

Organic fouling control through magnetic ion exchange nanofiltration (MIEX-NF) in water treatment

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35

36 **Keywords**

37 Nanofiltration, Fouling, Helium-Ion-Microscopy, Magnetic ion exchange (MIEX[®]), Humic acid

38

39 **1. Introduction**

40 Application of nanofiltration (NF) in drinking water applications is constantly growing as this membrane
41 process can separate divalent salts and small organic molecules to produce high quality water [1-3].
42 Natural organic matter (NOM) is one of the most common contaminants present in all water resources.
43 Removing NOM is important because of its undesirable odor, taste and color, and because it is
44 responsible for bacterial re-growth and reaction with chlorine disinfectants to produce disinfection-by-
45 products (DBPs) [4, 5]. Long-term adverse health effects of DBPs are widely reported in the literature and
46 the amount of these substances in drinking water is regulated strictly [6-8].

47 A large fraction of NOM, e.g. polysaccharides and humic acids (HA), is highly retained by NF/RO
48 membranes mostly due to size exclusion, charge repulsion, and hydrophobic interactions [9-11]. Further,
49 NOM is the main culprit of membrane organic fouling, which reduces system performance as a
50 consequence of the deposition of suspended and dissolved organic substances onto the membrane surface
51 and within its pores [12]. Fouling is associated with reduced productivity and deterioration of product
52 water quality, increased energy demand and maintenance costs, membrane degradation, and reduced
53 membrane life [13]. Indeed, fouling is a great challenge that engineers struggle to overcome for the full
54 implementation of membrane technology in drinking water production, especially when treating water
55 sources containing high concentrations of NOM and other organic substances [14, 15].

56 The main factors influencing membrane fouling by NOM are: i) the surface structure and the chemical
57 properties of the membrane [16-19], ii) the chemical composition of the feed solution [13, 20-22] and iii)
58 the operating conditions [20-24]. Several studies have reported an increase in fouling in the presence of
59 divalent cations, especially calcium, due to the related reduction of organic dissolution rate [25] and to
60 bridging interactions of NOM functional groups (mainly COOH and OH) with those of the membrane
61 surface [21, 26-30]. This effect is more pronounced under alkaline pH conditions, as ionization of
62 carboxyl groups promotes complexation with calcium cations [31] and the solubility of calcium is lower
63 [27]. Wang *et al.* [31] observed that Ca-HA complexes are highly sensitive to pH changes and to calcium
64 concentration; they suggested the existence of a critical foulant size of roughly 300-400 nm. Mo *et al.*
65 [32] demonstrated that the density of available surface carboxyls at the membrane-solution interface plays
66 a key role in promoting fouling by NOM. Specifically, lower flux decline, greater fouling reversibility

67 and cleaning efficiency were observed when the carboxyl group density was lower. However, at acidic
68 pH and especially at high ionic strength, the electrostatic repulsion between the membrane and NOM
69 molecules is reduced, resulting in more favorable organic deposition on the membrane surface [10, 26].

70 While important progress has been achieved to understand fouling mechanisms and to develop anti-
71 fouling membranes, organic fouling remains of critical concern in NF. New strategies are required for
72 fouling mitigation as well as for optimization of pre-treatment. Feed pre-treatment (including coagulation,
73 activated carbon, ozonation, H₂O₂/UV oxidation, and ion exchange) modifies NOM characteristics with
74 the goal to reduce its interactions with the membrane [13]. Advanced oxidation processes modify the
75 functional groups and the structure of NOM to yield less hydrophobic and sorbable compounds [33, 34].
76 Coagulants (e.g., iron or aluminum salts) and granular activated carbon remove high molecular weight
77 and hydrophobic organic compounds, respectively, resulting in reduced membrane fouling [35-38]. Ion
78 exchange resins have been applied successfully in feed pre-treatment due to their high NOM removal
79 capacity [39-41]. Magnetic ion exchange resins (MIEX) were developed specifically for the removal of
80 NOM in drinking water treatment [42-45]. These resins are advantageous compared with conventional ion
81 exchange resins due to: i) their smaller size, ii) easy downstream recovery made possible by their
82 magnetic properties, and iii) higher kinetics of NOM adsorption and surface regeneration due to the larger
83 specific area and more active exchange sites [46, 47].

84 MIEX resins have been used in combination with biological activated carbon to pre-treat secondary
85 wastewater effluents, thus reducing NF membrane fouling [48, 49]. Son *et al.* [50] investigated MIEX
86 application to mitigate fouling of UF membranes. The removal efficiency of MIEX was shown to be
87 higher for the low molecular weight organic fraction (< 10 kDa). This is of great importance for pre-
88 treatment in NF process where convective transport of the low molecular fraction of NOM occurs at high
89 recovery rates [9]. MIEX packed in fluidized bed column was combined with submerged NF membranes
90 [39]. MIEX significantly removed NOM compounds characterized by low specific ultraviolet absorbance
91 (SUVA) values (mainly phenolic compounds, aliphatic hydrocarbon, and amino sugars). Lower removal
92 efficiency was determined for carboxyl-containing substances. Flux decline in the subsequent NF step
93 was reduced by 30% and MIEX use also resulted in reduced biofouling, suggesting MIEX as an effective
94 pre-treatment for NF.

95 In the present study, MIEX and NF are combined in one single process to investigate and mitigate fouling
96 by HA. Previously, MIEX was used mostly in feed pre-treatment, while no studies about direct
97 application in the membrane system has been reported. Further, compared with fluidized bed columns,
98 stirred reactors increase turbulence, thus decreasing the resistance to liquid phase mass transfer and
99 leading to better interaction of MIEX and HA. Initially, static adsorption studies of HA by MIEX are

100 discussed to elucidate MIEX-HA interactions. MIEX effectiveness in controlling NF fouling is thus
101 investigated. Two types of widely employed commercial NF membranes (a loose and a tight membrane
102 with different salt retention properties and fouling propensity) are evaluated in order to investigate MIEX
103 effectiveness under different fouling conditions and water chemistries. The main hypotheses to be tested
104 are that MIEX may be deployed effectively to reduce fouling for different water-membrane systems and
105 that operating conditions are critical to enhance effective interaction mechanism with HA. The latter
106 aspect is of great importance to achieve fouling control under real water chemistries in NF sources for
107 drinking water production.

108 **2. Materials and Methods**

109 **2.1 Chemicals**

110 The humic acid (HA, purchased from Sigma Aldrich, Germany) stock solution (500 mg/L) was prepared
111 by dissolving 1.5 g of HA and 2.5 g NaOH in ultrapure water (pH 8) and stirring for 24 hours. The
112 dissolved organic carbon (DOC) fraction was obtained by filtering the stock solution with a 0.45 μm
113 PTFE (poly-tetra-fluoro-ethylene) filter. A buffer solution containing 2.5 mM CaCl_2 (Berndt Kraft,
114 Germany), 1 mM NaHCO_3 (VWR Chemicals, Germany), 10 mM NaCl (VWR Chemicals, Germany), and
115 12.5 mgC/L of HA was used for the static adsorption experiments with MIEX as well as for membrane
116 filtration experiments. HCl (1 M) and NaOH (1 M) were used to adjust the pH of the solutions varying
117 from 2 to 10. Metabisulfite (Alfa Aesar, Germany) solution of 10 g/L was used to prevent bacterial
118 growth on the used membrane. MilliQ water (MilliQ A+ system, Merck Millipore, Germany) was used to
119 prepare solutions.

120 **2.2 MIEX characteristics**

121 Two types of MIEX resin beads (MIEX_{DOC} and $\text{MIEX}_{\text{GOLD}}$) were provided by Orica Watercare
122 (Melbourne, Australia). MIEX_{DOC} and $\text{MIEX}_{\text{GOLD}}$ resins were compared in static adsorption experiments
123 and only MIEX_{DOC} were used in the filtration experiments. The main differences between the two resins,
124 as reported by the supplier, are the rougher and higher surface area of $\text{MIEX}_{\text{GOLD}}$ and its larger pore
125 openings, which allow easier access to inner bead area and increased exchange capacity, according to the
126 manufacturer. For this reason, $\text{MIEX}_{\text{GOLD}}$ are able to remove low molecular weight organic material (<
127 5000 Da) compared with MIEX_{DOC} [51]. Particle size and surface morphology of both resins were
128 analyzed by environmental scanning electron microscopy (ESEM) and the micrographs are presented in
129 the Supporting Information (see Figure S12). In these images, both resins display a porous and smooth
130 surface. $\text{MIEX}_{\text{GOLD}}$ is heterogeneous in size and shape with larger particles ranging from roughly 50 μm
131 to 400 μm . MIEX_{DOC} appear more homogeneous with an average diameter of about 140 μm , which is in
132 accordance with values reported in the literature (150-180 μm) [52]. The Zeta potential of the resins was

133 measured at pH ranging from 2 to 10 and results are presented in Figure S13 of the Supporting
 134 Information. The resins showed slightly positive potentials at pH>6 (1-6 mV) while the zeta potential is
 135 close to zero at pH<6. This trend might be attributed to the high ionic conductance typical of ion
 136 exchange material, which significantly reduces the streaming potential signal and thus the magnitude of
 137 the measured zeta potential. Hence, measurement of streaming potential current were conducted in an
 138 electrolyte solution with similar electrical conductivity of that of the resin.

139 MIEX are usually acquired as a suspension having an organic content of 19 mgC/L. Therefore, a washing
 140 step was necessary prior to use in order to remove dissolved carbon-containing substances. The washing
 141 procedure was performed by diluting the MIEX with NaCl solution (1%) and mixing for 1 min.
 142 Subsequently, the resin was sedimented with a magnet, the supernatant removed, and the resin recovered.
 143 Finally, the resins were rinsed with MilliQ water and used for experiments.

144 2.3 Static adsorption tests of humic acid on MIEX resins

145 Static adsorption of HA on MIEX resins was investigated under different physico-chemical water
 146 conditions. The composition of the solutions used in the static adsorption study is summarized in Table 1.

147 Table 1. Buffer solution composition for the static adsorption experiments

Parameters	Concentration range (mM)	Buffer solution composition
CaCl ₂	0-0.5-1-2.5- 3.5- 4	12.5 mgC/L HA, 10 mM NaCl, 1 mM NaHCO ₃
NaCl	0.1-0.5-5-10-20-30-50	12.5 mg/L humic acid, 2.5 mM CaCl ₂ , 1 mM NaHCO ₃
HA	4- 6-12.5-25-45 mgC/L	2.5 mM CaCl ₂ , 10 mM NaCl, 1mM NaHCO ₃

148
 149 Rinsed resins were settled for 5 minutes in a 10 mL syringe and 1.5 mL of suspension was added into a
 150 conical flask containing 150 mL of buffer solution to obtain a final resin concentration of 10 mL/L.
 151 Previous studies have shown that this concentration is optimal for NOM removal [53]. The flasks were
 152 shaken (New Brunswick™ Innova® 43) at the speed of 260 rpm for 60 min at 25 °C. MIEX adsorption
 153 was tested firstly for 4 hours: fast adsorption kinetics were observed and equilibrium was reached within
 154 20 minutes (see Figure S15 in Supporting Information); therefore, 60 min was set as suitable time to
 155 evaluate static equilibrium adsorption. Samples of 10 mL were drawn at regular intervals for total organic
 156 carbon analysis. HA uptake (%) was calculated using Equation (1):

$$157 \text{ HA uptake (\%)} = \left(1 - \frac{C_t}{C_i}\right) \cdot 100 \quad (1)$$

158 Where C_i (mg/L) is the initial HA concentration prior to resin addition, C_t (mg/L) is HA concentration at
 159 any given time, t. The mass of HA removed per mass of resin added, Q (mg/g), was calculated using
 160 Equation (2):

161
$$Q = \frac{(C_i - C_f) \cdot V_w}{M} \quad (2)$$

162 where V_w (L) is the solution volume at any given time, t , and M is the mass of resin added (g).

