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A Reverse-Selective Ion Exchange Nanocomposite Membrane: Selective Phosphate Recovery via an Outer Sphere Complexation-Diffusion Pathway

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Abstract: Polymer nanocomposite materials are used across multiple fields such as energy storage, power generation, water treatment, and resource extraction. Here, we report on a new discovery that enables phosphate-specific, reverse selectivity in cation exchange membranes. Compared to other phosphate removal/recovery methods that require chemical addition, are batch processes, and/or require multiple processing steps to recover pure phosphate, the process developed here allows for continuous recovery of phosphate with high selectivity. The specific selectivity is enabled through the in-situ growth of hydrous manganese oxide (HMO) nanoparticles (NPs) throughout a cation exchange membrane material that provide a diffusion pathway for phosphate, via specific reversible outer-sphere interaction. Upon incorporating the HMO NPs, the membrane's phosphate permeability increased compared to an unmodified membrane, and the membrane showed improved selectivity of 47, 100, and 20 for phosphate over other competing anions such as sulfate, nitrate, and chloride, respectively. Compared to other membrane separation processes such as an anion exchange membrane, with phosphate selectivity of 5, 1.5, and 1 for sulfate, nitrate, and chloride respectively, this modified cation exchange membrane provides improved selectivity for phosphate. By pairing the interactions of target ions with specific NPs, such nanocomposite ion exchange materials represent a new route for the synthesis of highly selective membranes capable of targeting a range of target ions for multiple applications.

Introduction

Ion selective separation membranes are used in clinical, environmental, food, and analytical applications. However, despite their extensive use, high-precision separations using membranes

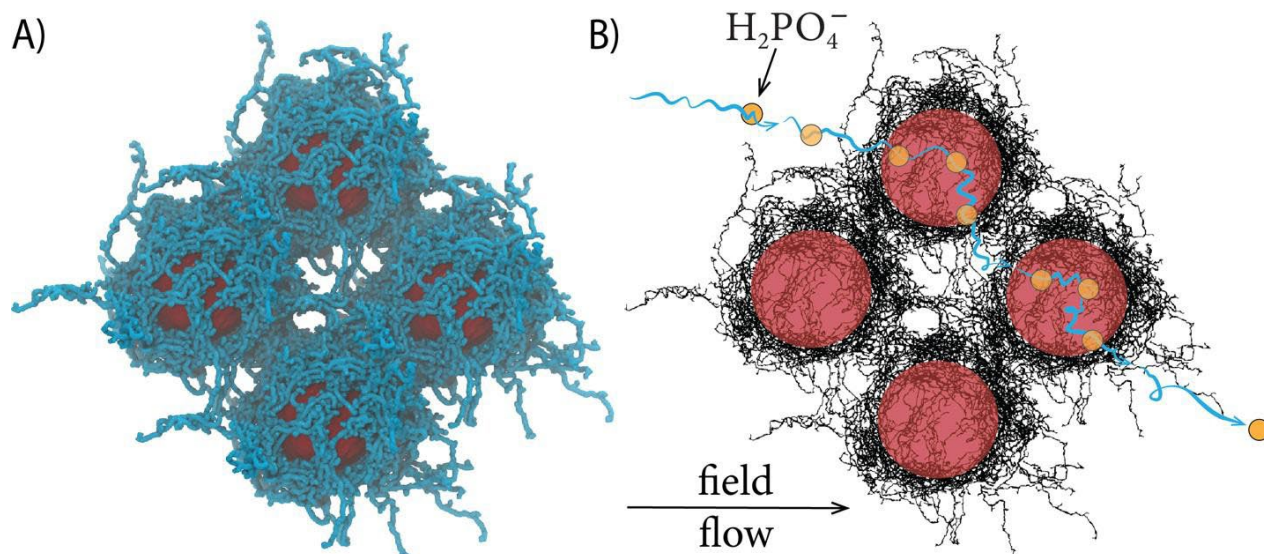
41 remains a challenge. Fine-tuning the selectivity of membranes could increase the efficiency of
42 existing applications and enable novel processes in new fields such as smart materials,
43 electronics, renewable energy, and resource extraction.¹ Increasing demand for resources and the
44 depletion of natural reserves have made it imperative to find alternate sources and technologies
45 to meet the growing need of a modern society.² For instance, deposits of phosphorus and
46 potassium, critical ingredients in fertilizers, are expected to be significantly depleted by the end
47 of the century.^{3,4} Phosphate sequestration has been achieved through precipitation (as struvite),
48 or extraction using organic solvents. These processes require substantial infrastructure
49 investment, high maintenance costs, and may require further separation procedures.⁵ Adsorption
50 of phosphate onto various substrates has been extensively described. Phosphate-specific sorbents
51 include zeolites, slag (produced during steel refining), and metal (hydro)oxides.⁶⁻⁸ However, the
52 recovery of phosphate from these adsorbents requires dramatic pH swings, making the process a
53 batch process by nature. Furthermore, the use of strong acids/bases to drive the pH swing can
54 damage the adsorbent, reducing its lifetime and requiring frequent replenishment.^{6,9} In contrast, a
55 membrane-based phosphate separation process will enable the continuous extraction of
56 phosphate from wastewater without the need for material regeneration or the addition of
57 chemicals to drive a pH swing, enabling the treatment of an environmental contaminant
58 responsible for water resource eutrophication, and the production of a valuable commodity
59 chemical.^{5,6,10,11} However, few reports on membranes that are exclusively selective towards
60 specific anions such as phosphate exist.^{3,4,12-15} In addition, while phosphate is almost always
61 mined, the continuous extraction of phosphate ions from waste streams (such as municipal
62 wastewater) would enable simultaneous treatment of an environmental contaminant responsible
63 for water eutrophication and production of a valuable commodity chemical.^{5,6,10,11}