163 **2.4 NF membranes**

164 Two commercial NF membranes, NF270 and NF90 (provided as flat sheet samples by The Dow
165 Chemical Company, Germany), were used for the fouling experiments. NF270 and NF90 consist of a
166 semi-aromatic piperazine-based polyamide and a fully aromatic polyamide active layer, respectively [54].

167 The main properties of the membranes are summarized in Table 2.

168 Table 2. NF membrane characteristics used in the fouling experiments (MWCO= Molecular-weight-cut-off, IEP=
169 isoelectric point, Lp= permeability)

Membrane	MWCO (Da) ^{*1}	Ref.	IEP	Lp (L m ⁻² h ⁻¹ bar ⁻¹)	Pore radius (nm) ^{*2}	Ref.
NF90	90-180	[55-58]	~3.5	6 - 11	0.31-0.38	[56, 57, 59]
NF270	150-340	[55-57, 60]	~3	17-19	0.36-0.44	[56, 57, 61]

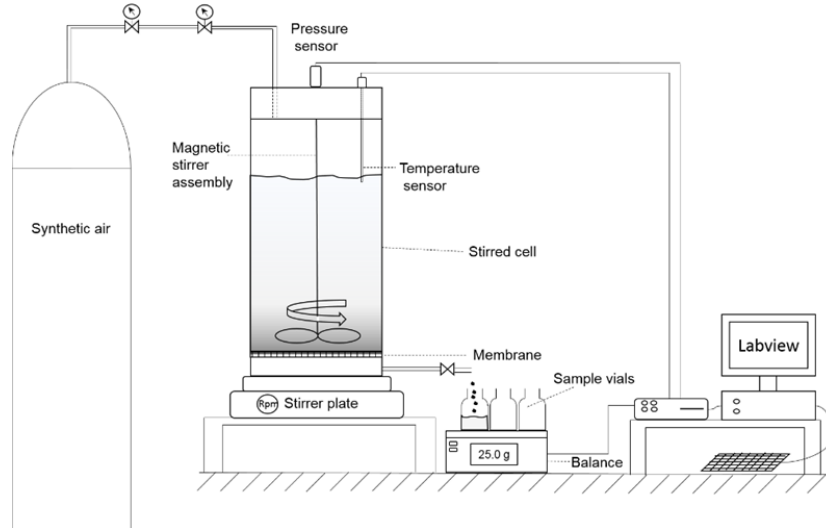
170 ^{*1,2} MWCO was determined by filtration of organic solutes (poly-ethylene glycol and sugars), pore size was estimated by
171 applying the steric hindrance pore model

172 A new membrane coupon was used for each experiment; this coupon was soaked in NaCl 10 mM for 1
173 hour prior to use, then compacted by filtering MilliQ water at 9.6 bar for 1 hour. Soaking in NaCl
174 enhances opening of the pores and swelling of the active layer due to interaction of electrolytes with the
175 polyamide layer [62]. Normalized permeate flux (J_n) was calculated using Equation (3):

176
$$J_n = \frac{J_t}{J_{wo}} \quad (3)$$

177 The initial pure water flux, J_{wo} (L m⁻²h⁻¹) was measured at steady-state before the filtration, while J_t (L m⁻²h⁻¹)
178 was the observed flux during fouling. The pure water flux was chosen as reference value due to
179 practical limitations in the determination of a consistent value of flux in the presence of foulants at the
180 very start of fouling experiments. The flux obtained by normalization with reference to J_{t0} , the flux at the
181 beginning of the fouling experiment, is compared to the normalized permeate flux, J_n , in Figure S18
182 (Supporting Information). The filtration experiments were performed using a stainless steel stirred cell
183 (capacity 900 mL) with an internal diameter of 7 cm, corresponding to an active membrane area of 38.48
184 cm². The cell was pressurized using synthetic compressed air that was supplied from the top of the cell.

185 The mass of permeate, as well as the feed pressure and the temperature, were monitored continuously and
 186 data were registered by using LabVIEW software (version 2014, National Instruments). A schematic
 187 representation of the system is reported in Figure 1.



188
 189 **Figure 1.** Stainless steel stirred cell system
 190

191 For fouling experiments, 400 mL of feed solution containing HA (12.5 mgC/L), NaCl (10 mM), NaHCO₃
 192 (1 mM), and CaCl₂ (2.5 mM), with or without a suspension of MIEX at 10 mL/L, was introduced into the
 193 cell and stirred at 400 rpm using a stirrer (model SU1300, Sunlab, Germany). Filtration was carried out at
 194 a trans-membrane pressure of 9.6 bar up to a recovery of 70 %. Nine permeate samples were collected
 195 during each test for a total volume of 280 mL and used for DOC analysis in order to measure the free HA
 196 concentration. HA retention was calculated using Equation (4):

197
$$R (\%) = \left(1 - \frac{C_p}{C_b} \right) \cdot 100 \quad (4)$$

198 Where C_p (g/L) is HA concentration in the permeate, C_b (g/L) is HA concentration in the stirred cell,
 199 which changes over time and it is calculated as a function of permeate volume and concentration using
 200 Equation (5):

201
$$C_b = \frac{C_{FD} \cdot V_{FD} - \sum C_{Pi} \cdot V_{Pi}}{V_R} \quad (5)$$

202 where C_{FD} (g/L) is the initial HA concentration in the feed solution, C_{Pi} (g/L) is HA concentration in the
 203 permeate sample i , V_R (L) is the retentate volume (L), V_{FD} (L) is the initial feed volume, and V_{Pi} (L) is the
 204 permeate volume of sample i . After each fouling experiment, the cell containing the membrane was rinsed

205 gently with MilliQ water. The rinsing protocol consisted of filling the cell with MilliQ water (400 mL)
206 without removing the membrane, rinsing manually and emptying. The rinsing was followed by evaluation
207 of the pure water flux, J_w , by measuring steady-state permeation of MilliQ water at an applied pressure of
208 9.6 bar. The water flux reduction due to previous fouling, FR , was calculated using Equation (6):

$$209 \quad FR(\%) = \frac{J_{w0} - J_w}{J_{w0}} \cdot 100 \quad (6)$$

210 The fouled membrane samples were stored at 4 °C after treatment with sodium metabisulfite (10 g/L) in
211 order to avoid bacterial growth prior to later imaging.

212 **2.5 HA and IC analysis**

213 HA and IC (inorganic carbon) concentrations in the solutions used for static adsorption tests, as well as in
214 permeate, feed, and retentate samples of fouling tests, were measured with a GE Sievers M9 TOC
215 Analyser (GE Analytical Instruments, UK). Feed and retentate samples were diluted 2 and 10 times,
216 respectively, in order to ensure that concentrations were within the range of the calibration curve made
217 with standard HA solutions (range 0-10 mgC/L). Samples were analyzed using an acid (H_2SO_4) and
218 oxidizer (ammonium persulfate) flow rate of 1 μ L/min.

219 **2.6 Calcium analysis**

220 Calcium concentration was measured by inductively coupled plasma optical emission spectrometry (ICP-
221 OES, model Optima 8300DV, Perkin Elmer, Germany). Samples were diluted 10 times due to
222 acidification with HNO_3 (5%) and treatment with Triton-X 100 before measurement.

223 **2.7 Microscopy imaging**

224 Environmental scanning electron microscopy (ESEM) (model Phillips ESEM-FEG XL30) was used to
225 visualize MIEX resin beads morphology and particle surface. Fouling layer thickness was determined
226 using scanning helium ion microscopy (HIM, ORION NanoFab, Carl Zeiss AG, Germany). The
227 membrane samples were analyzed after the rinsing procedure explained in paragraph 2.4 in order to
228 analyze only the material adsorbed irreversibly on the membrane surface. Cross-sections of the membrane
229 discs were prepared manually using a sharp razor blade to minimize damage of the membrane surface.
230 The HIM microscope was operated at an acceleration voltage and beam current of 30 kV and 0.3 pA,
231 respectively, and the samples were imaged without any additional conductive coating with the aid of an
232 electron flood gun.

233 **2.8 Zeta potential analysis**

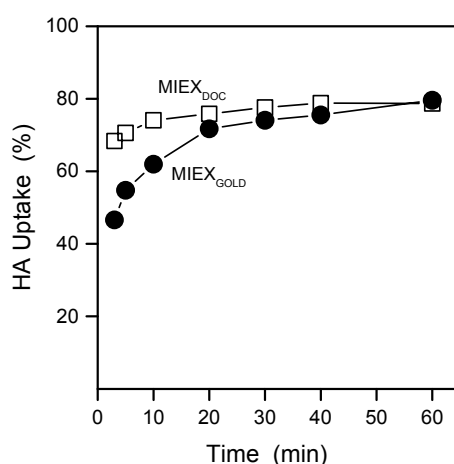
234 The Zeta potential of MIEX beads and membranes was measured with an electrokinetic analyzer
235 (SURPASSTM, Anton Paar, Austria). The measurements of MIEX zeta potential were carried out with a
236 background electrolyte solution of KCl (1 mM, VWR Chemicals, Germany) and at a temperature of 22
237 °C. The pH was adjusted using HCl or NaOH (50 mM). The MIEX bead powder was placed in a
238 cylindrical measuring cell and the electrolyte solution flowed through the cell. An appropriate amount of
239 powder was used in order to have a pressure of 200 mbar between the inlet and the outlet of the
240 cylindrical cell and a flow rate in a range of 50 to 70 mL/min.

241 Zeta potential measurements of the membranes were carried in solutions containing NaCl only (15 mM),
242 NaCl and HA, or in the same solutions used for fouling experiments that contained NaCl, CaCl₂, and HA.
243 The method was similar to that described elsewhere [63]. Streaming potential measurements were carried
244 out from at increasing pH starting from a value of 2 until a plateau in the magnitude of zeta potential was
245 reached and no further change in potential was expected by increasing the pH of the solution.

246 3. Results and discussion

247 3.1 Comparison uptake of MIEX_{DOC} and MIEX_{GOLD} in static adsorption

248 Morphological analysis of MIEX_{DOC} and MIEX_{GOLD} resins revealed higher heterogeneity of particle size
249 and shape of MIEX_{GOLD} compared with MIEX_{DOC} (see Figure S12 of the Supporting Information).
250 MIEX_{GOLD} is characterized by higher ion exchange capacity according to the manufacturer. The
251 adsorption of HA was investigated with both types of resin to determine their possible difference in
252 performance and the sorption kinetics are reported in Figure 2.

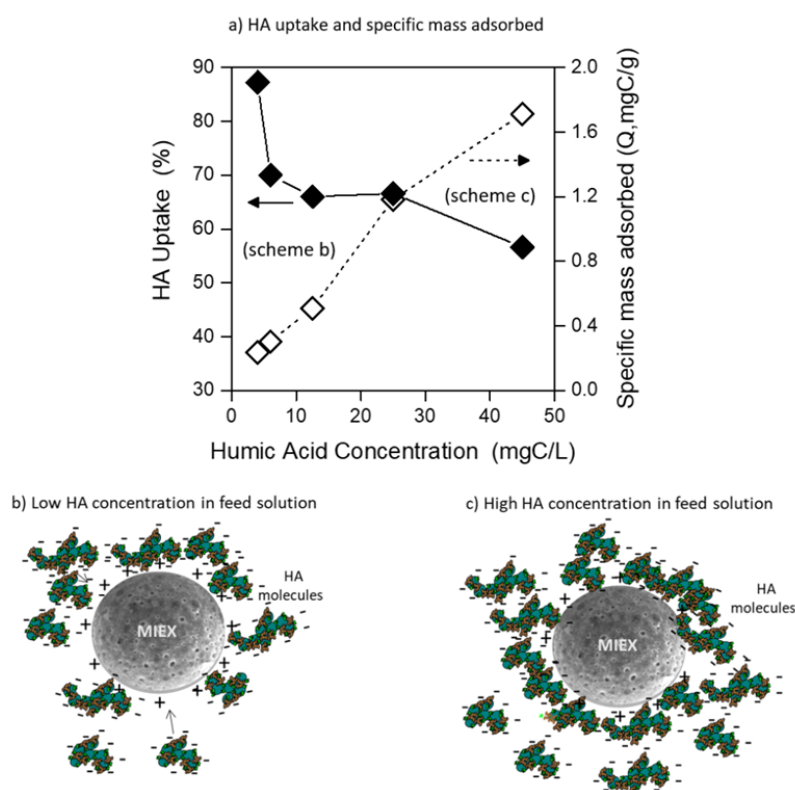


253
254 **Figure 2.** HA uptake (%) of two types of MIEX (12.5 mgC/L HA, 2.5 mM CaCl₂, 1 mM NaHCO₃, 10 mM NaCl, 10
255 mL/L MIEX, 150 mL, 20 °C, 260 rpm, pH 6)

256 Near steady-state was reached for both types of resin after about 20 min. Fast sorption kinetics resulted in
 257 uptake of more than 40% of the organic material after few minutes and 80% of organics at the end of the
 258 experiments. These data are consistent with adsorption driven by electrostatic attraction of negatively
 259 charged HA molecules and positively charged MIEX surfaces at pH 6 and are in accordance with
 260 previous reports [52, 64]. Overall, adsorption was slightly faster with MIEX_{DOC} and this type of MIEX
 261 resin was thus chosen to conduct subsequent experiments.

262 3.2 Influence of HA concentration on HA-MIEX interaction

263 The variation of HA uptake at increased HA concentration was investigated to estimate the amount of HA
 264 adsorbed per unit mass of resin. This is relevant to understand HA-MIEX interaction in the dead-end
 265 stirred cell, where HA is concentrated within the cell during NF. HA uptake and specific mass adsorbed
 266 per mass of MIEX (Q) are reported in Figure 3a as a function of HA concentration. These data refer to the
 267 uptake at equilibrium (after 1 hour). HA uptake kinetics is reported in Figure S16 of the Supporting
 268 Information.



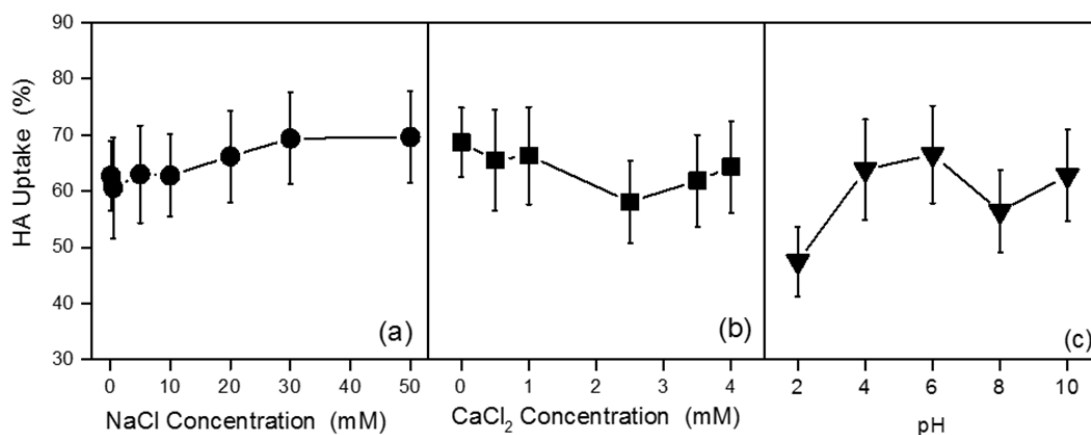
269
 270 **Figure 3.** HA uptake and specific mass adsorbed of HA at increased HA concentration (12.5 mgC/L HA, 2.5 mM
 271 CaCl₂, 1 mM NaHCO₃, 10 mM NaCl, 10 mL/L MIEX, 150 mL, 20 °C, 260 rpm, pH 6, 60 min adsorption)

272 HA uptake decreased from 89 to 56 % with increasing HA concentration, while HA mass adsorbed per
273 unit mass of MIEX increased clearly from 0.2 to 1.7 mgC/g. At low HA concentration, the MIEX surface
274 remained available for adsorption until all available HA in solution was consumed (Figure 3b). In a
275 middle range of HA concentrations, 6-25 mgC/L, HA uptake was constant at approximately 66% after 1
276 hour, independently of initial HA concentration in solution. Under these conditions, adsorption was not
277 driven by interactions of suspended HA molecules with MIEX surfaces, but by interaction with already
278 deposited HA molecules. This mechanism led to an increase of the overall amount of adsorbed HA
279 (Figure 2c), even though the uptake did not change.

280 **3.3 HA adsorption by MIEX as a function of water chemistry: ionic strength, hardness and pH**

281 HA interactions with MIEX are mainly dominated by ion exchange mechanisms due to oppositely
282 charged functional groups of HA molecules and MIEX surface. Thus, ionic strength, calcium
283 concentration and pH are expected to play an important role by changing the charge density of HA
284 molecules and by screening the electrostatic interactions. Furthermore, NaCl is used to regenerate
285 saturated MIEX, based on the exchange of adsorbed materials with Cl⁻. To promote regeneration, NaCl
286 concentration is increased by one order of magnitude, based on the exchange capacity of 0.52 meq/mL
287 [43]. 10 mL/L of MIEX corresponds to an exchange capacity of 5.2 meq/L (or 5.2 meq/L), therefore the
288 regeneration concentration should be 50 mM, which was chosen in this study as highest ionic strength
289 during experiments.

290 **Ionic strength:** a NaCl concentration range of 0 to 10 mM was chosen in order to determine when NaCl
291 reduces HA uptake by MIEX and regeneration takes place. HA uptake as a function of NaCl
292 concentration at equilibrium is reported in Figure 4a (HA uptake kinetic is reported in Figure S14 of the
293 Supporting Information). Contrary to expectations, constant high HA uptake (about 65%) was observed
294 with increasing NaCl concentration. Gosh *et al.* reported that HA molecules have a rigid sphero-colloid
295 structure at high concentration of electrolytes and behave like uncharged polymers [65]. This effect
296 appears to be dominant over the exchange mechanism at this concentration, thus allowing for denser
297 packing of molecules on MIEX surface and resulting in higher adsorption values, as observed in other
298 studies [66, 67]. Similar DOC removal was observed also by Apell *et al.* [43] during the regeneration
299 process.



300
 301 **Figure 4.** Effect of water chemistry on HA uptake after 60 min of adsorption: (a) ionic strength (2.5 mM CaCl₂,
 302 12.5 mgC/L HA, 1 mM NaHCO₃, 10 mL/L MIEX), (b) calcium (CaCl₂) (10 mM NaCl, 12.5 mgC/L HA, 1 mM
 303 NaHCO₃, 10 mL/L MIEX), (c) pH (2.5 mM CaCl₂, 12.5 mgC/L HA, 10 mM NaCl, 1 mM NaHCO₃, 10 mL/L
 304 MIEX). 20 °C, 150 mL, 260 rpm.

305 **Calcium concentration:** In Figure 4b, HA uptake is reported as a function of CaCl₂ concentration. The
 306 range of calcium concentration was defined to investigate HA uptake in both soft (< 0.4 mM) and hard
 307 waters (≥ 4 mM). Calcium is ubiquitously present in drinking water. Tap and bottled water sources have
 308 a wide range of calcium concentration between 5 to above 200 mg/L (0.4-4.5 mM) [68]. Calcium ions
 309 interact strongly with the negatively charged groups of HA molecules reducing the electrostatic repulsion
 310 and the dissolution rate [25]. However, no significant change in HA uptake by MIEX was observed,
 311 suggesting that HA-MIEX interaction was not affected by calcium concentration.

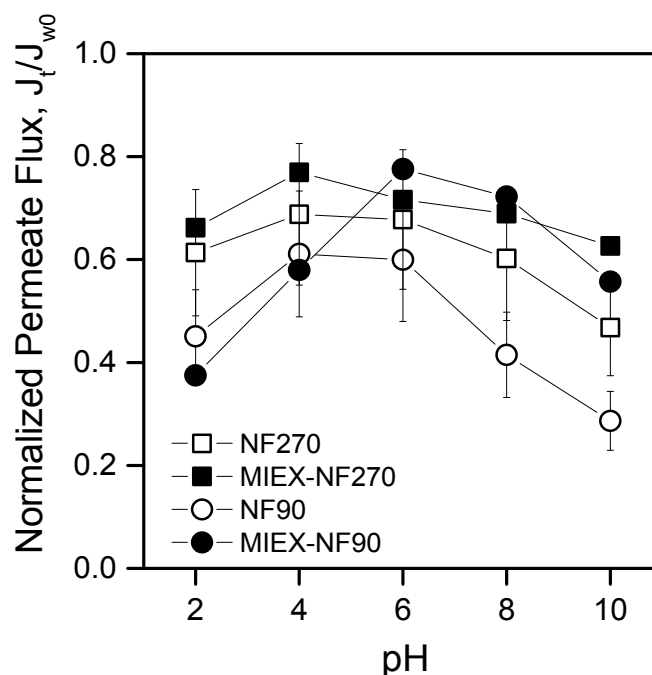
312 **pH:** HA changes charge density, size and shape in different pH solutions [25, 69]. MIEX have a
 313 macroporous poly-acrylate shell with quaternary ammonium functional groups for ion exchange [64].
 314 Ammonium (NH₄⁺, pKa 9.25) is a strong base and is ionized completely in the pH range studied. The
 315 observed HA uptake as a function of pH is reported in Figure 4c. A slight increase from 47% to 66% was
 316 observed by increasing pH from 2 to 10. HA molecules contain mainly carboxyl and phenolic groups,
 317 which are deprotonated at pH 4-5 and pH 8-9, respectively [25]. At pH 2, charge density and dissolution
 318 rate of HA molecules is low, resulting in aggregation into molecular clusters [69]. These phenomena
 319 reduced the interaction with MIEX, leading to lower uptake. The increase of the negative charge density
 320 with increasing pH enhanced instead the interaction with the positively charged functional groups of
 321 MIEX resins and resulted in higher uptake. Taken together, results as a function of water composition
 322 suggested no significant effect of water chemistries on HA uptake due to stronger HA-MIEX interaction.

323 **3.4 Flux decline during filtration in combined MIEX-NF process**

324 Fouling studies were conducted using NF270 and NF90 membranes, which are loose and tight NF
325 membranes, respectively. NaCl and CaCl₂ retention (without HA) is higher for NF90 (~85-90%)
326 compared with NF270 (40-60%) [57, 58, 70], while both membranes have high HA rejection. This may
327 be attributed to size exclusion of the high molecular weight compounds (measured retention was in the
328 range 80-95% in this study, see Figure S17 of the Supporting Information). Calcium ions enhance NF
329 membrane fouling by bridging the negative functional groups of the membrane surface with the HA
330 molecules [26-29]. The pH of feed solution is also an important parameter affecting membrane-HA
331 interaction, Ca-HA complexes, as well as HA-MIEX interactions [27, 31].