64 Facilitated transport membranes (FTM) have been used to increase the selectivity of membranes
65 towards specific targets by pairing the target molecule with “extractant” particles/functional
66 groups embedded within the membrane matrix.¹⁶⁻¹⁹ These extractants selectively bind with the
67 target molecule or ion to form a complex, and transport of the target is then facilitated by either
68 the motion of the complex (mobile carrier FTM) or hopping of the target from one carrier to
69 another (fixed carrier/fixed-site FTM).¹⁷ For ion separation, facilitated transport has been
70 demonstrated using polymer inclusion or liquid membranes, but they suffer from poor
71 stability.^{20,21} To solve this stability limitation, we synthesized a novel organic/inorganic
72 composite that enables facilitated transport of target ions through specific outer-sphere
73 interactions between the target and an inorganic component within the membrane. Many
74 transition metals, such as Zr, Cu, and Fe, have hard Lewis acid properties and exhibit preferential
75 adsorptive selectivity toward phosphate.^{22,23} Hydrous manganese oxide (HMO) has also been
76 demonstrated to be an effective phosphate sorbent.^{6,24-26} However, unlike other transition metals,
77 HMO forms weaker outer-sphere complexes with phosphate, which can allow for phosphate ion
78 hopping between adjacent manganese (di/hydro)oxide groups.^{25,27} Embedding HMO NPs
79 throughout a cation exchange membrane (CEM) (Figure 1A), which contains multiple fixed
80 negative charges (e.g., from sulfonate groups) attached to the polymer backbone, creates a
81 diffusion pathway for phosphate across the polymer matrix; other anions (e.g., Cl⁻, NO₃⁻, SO₄²⁻)
82 that do not form complexes with HMO are denied passage due to charge exclusion forces exerted
83 by the CEM’s fixed negative functional groups (Figure 1B).

84 Here we report on the synthesis, testing, and characterization of a facilitated transport mixed
85 matrix membrane capable of selectively extracting phosphate from a mixed anion solution. The
86 membrane is fabricated via *in situ* oxidation of manganese in a CEM to form HMO NPs

87 embedded throughout the CEM (HMO-CEM). Through a combination of experimental and
88 theoretical analysis, we characterize the transport properties of the hybrid material towards
89 phosphate, explain the mechanisms responsible for phosphate transport, and determine that the
90 rate-limiting step for phosphate transport is the complexation reaction between the HMO NPs
91 and phosphate ions. This study explores the fundamental principles behind the selective transport
92 of ions, and paves the way towards a new class of selective membrane materials.