332 In Figure 5, flux decline at the end of the experiments in NF and combined MIEX-NF is reported as a
333 function of pH for both membranes. Normalization of flux decline was carried out considering J_{w0} . Based
334 on the rejection capabilities of the two types of membrane, a maximum loss in driving force of 10% and
335 16% due to concentration of feed solutes in the dead-end cell is estimated at the end of the tests with
336 NF270 and NF90, respectively. The van't Hoff equation was used to calculate osmotic pressure from
337 concentrate salt concentrations, which was then deducted from the applied pressure. Normalized flux
338 declines below 0.9 and 0.84 for NF270 and NF90, respectively, should be attributable to fouling. Flux
339 decline was more pronounced with NF90 membranes compared to NF270 membranes. However, the
340 same trend with pH was observed, with higher decline in acidic (pH 2) and alkaline (pH 8, 10) solutions.
341 At pH 2, the electrostatic repulsion between HA molecules and HA-membranes is reduced due to lower
342 charge density of both materials. Therefore, deposition on the membrane surface of HA aggregates was
343 promoted [22]. Lower flux declines were observed at pH 4 and 6, whereby carboxylic groups of both
344 membranes and HA molecules are weakly ionized. Indeed, IEP of 3.5 was measured for NF90 and
345 carboxyl groups of HA are deprotonated at pH 4-5. Brigante *et al.* observed that the dissolution rate of
346 HA increases by more than two orders of magnitude by increasing the pH from 4 to 11 due to the
347 disruption of hydrogen bonds between HA molecules [25]. As such, the lower flux decline might be
348 attributed to weaker deposition of HA aggregates on the membrane. At higher pH values (8 and 10), the
349 density of deprotonated carboxyl groups is higher and complexation of Ca-HA molecules becomes
350 significant. Indeed, complexation of Ca-HA molecules as well as HA-membrane bridging have been
351 reported to be stronger at high pH due to availability of more deprotonated carboxyl groups on both the
352 membrane surface and HA molecules [12, 26]. As a result, highest flux declines were observed at pH 8
353 and 10 (normalized flux of 0.3 and 0.4 at the end of the test, respectively, for NF90 samples),
354 corroborating the significant role of calcium ions in membrane fouling.

355



356

357 **Figure 5.** Normalized permeate flux as a function of pH (12.5 mg/L HA, 2.5 mM CaCl₂, 1 mM NaHCO₃, 10 mM
358 NaCl, 10 mL/L MIEX, 9.6 bar, 400 rpm, 22 °C, 70% recovery)

359 At high pH, calcium can also contribute to membrane fouling by precipitation as calcite on the membrane
360 surface and subsequent adsorption of HA molecules on the calcite. Schäfer *et al.* observed calcite
361 formation at pH > 8 and 3 mM of calcium chloride [27]. In the present study, the initial feed solution
362 contained 2.5 mM of calcium chloride and calcium concentration increased continuously in the stirred
363 cell during filtration. Therefore, calcite precipitation is likely to occur at high rate at pH 10, resulting in
364 severe flux decline (final normalized flux of 0.3 with NF90). This phenomenon may explain the lower
365 decline observed with NF270 membranes (range of normalized flux 0.7-0.5), which are less capable of
366 rejecting calcium (75% versus 98%). Membrane surface properties (e.g., hydrophobicity and roughness)
367 contribute to membrane fouling. Boussu *et al.* reported that NF270 has higher hydrophilicity, smoother
368 surface and higher charge density than NF90 [58]. However, contrasting results are present in the
369 literature concerning fouling of NF270 and NF90. Some previous studies reported less fouling for NF270
370 compared to NF90 due to the smoother surface and higher hydrophilicity of the former membranes [24,
371 58]. On the contrary, other studies reported higher flux reduction for NF270 (33%) than NF90 (24%) due
372 to its higher permeability, which resulted in greater initial flux when operating at the same applied
373 pressure and hence higher concentration polarization [22]. Nghiem *et al.* identified calcium concentration
374 as the major factor governing fouling by HA and similar flux decline was observed for both NF90 and
375 NF270 at the same calcium concentration [71]. In this study, a larger flux decline was observed at high

376 pH values, where complexation and bridging Ca-HA with the membrane surface plays a major role in
377 membrane fouling.

378 In the combined MIEX-NF process, system performance was improved. In the case of NF90, higher
379 efficiency of MIEX addition was observed at high pH. Specifically, at pH 8 the final value of normalized
380 flux increased from 0.4 to 0.7, while at pH 10 it increased from 0.3 to 0.6. This result is in accordance
381 with the static adsorption study where higher HA uptake by MIEX was measured at high pH. The lower
382 flux decline suggested that the presence of MIEX reduced the complexation of Ca-HA molecules and
383 bridging or deposition onto the membrane surface. This is due to the stronger HA-MIEX interaction,
384 which reduces the amount of free HA molecules to interact with calcium. MIEX effectiveness was low at
385 acidic pH (2 and 4), as flux decline was only slightly reduced. According to the static adsorption tests,
386 HA-MIEX interactions are weaker in acidic condition and HA molecules are mainly in the form of
387 aggregates, which can deposit on the membrane surface during filtration, as discussed above.

388 In the case of NF270, the effect of MIEX addition was as significant as with the tighter membranes,
389 resulting overall in significantly lower flux decline. The effect of MIEX was strongest at pH 10, with the
390 final value of normalized flux increasing from 0.4 to 0.6 upon addition of MIEX. This result supports the
391 hypothesis that the resin inhibited the adsorption of HA on the calcium precipitated onto the membrane
392 surface due to stronger HA-MIEX interaction.

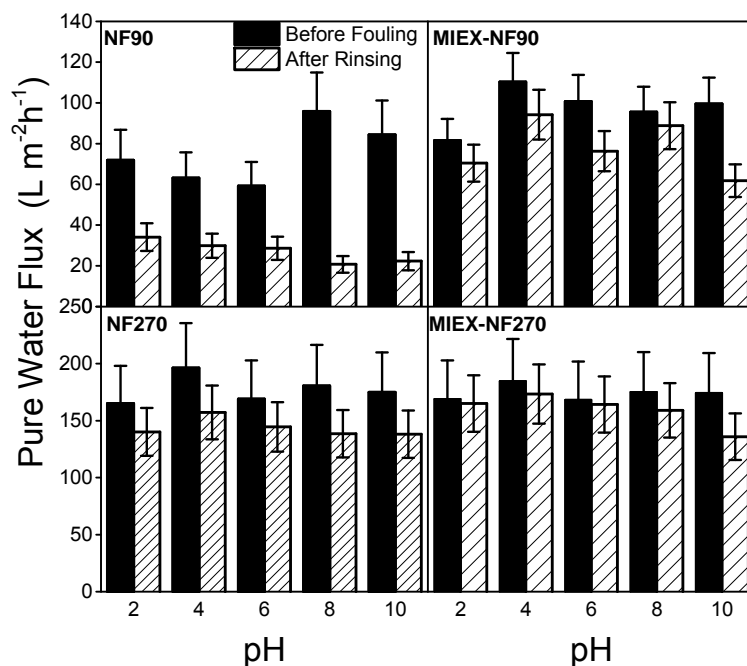
393 **3.5 Flux reduction due to irreversible fouling in combined MIEX-NF process**

394 Flux decline is an indication of loss of driving force, concentration polarization, and accumulation of
395 organic material on the membrane surface (thus fouling) during operation. However, flux decline does not
396 indicate whether fouling is reversible or irreversible. In the present study, the flux reduction, i.e., the loss
397 of flux following fouling and rinsing of the membrane, was investigated to this purpose. Further, flux
398 reduction in presence of MIEX was investigated at different pH values in order to evaluate optimal
399 conditions for MIEX effectiveness. In Figure 6, pure water flux measured before and after the filtration of
400 HA solution at different pH values is shown for both types of membrane in NF and combined MIEX NF
401 processes.

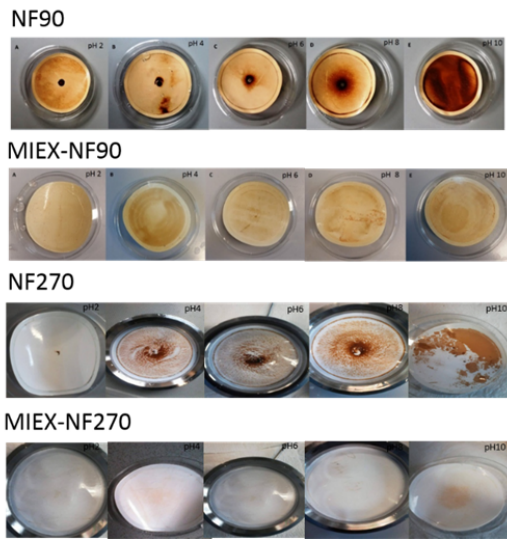
402 High water flux reduction in a range between 53-78% was observed when NF90 was used without MIEX.
403 Therefore, irreversible fouling was dominant, which was confirmed by the dark coloration of the
404 membrane discs after rinsing, especially at alkaline pH values (8-10) (Figure 7). The results may be
405 rationalized with the strong complexation of Ca-HA molecules on the membrane surface as mainly
406 responsible of irreversible fouling during filtration by NF90. Lower water flux reduction (15-23%) was
407 observed for NF270, independent of pH. This result suggests less irreversible fouling with the less

408 rejecting membrane. This is in agreement with the lower flux decline reported in Figure 5 as well as the
 409 cleaner membrane samples compared with NF90 after rinsing. The lower calcium retention reported in
 410 the literature for NF270 [57, 58, 70] as well as higher hydrophilicity and smoother surface [58] might
 411 explain the lower and reversible fouling observed with this membrane.

412 In the case of MIEX-NF90, the irreversible water flux reduction was 2 times lower (14-34%). Flux
 413 reduction of 34% was observed at pH 10, suggesting the inhibition of calcium effect by the resins:
 414 stronger interaction between MIEX and HA occurred, thus preventing calcium-organic complex
 415 formation. At pH 2, flux reduction was about 14%, in contrast with the high flux decline observed during
 416 filtration and reported above in Figure 5. This means that fouling was mostly reversible at pH 2. Indeed,
 417 HA aggregate deposits were bound weakly to the membrane and flux could be recovered by gentle rinsing
 418 with MilliQ water. This was supported by the qualitative analysis of the membrane disc, which did not
 419 appear heavily fouled at pH 2 following experiments conducted in the presence of MIEX (Figure 7). In
 420 the case of MIEX-NF270, the water flux was recovered fully after filtration, indicating that HA-MIEX
 421 interactions minimized HA layer deposition on the membrane. These results suggest that MIEX can
 422 effectively reduce irreversible fouling with both membranes.



423
 424 **Figure 6.** Water flux measured before and after filtration in NF and combined NF-MIEX at different pH values
 425 (12.5 mg/L HA, 2.5 mM CaCl₂, 1 mM NaHCO₃, 10 mM NaCl, 10 mL/L MIEX, 9.6 bar, 400 rpm, 22 °C, 70%
 426 recovery)

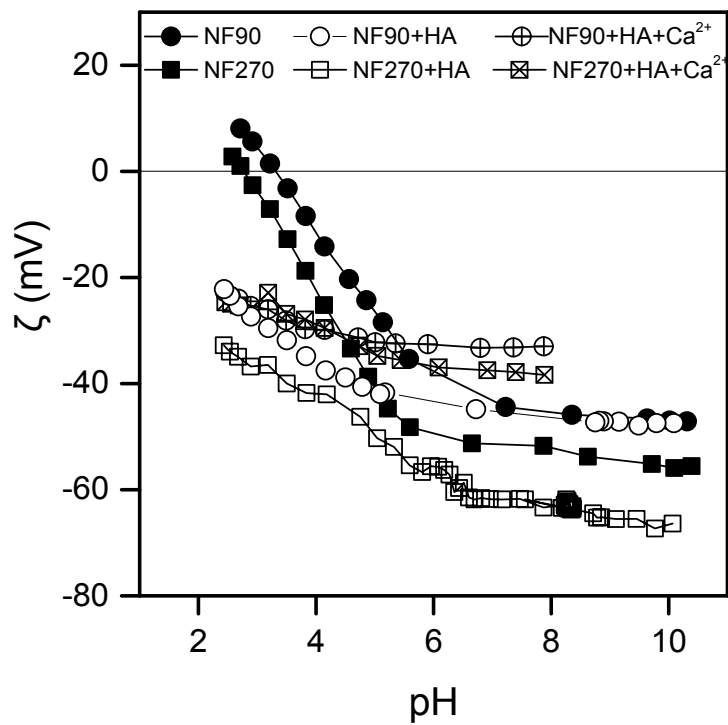


427

428 **Figure 7.** Appearance of the membrane discs after rinsing with MilliQ water

429 **3.6 Impact of calcium on membrane zeta potential in fouling condition**

430 The zeta potential of NF90 and NF270 in the presence of HA with and without calcium ions was
 431 measured in order to determine the impact of calcium on surface charge. Figure 8 summarizes zeta
 432 potential values measured in 15 mM NaCl, in HA solution, as well as HA+Ca solution.



433

434 **Figure 8.** Zeta potential of NF270 and NF90 as a function of pH in different solutions containing (i) electrolytes
435 only (NaCl 15 mM), (ii) electrolytes and HA (12.5 mgC/L HA, 1 mM NaHCO₃, 10 mM NaCl), or (iii) electrolytes,
436 HA and calcium (12.5 mgC/L HA, 1 mM NaHCO₃, 10 mM NaCl and 2.5 mM CaCl₂)
437

438 Comparison of the pristine membranes showed slightly higher negative charge of NF270 compared with
439 NF90 and IEP of about 3-3.5, which was in accordance with other previous studies [63, 72]. The negative
440 charge was related with deprotonation of the carboxylic group of the active polyamide layer [73]. The
441 presence of HA increased the negative charge of both membranes over the entire pH range, indicating that
442 interactions between HA and membranes occurred in both acidic and alkaline conditions. The same
443 phenomenon was observed also in previous studies by streaming potential measurements [26, 74, 75]. HA
444 molecules contain mainly carboxyl and phenolic groups, which are deprotonated at pH 4-5 and pH 8-9,
445 respectively [25]. This explained the strong negative charge of the HA layer adsorbed on the membrane
446 which dominates the membrane surface charge. As reported by Childress *et al.* [74, 75], HA adsorption
447 on the membrane is mainly driven by hydrophobic interaction at higher pH values, where membrane and
448 HA molecules are both negatively charged and electrostatic repulsion is present

449 In presence of calcium ions, a reduction in the magnitude of the zeta potential was observed for both
450 NF90 and NF270, which can be correlated to the interaction of positively charged calcium ions with HA
451 molecules at the membrane surface. This phenomenon appeared to be more pronounced for NF90 than
452 NF270. These results contradict the results reported by Childress *et al.* [74] who observed an increase of
453 the negative charge in presence of HA and calcium. This was attributed to higher HA adsorption due to
454 complexation with calcium and bridging with the membrane surface. In another study by Hong *et al.* [26]
455 a reduction of the negative membrane charge was observed by increasing calcium concentration in the
456 presence of humic acid, which highlights the importance of the feed composition on the results obtained
457 by streaming potential measurement. In the present study, the concentration of calcium is twice compared
458 with the study carried out by Childress. Therefore, more calcium ions are available to interact with both
459 negative functional groups of the membrane and functional groups of the adsorbed HA layer, thus
460 reducing the overall magnitude of the negative potential.

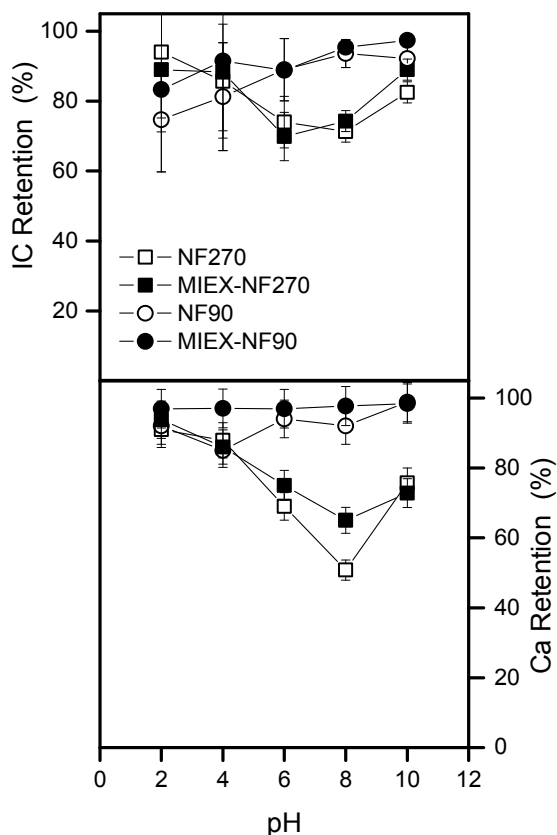
461 In conclusion, the surface potential data supported the hypothesis that the complexation of Ca-HA
462 molecules on the membrane surface was important in the fouling mechanism. This is in accordance with
463 the previous results of flux decline and flux reduction that demonstrated major fouling under alkaline
464 conditions.

465 **4. Calcium and inorganic carbon (IC) retention in NF and combined NF-MIEX**

466 Several studies suggest calcium as one of the main parameters responsible for membrane fouling by HA
467 complexation and bridging with the membrane functional groups, especially at alkaline pH and with the

468 tighter NF membranes [21, 26-28, 30, 71]. Further, calcium interacts with carbonate species at alkaline
469 pH and precipitation of calcite occurs when the solubility limit of species is exceeded (what are those
470 solubility limit then you can estimate) [76]. Published studies reported higher retention of calcium by
471 NF90 (~85-90%) compared with NF270 (40-60%) in absence of organics [57, 58, 70], which is
472 correlated with different calcium concentration at the membrane/feed interface.

473 HA-Ca interaction is expected to increase calcium retention. In consequence, calcium and IC retention
474 was determined in presence of HA during fouling tests. In Figure 9, IC and calcium retention as a
475 function of pH is compared. High IC (75-97%) and calcium retention (92-98%) was determined for NF90
476 independent of pH, while low calcium (65-75%) and IC (75-89%) retention was observed for NF270 at
477 alkaline pH. The calcium concentration measured at the end of the tests after 70% recovery, reported in
478 Figure S20 (Supporting Information), was roughly 4 and 4.8 mM for NF270 and NF90, respectively.
479 Schäfer et al. observed precipitation of calcite at $\text{pH} > 8$ and 3 mM CaCl_2 using a background solution of 1
480 mM NaHCO_3 , 20 mM NaCl [27]. Concentration at the membrane/solution interface will be even higher
481 than the reported values due to concentration polarization and as recovery increases.

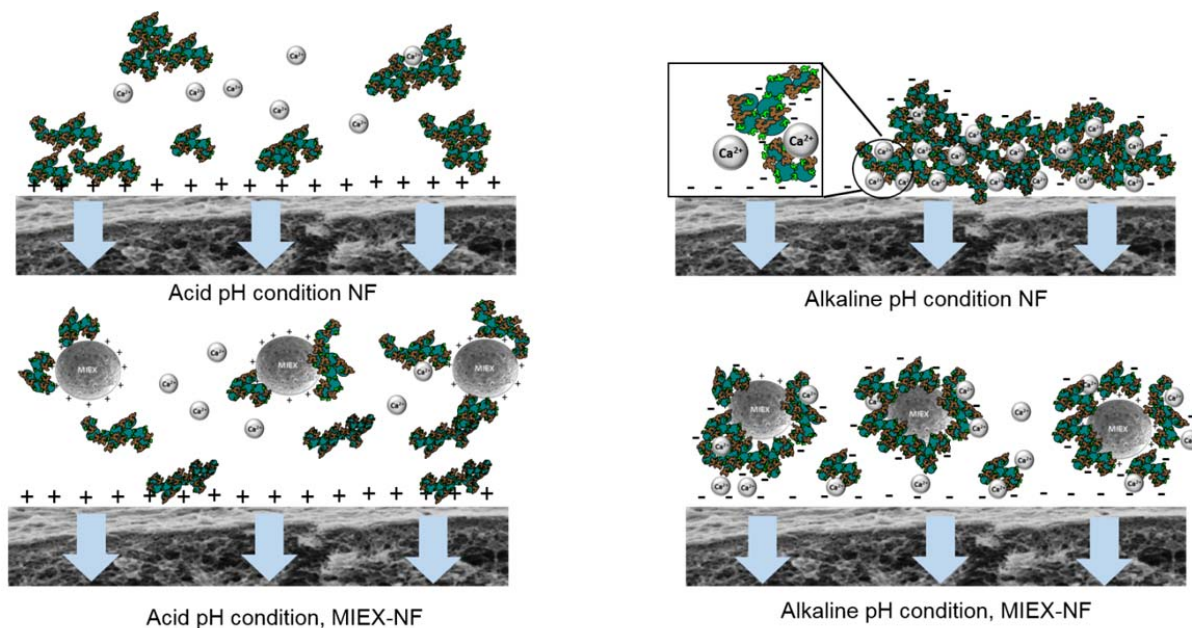


482
 483 **Figure 9.** Calcium and IC retention as a function of pH (12.5 mg/L HA, 2.5 mM CaCl₂, 1 mM NaHCO₃, 10 mM
 484 NaCl, 10 mL/L MIEX, 9.6 bar, 400 rpm, 22 °C, 70% recovery)

485 Both membranes shown different response to pH changes, which may be rationalized with different
 486 retention mechanisms. For the tight NF90 membrane, retention of both carbonate species and calcium was
 487 not affected significantly by pH meaning that 1) there is no evident impact of carbonate speciation on
 488 retention, and 2) electrostatic repulsion is not the dominant retention mechanism of these species.
 489 Hydrated radius for Ca²⁺ and carbonate species (HCO₃⁻ and CO₃²⁻) has been reported to be in a range of
 490 0.26-0.41 nm [9, 77] and 0.26-0.39 nm [78, 79], respectively. NF90 has pore size in the range of 0.31-0.38
 491 nm, suggesting that size exclusion is dominant in retaining carbonate and calcium. In contrast, for the
 492 NF270 membrane, charge repulsion appears to be significant. In fact, the highest calcium retention was
 493 observed at pH 2 and 4 (88-94%) due to the positive charge at the membrane surface (IEP 3). The lowest
 494 retention of both calcium (60-69 %) and IC (70-74%) was observed at pH 6 and 8 when the membrane is
 495 negatively charged. Calcium retention increased to 75% at pH 10 probably due to stronger complexation
 496 with the negatively charged HA molecules and precipitation of calcite. Similar trend for both calcium and
 497 IC is reported in other studies where membrane charge was demonstrated to play major role in solute

498 retention [9, 63]. Retention experiments imply that a larger concentration of calcium is present at the
 499 membrane solution/interface for tighter NF90 membranes than for looser NF270 membranes (how were
 500 you able to exclude flux effects?). In consequence, irreversible organic fouling, was more pronounced for
 501 the NF90.