93



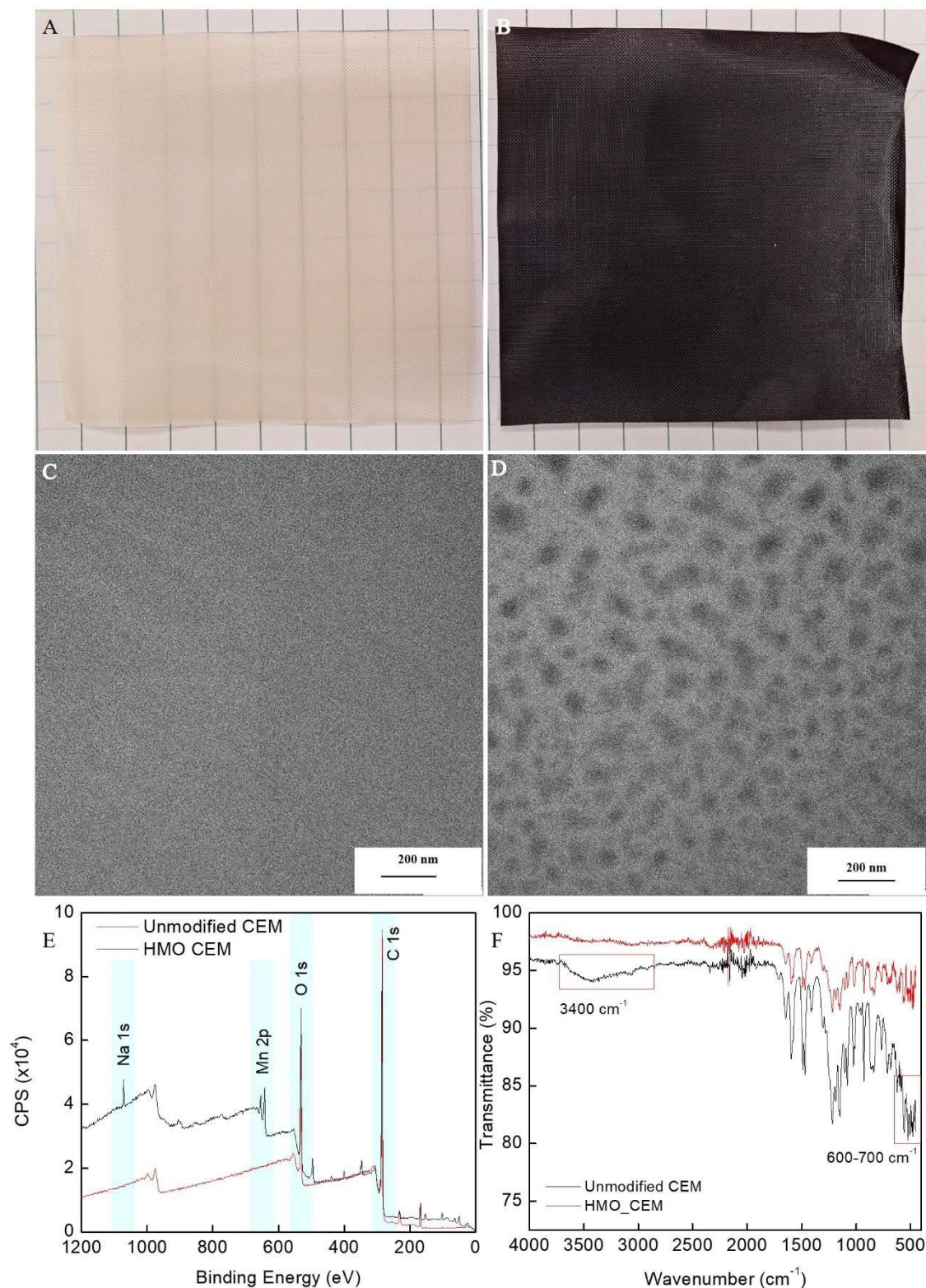
94
95 Figure 1: Molecular representation of the HMO-CEM membrane (A) and proposed mechanism
96 of selective phosphate transport. The weak outer-sphere complexes $H_2PO_4^-/HMO$ are formed
97 within the Stern part of the EDL, which are relatively mobile and can migrate around HMO
98 particle if subjected to external driving force like flow or weak electric field. The $H_2PO_4^-$ ions
99 jump from one HMO particle to another through the intergel solution phase, that is, through the
100 fluid-saturated micro and mesopore spaces. The phosphate ions adsorbed to HMO diffuse within
101 the particle EDL in the direction of the flow or applied electric field.

102 Results & Discussion

103 HMO loading for the two membranes, high loading HMO-CEM and low loading HMO-CEM,
104 was determined to be 117 mg MnO_2/g of membrane and 69 mg MnO_2/g of membrane,
105 respectively. The effect of increasing the HMO loading on the membrane properties such as ion
106 exchange capacity, water uptake, and volume fraction have been described in the SI (Table S1).