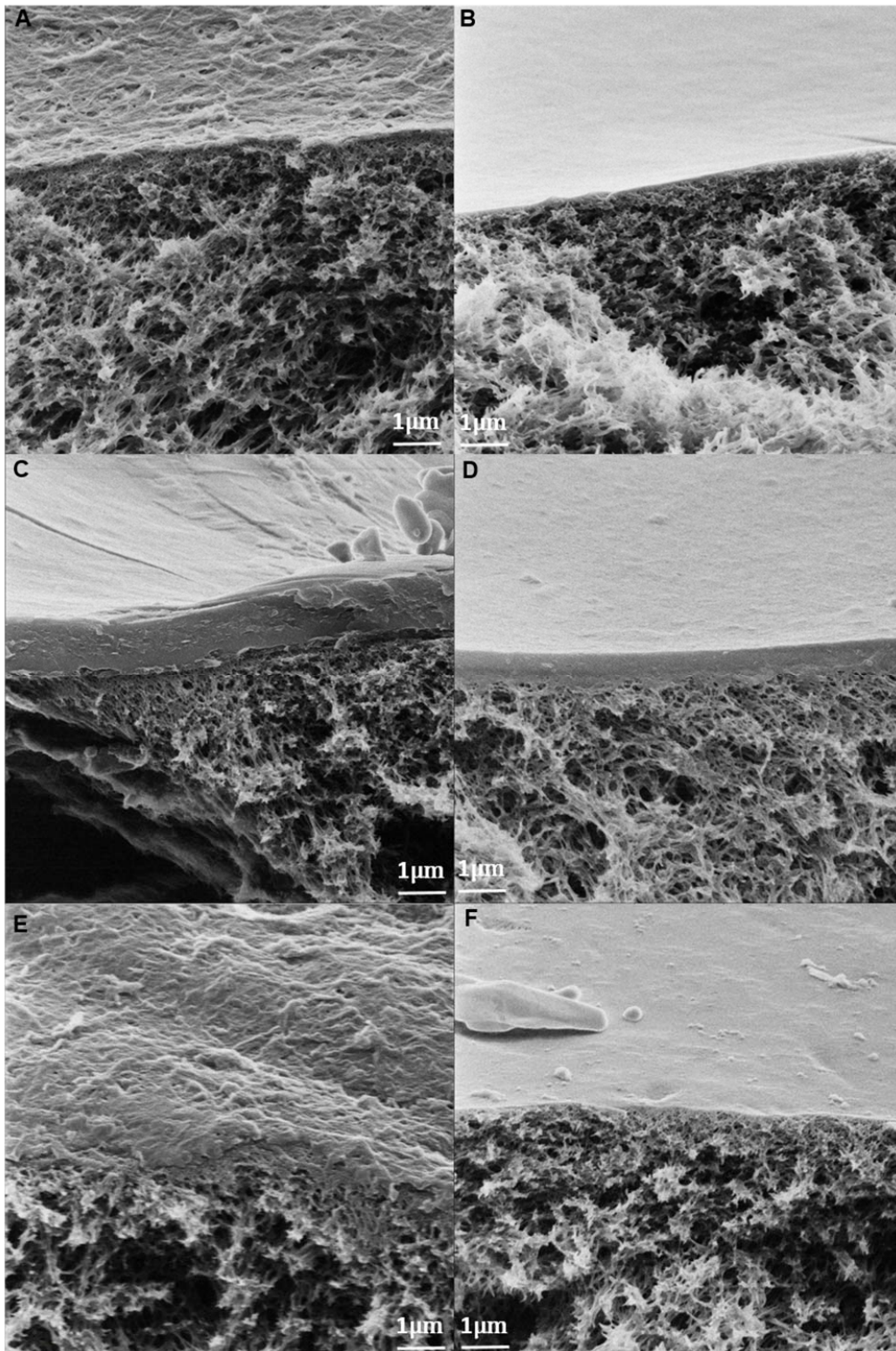
502 A schematic is presented in Figure 10 to summarize the overall HA-Ca-membrane and HA-MIEX
 503 interactions that cause reversible or irreversible fouling under both alkaline and acid pH conditions. In
 504 acidic pH, Ca-HA interactions are negligible due to low HA charge density and fouling is mainly caused
 505 by deposition of HA aggregates, which only interact weakly with the membrane surface. Equally, HA-
 506 MIEX interaction is weak under acidic conditions, while aggregate deposits can be removed by water
 507 rinsing. At neutral to alkaline pH values, relevant for most water sources, HA-Ca complexation as well as
 508 calcium-mediated bridging with the membrane occur due to the negative charges of both membrane
 509 surfaces and HA molecules, resulting in irreversible deposits. This was more significant for the tight
 510 membrane leading to higher calcium concentrations at the membrane/solution interface. However, HA-
 511 MIEX interactions are stronger than Ca-HA interaction, resulting in less favourable HA layer deposition
 512 and lower irreversible fouling of the membrane when resins are present.



513
 514 **Figure 10.** Schematic of HA-Ca-membranes and HA-MIEX interaction mechanisms HA-Ca-membranes
 515 and HA-MIEX in NF and combined NF-MIEX at alkaline and acidic pH condition

516 **3.8 Impact of MIEX on fouling layer morphology analyzed using HIM (or HeIM)**

517 To visualize the fouling layer thicknesses HIM analysis of membrane cross-section was performed. HIM
518 microscope offers several benefits in terms of resolution, material contrast and surface sensitivity due to
519 the unique physics of the interaction of moderate energy helium ions with material surfaces [80]. This
520 offers the possibility to observe the membrane structure without conductive coating, which is instead
521 necessary prior to traditional SEM analysis. Therefore, the fouling layer of HA deposited on the
522 membrane could be preserved and imaged without artifacts resulting from such sample preparation.
523 Figure 11 presents micrographs of the cross-sections of the pristine NF90 and NF270 membranes (Figure
524 11 A and B, respectively), the membranes fouled by HA at pH 8 without MIEX (Figure 11 C and D), and
525 in the combined MIEX-NF process (Figure 11 E and F). Samples at pH 8 were selected as representative
526 of natural water conditions. Both NF90 and NF270 are composed of a polyester support, polysulfone
527 middle layer, and a thin polyamide active layer [81]. In Figure 11 A and B, the thin active layer and the
528 porous substrate were clearly visible in the cross-sectional micrographs. NF90 was characterized by a
529 rough surface while NF270 surface was much smoother, as reported also by Boussu *tr* [58]. A packed and
530 dense deposited layer of HA is visible for NF90 and NF270 in Figure 11 C and D, respectively. However,
531 in the case of NF90 (Figure 11 C), the fouling layer thickness was about 1.1 μm , while it was roughly
532 0.65 μm for NF270, that is, almost 2 times lower. The difference of fouling layer thickness confirmed the
533 data discussed above showing significant flux decline and irreversible fouling for NF90 and less fouling
534 for NF270. At neutral and alkaline pH, HA-Ca complexation enhanced the formation of a densely packed
535 layer on the membrane surface and this effect is more significant for NF90. Moreover, membrane
536 roughness has been reported to be an important parameter affecting fouling of NF membranes [17, 58].
537 Since NF270 is much smoother than NF90, less fouling has been reported in previous studies [24, 58] and
538 this confirms the results obtained in this study where reversible fouling was observed for NF270. Figure
539 11 E and F displays membrane cross-section from the combined MIEX-NF. The densely packed layer of
540 HA observed for fouled membranes in the single NF process was no longer present. In Figure 11 E, the
541 membrane surface of NF90 was comparable with the pristine membrane, meaning that the fouling layer
542 was mostly removed after the rinsing process. This is in agreement with the data discussed above showing
543 low water flux reduction in the presence of MIEX (14-34%). In Figure 11F, the smoother surface of
544 NF270 was apparent and no significant layer deposition was identified. These results corroborate the
545 effectiveness of MIEX to reduce HA layer deposition on the membrane due to either reversible or
546 irreversible fouling.



547

548 **Figure 11.** HIM micrographs of membrane cross-sections: A) clean NF90, B) clean NF270, C) fouled
549 NF90 (pH 8), D) fouled NF270 (pH 8), E) fouled NF90-MIEX (pH 8), F) fouled NF270-MIEX (pH 8).
550 Scale bar is 1 μm

551

552 **4. Conclusions**

553 Magnetic ion-exchange particles (MIEX) and nanofiltration (NF) were combined in one single process to
554 reduce fouling by humic acids (HA). MIEX effectiveness was investigated under different pH conditions
555 and with different membranes (tight and loose) in order to identify interaction mechanisms and optimal
556 operative conditions. Without MIEX, significant fouling by deposition of HA was observed, resulting in
557 high flux decline during operation (30-70%) and irreversible flux reduction (53-78%), especially with the
558 tight membrane (NF90). This phenomenon was more pronounced at alkaline pH: HA-Ca complexation
559 and bridging with the membrane were identified as the main phenomenon responsible for irreversible
560 membrane fouling. A dense and thickly packed HA fouling layer was characterized on the membrane by
561 He-microscope following these experiments. Lower but significant fouling was observed for the looser
562 membrane (NF270) in the absence of MIEX: in this case, the flux decline was 20-50%, and fouling was
563 mostly reversible, as pure water flux reduction after rinsing was 15-23%. These results were confirmed
564 by a fouling layer thickness 2 times lower compared with the deposited layer observed for NF90.

565 One of the main reasons for the different fouling behavior of the two membranes was their different
566 calcium retention. Calcium plays a major role in fouling of the membrane as interaction with HA
567 molecules and membrane surface is stronger in its presence. Calcium retention by NF90 was > 95%,
568 independently of pH, while lower calcium retention (65-75%) was reported for NF270 at neutral to
569 alkaline pH. This implies a larger concentration of the divalent cation at the membrane/solution interface
570 for the tighter membrane, especially at high recovery rates, thus explaining the larger fouling observed
571 with NF90.

572 In the combined MIEX-NF, fouling was significantly reduced, resulting in both lower flux decline during
573 operation and lower irreversible loss of flux. In particular, irreversible flux reduction decreased
574 significantly for NF90, and water flux was fully recovered with NF270. Strong HA-MIEX interactions
575 were especially effective in minimizing calcium complexation and HA layer deposition at neutral and
576 alkaline pH, relevant for real applications. Results demonstrated the effectiveness of MIEX to minimize
577 fouling of NF membrane with different feed chemical compositions and the possibility to apply these
578 resins directly in the membrane system, minimizing or possibly eliminating any feed pre-treatment. This
579 is of great importance considering the wide variability of real water chemistries of sources tapped for
580 drinking water production by NF. Further, addition of MIEX may be an interesting application in tubular
581 or hollow fibre systems as well.

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798 **Organic Fouling through Magnetic Ion Exchange-Nanofiltration (MIEX-NF) in Water Treatment**

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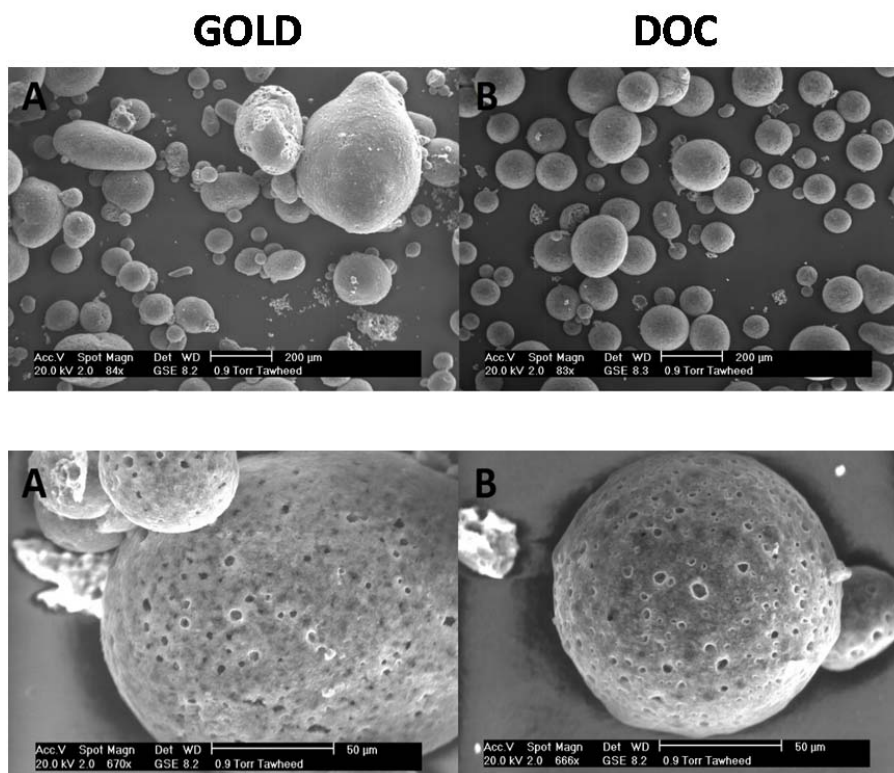
807 ^dKarlsruhe Nano Micro Facility (KNMF), Karlsruhe Institute of Technology (KIT), Hermann-von-
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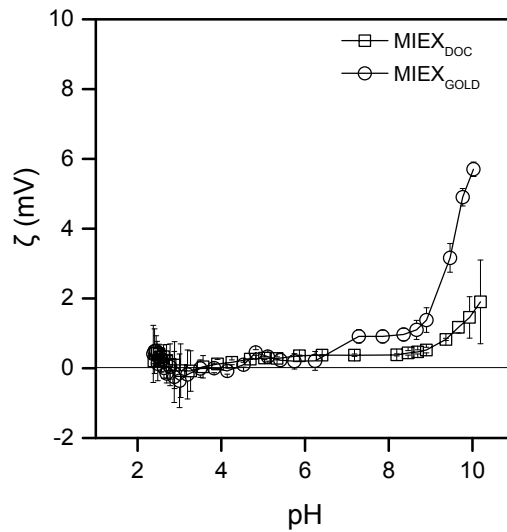
811 SUPPORTING INFORMATION

812 1. ESEM characterization of MIEX_{DOC} and MIEX_{GOLD}



813

814 **Figure S12.** ESEM micrographs of (A) MIEX_{GOLD} and (B) MIEX_{DOC} at different magnifications.



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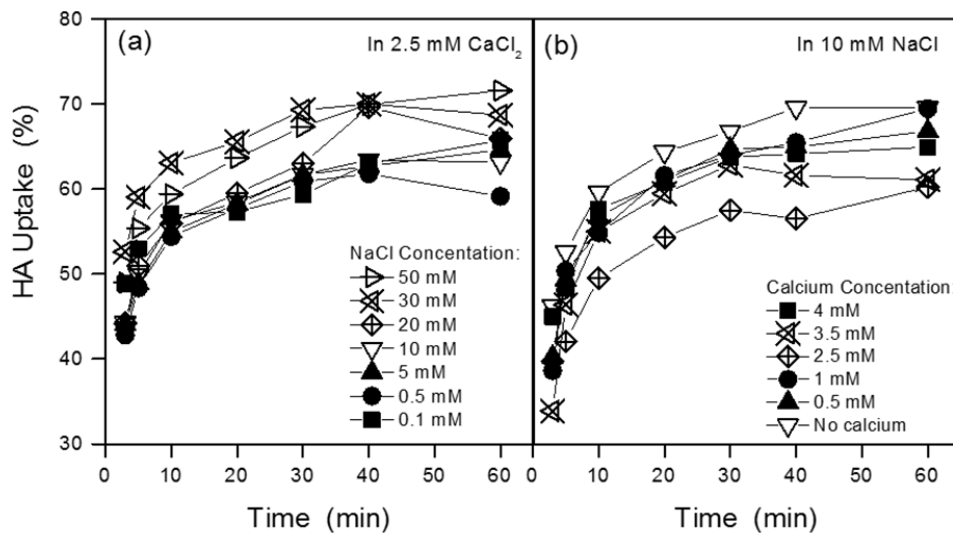
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Figure S13. Zeta potential of MIEX_{DOC} and MIEX_{GOLD} in 1 mM KCl electrolyte solution

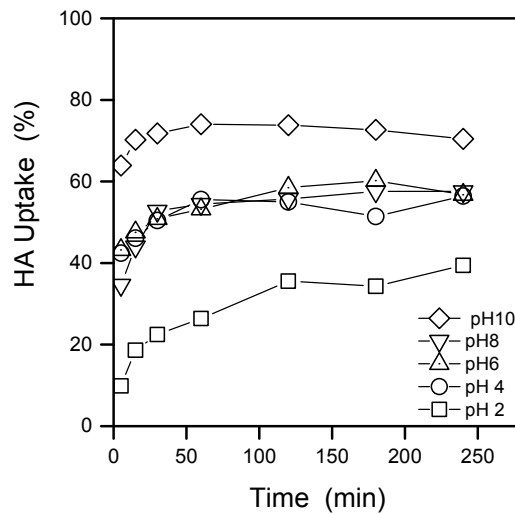
818 **2. Adsorption kinetic of HA by MIEX at different water chemistry: ionic strength, calcium, pH**
 819 **and HA concentration**

820 HA adsorption kinetics by MIEX_{DOC} was determined at different concentrations of NaCl (range 0-50
 821 mM) and calcium (0-4 mM), at different pH (range 2-10) and HA concentration (4-45 mgC/L)



822

823 **Figure S14.** HA uptake kinetics. Influence of (a) Ionic strength (NaCl concentration) and (b) Calcium
 824 concentration (12.5 mg/L HA, 1 mM NaHCO₃, 10 mL/L MIEX, 20 °C, 260 rpm, pH 6)



825

826 **Figure S15.** HA uptake as a function of time at different pH (12.5 mgC/L HA, 2.5 mM CaCl₂, 1 mM
 827 NaHCO₃, 10 mM NaCl, 10 mL/LMIEX, 20 °C, 260 rpm)

828

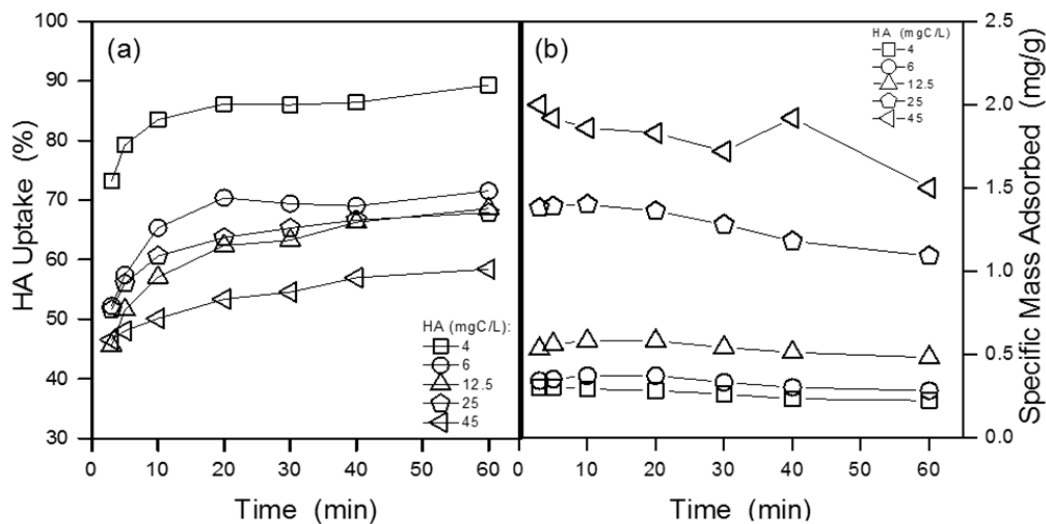
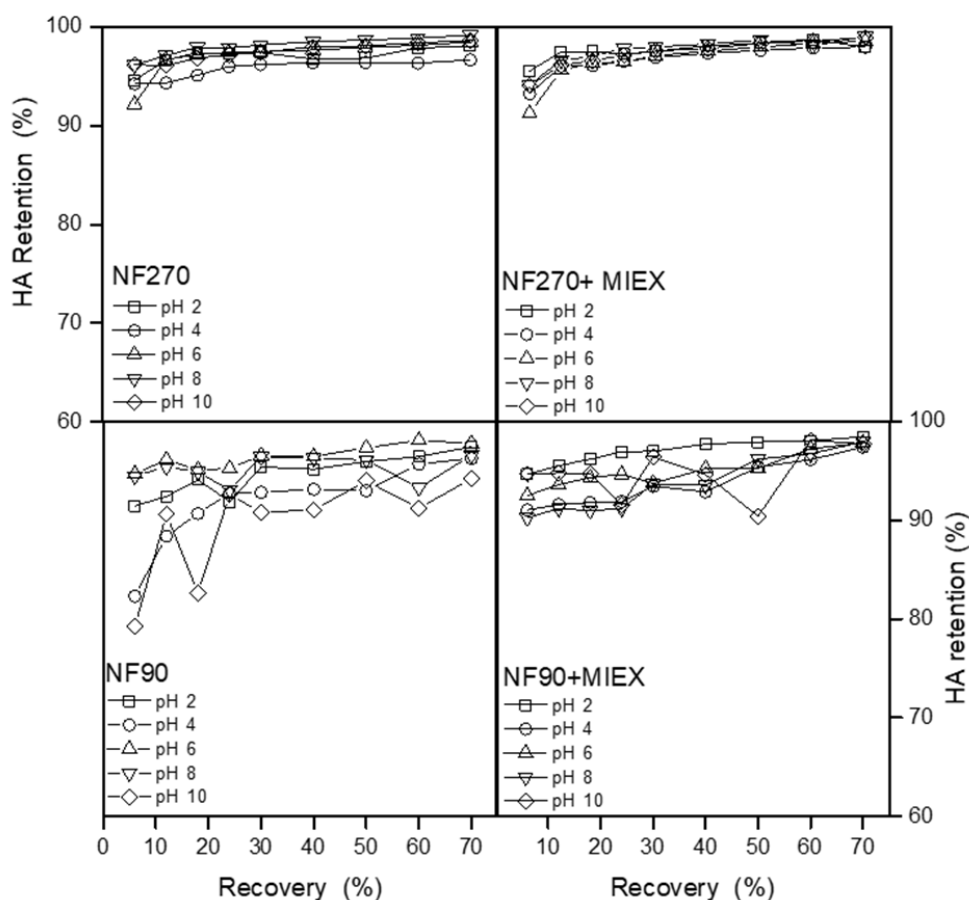


Figure S16. a) HA uptake kinetics at different HA concentrations; b) HA mass adsorbed per unit mass of
 MIEX as a function of time at different HA concentrations (2.5 mM CaCl₂, 1 mM NaHCO₃, 10 mM
 NaCl, 10 mL/L resin, 20 °C, 260 rpm, pH 6)

3. Retention of HA in NF and combined NF-MIEX process

829 Retention of HA as a function of recovery was measured in both NF and NF-MIEX processes.

830 Figure S17 presents HA retention for both membranes (NF90 and NF270) and both processes (NF and
 831 combined NF-MIEX).