107 Visual investigation of the membranes demonstrates the successful modification of the CEM
108 with HMO; while the pristine CEM is a white, slightly transparent material, the HMO-CEM is
109 transformed into a solid black material (Figure 2A, B). The structure and uniformity of the HMO
110 immobilized within the membrane was investigated using transmission electron microscopy
111 (TEM), and X-ray photoelectron spectroscopy (XPS), and X-ray diffraction (XRD). Cross-
112 sectional TEM micrographs of the HMO-CEM clearly show the presence of HMO NPs
113 distributed uniformly throughout the membrane, with an average size of approximately 79.4
114 ± 23.1 nm, while TEM micrographs of the unmodified CEM show no distinguishing features
115 (Figures 2C, D). XRD analysis of the particles and HMO-CEM membrane showed no
116 distinguishing peaks associated with the HMO particles, suggesting that the particle had an

117 amorphous structure (Figure S1). The XPS spectrum of the modified HMO-CEM shows a
118 distinct Mn peak at ~ 642.8 eV, demonstrating the successful incorporation of Mn, at least at the
119 surface of the material (Figure 2E).^{28,29} Fourier transform infrared spectroscopy (FTIR) peaks
120 (Figure 2F) of the HMO-CEM show a weak broad band with a peak centered around 3400 cm^{-1}
121 resulting from the stretching vibrations of $-\text{OH}$ following HMO loading, a broadening of a peak
122 at 600 cm^{-1} , and two additional peaks at 712 cm^{-1} and 681 cm^{-1} , corresponding to the MnO_x
123 stretching, bending, and wagging vibrations, respectively.^{30,31}



124
 125 Figure 2: Photographs of the A) unmodified CEM and B) HMO-CEM. Cross-sectional TEM
 126 micrographs for C) unmodified CEM and D) HMO-CEM show Mn nanoparticles embedded
 127 uniformly within the HMO-CEM matrix with an average particle size of $\sim 79.4 \pm 23.1$ nm. XPS
 128 spectra (E) shows the Mn peak of the HMO-CEM at ~ 642.8 eV, demonstrating successful

129 incorporation of Mn into the CEM; and FTIR spectra (F) shows a weak band at 3400 cm^{-1}
130 resulting from stretching of $-\text{OH}$, and peak broadening at $600\text{-}700\text{ cm}^{-1}$ corresponding to MnO_x
131 stretching and bending vibrations.