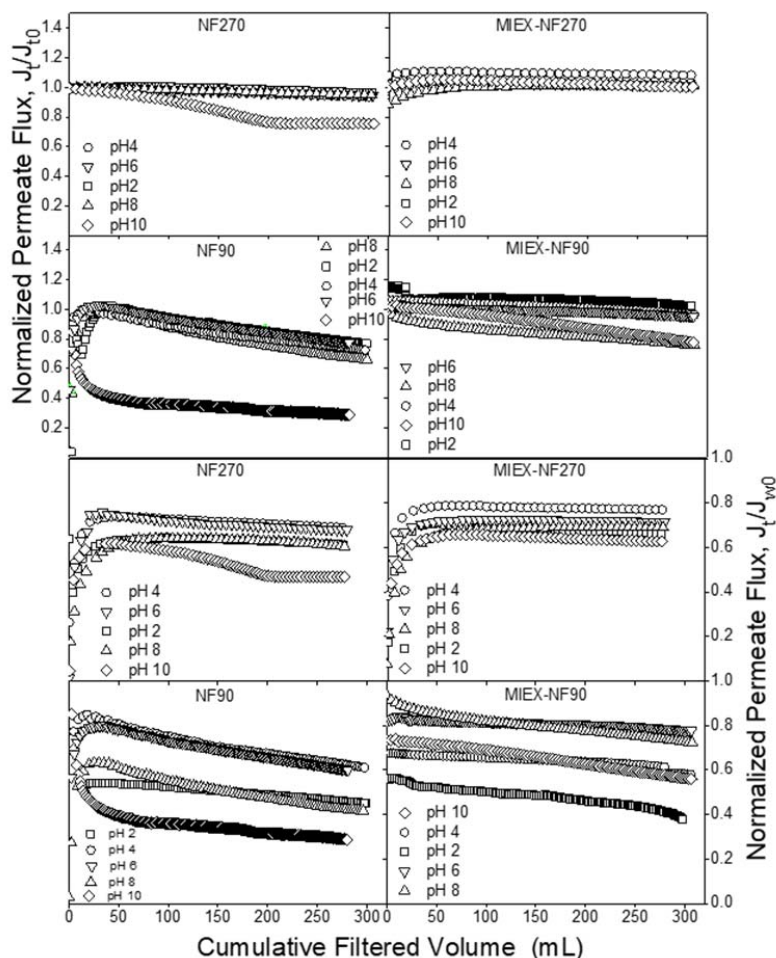


832
 833 **Figure S17.** HA retention as a function of recovery at different pH (12.5 mg/L HA, 2.5 mM CaCl₂, 1
 834 mM NaHCO₃, 10 mM NaCl, 10 mL/L MIEX, 9.6 bar, 400 rpm, 22 °C, 70% recovery)

835 **4. Comparison of normalized permeate flux versus pure water flux (J_{w0}) and initial filtration flux**
 836 **(J_{i0})**

837 Flux decline as a function of filtered volume was calculated by normalizing the permeate flux (J_t) versus
 838 J_{i0} (initial filtration flux) or J_{w0} (pure water flux) in order to evaluate comparability and limitations of both
 839 methods and the influence of the osmotic pressure. Flux decline in NF and combined MIEX-NF for both
 840 NF270 and NF90 membrane samples and at different pH values is reported in Figure S18. When J_{i0} was
 841 used to normalize the flux the effect of osmotic pressure was excluded and flux decline started from 1 for
 842 each experiment. However, as mentioned in the Material and Methods section, in dead-end system initial
 843 unstable conditions occurred due to system adjustment, which introduces limitation to determine precisely
 844 J_{i0} . This was visible in the initial part of the graph where an increase in normalized flux was determined
 845 due to pressure adjustment. In order to establish a J_{i0} value for each experiment, the flux measured at
 846 corresponding pressure of 9.6 bar and stable conditions was considered. The overall trend of flux decline
 847 at different pH in both individual NF and combined NF-MIEX process was comparable with the flux
 848 decline calculated by using J_{w0} as reference value. In individual NF process, higher flux decline was
 849 visible at alkaline pH compared with acidic pH and flux decline was more significant for NF90 compared

850 with NF270. In combined MIEX-NF process, flux decline was reduced significantly for NF90, while it
 851 was negligible for NF270.

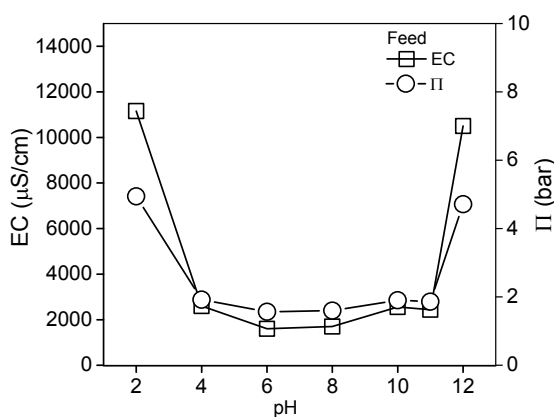


852
 853 **Figure S18.** Normalized flux versus J_{t0} (initial flux of fouling experiments) or J_{w0} (pure water flux) as a function of
 854 filtered volume
 855

856 When J_{w0} was used to normalize the flux, the osmotic pressure of the feed solutions was not taken into
 857 account. As a consequence, the beginning of the flux decline started in a range of 0.8 and 0.6 rather than
 858 1. An osmotic pressure of 0.7 bar is calculated using Van't Off equation by taking into account the
 859 concentration of salts in the feed solution (1 mM NaHCO_3 , 10 mM NaCl and 2.5 mM CaCl_2). However,
 860 the variation of pH, which caused variation of feed solution ionic strength, is not taken into account in the
 861 Van't Off equation. Therefore, conductivity of feed solution at different pH is measured and total
 862 dissolved solids (TDS, mg/L) is calculated from the conductivity (EC, $\mu\text{S}/\text{cm}$) by using the equation TDS
 863 $(\text{mg}/\text{L}) = \text{EC} (\mu\text{S}/\text{cm}) \cdot 0.5$ [82]. The osmotic pressure (Π , bar) of the feed solution at different pH was
 864 estimated by the total dissolved solids (TDS, mg/L) using Equation S1 [83]:

865
$$\Pi = \frac{(70.7 \cdot \text{TDS} \cdot 10^{-6}) + 0.1}{10^{-1}} \quad \text{Eq (S1)}$$

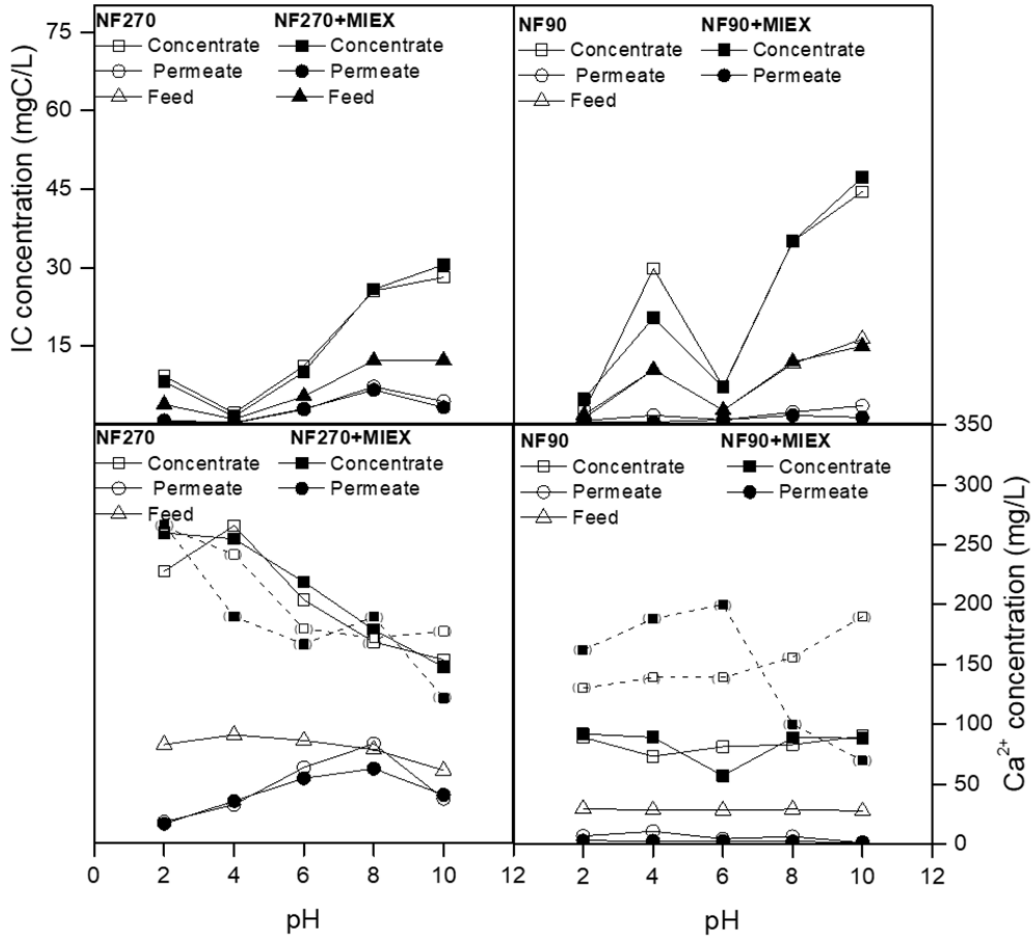
866
 867 Variation of osmotic pressure and conductivity of feed solution as a function of pH is reported in Figure
 868 S19. In the range of pH 4 to 10 conductivity and osmotic pressure were almost constant at values about
 869 2000 $\mu\text{S}/\text{cm}$ and 2 bar, respectively. At extreme pH values (e.g., pH 2 and 12) conductivity increased
 870 significantly and as consequence osmotic pressure of about 4.5 bar was estimated, that is about 2 times
 871 higher compared with the osmotic pressure calculated for the other pH. This variation of osmotic pressure
 872 in addition to permeability variability can be correlated with the variability of the initial trend of flux
 873 decline obtained when J_{w0} was used.



874
 875 **Figure S19.** Conductivity and osmotic pressure of feed solution as a function of pH. Osmotic pressure is calculated
 876 by using Eq. S1
 877

878 **5. Concentration of inorganic carbon (IC) in the feed, concentrate and permeate**

879 IC and calcium concentration were measured in the feed, concentrate, and permeate samples collected
 880 during filtration by NF90 or NF270 for both NF and combined NF-MIEX. The concentration as a
 881 function of pH is reported in Figure S20. Calcium concentration in retentate samples is reported both as
 882 values measured following filtration (points in bracket) and as values calculated based on mass balance
 883 from observed values of feed and permeate samples (using Equation 5 reported in the manuscript). For
 884 NF270, measured and calculated concentrations are in accordance, while a discrepancy was observed for
 885 NF90.



886

887 **Figure S20.** IC and Ca²⁺ concentration in the feed, permeate, and concentrate as a function of pH (12.5
 888 mg/L HA, 2.5 mM CaCl₂, 1 mM NaHCO₃, 10 mM NaCl, 10 mL/L MIEX, 9.6 bar, 400 rpm, 22 °C, 70%
 889 recovery)

890

891 **6. Error calculation**

892 The system error (ΔS) is calculated from the uncertainties of the various experimental parameters:

893

$$\Delta S = \sqrt{\Delta T^2 + \Delta V^2 + \Delta P^2}$$

894

895 where ΔT is the relative error due to temperature variation, ΔV is the relative error due to volume
 896 variation, ΔP is the relative error due to pressure variation.

897 The flux error (ΔJ) is estimated considering the system error and the variability of pure water flux
 898 (ΔJ_{w0}) for each membrane sample:

899

$$\Delta J = J \sqrt{\Delta J_{w0}^2 + \Delta S^2}$$

900

901 where J is the flux for each experiment. Error for HA uptake (ΔHA) by MIEX is estimated from the
902 uncertainties of the TOC analyzer (ΔTOC).

903

$$\Delta\text{HA} = \sqrt{\Delta\text{TOC}^2 + \Delta\text{TOC}^2}$$

904

905 ΔTOC is considered twice because concentration is considered twice in the calculation of HA uptake.

906 Error for IC retention (ΔIC) is estimated using the same method published in Supporting Information of
907 another study which takes into account also degassing of carbonate system at acidic pH [63].

908 Error for Ca^{2+} retention (ΔCa) is calculated from the uncertainties of the ICP-OES (ΔICP).

$$\Delta\text{Ca} = \sqrt{\Delta\text{ICP}^2 + \Delta\text{ICP}^2}$$

909

910 The error terms are reported in the table below:

911

ΔT (%)	ΔP (%)	ΔV (%)	ΔS (%)	ΔJ (%)	ΔTOC (%)	ΔHA (%)	ΔCa (%)
5.1	1.4	1.2	20.5	19.8	13.0	18.4	5.7

912

913