132 *Transport and Selectivity of Phosphate using HMO-CEM*

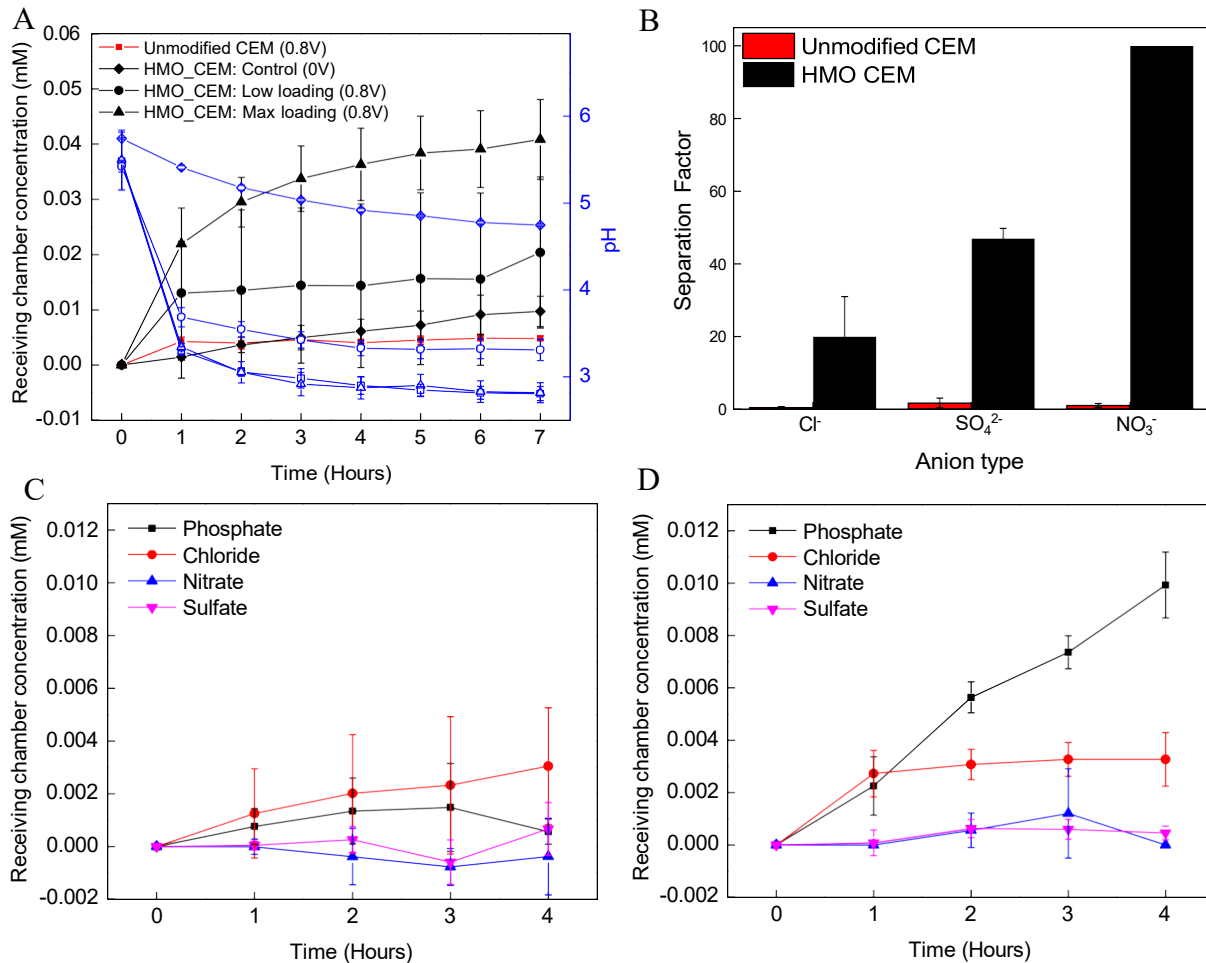
133 Phosphate transport across an unmodified CEM and HMO-CEM with two different HMO
134 loadings shows that the transport rate is highly dependent on HMO loading. The setup for these
135 experiments is described in supplementary materials (section 1) and follows the schematic in
136 Figure S2. As seen in Figure 3A, the unmodified CEM showed extremely low transport rates
137 ($0.8 \times 10^{-8}\text{ mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$, Figure 3A). This result is not surprising considering the high concentration
138 of fixed, negatively charged sulfonate groups within the polymer matrix, which prevent the
139 uptake and passage of phosphate anions. Phosphate transport across the HMO-CEM (with no
140 applied potential, i.e., Donnan dialysis, and with an applied potential, i.e., electro-dialysis) is
141 shown in Figure 3A and S. For both HMO-CEM loadings, the phosphate concentration in the
142 receiving compartment increased over time. For the high HMO loading case, under the effect of
143 the combined driving forces (concentration gradient + electric field; black triangles, Figure 3A),
144 phosphate concentration in the receiving (anolyte) compartment increased for the first three
145 hours, with a flux of $21.7 \times 10^{-8}\text{ mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ (while this flux is low compared to anion fluxes
146 through anion exchange membranes, the flux can be increased by increasing the driving force
147 and, in addition, the membrane exhibits dramatically enhanced selectivity towards phosphate –
148 more on this below). However, after three hours the flux declined to $5.4 \times 10^{-8}\text{ mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$. We
149 speculate that this flux decline is a result of pH-induced changes in phosphate speciation. As the
150 experiment progressed, the pH of the anolyte rapidly declined from 5.5 at $t=0\text{ h}$ to 2.9 at $t=3\text{ h}$ as
151 a result of water electrolysis (Figure 3A). Under the applied electric field, protons generated at
152 the anode migrate towards the cathode, penetrating the HMO-CEM as they migrate between the
153 two chambers, and reducing the inter-membrane pH. Since the pK_{a1} of phosphate is 2.1, as the
154 pH approaches this level, fewer phosphate molecules complexed with the HMO NPs are ionized
155 (H_2PO_4^- vs. H_3PO_4), making them less susceptible to the electrophoretic driving force and
156 slowing their transport across the membrane. Under Donnan dialysis conditions, the pH decline
157 was not as significant (possibly as a result of accumulation of phosphate ions) compared to the
158 pH under electro-dialysis conditions (pH declined to 4.7 from 5.7 after 7 hours). Because the pH
159 never dropped to extreme levels under these conditions, phosphate flux was constant throughout
160 the experiment ($5.1 \times 10^{-8}\text{ mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$). This is further evidenced by the lower phosphate flux and
161 pH drop under an applied potential when using an HMO-CEM with low HMO loading (2.6×10^{-8}
162 $\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$) (Figure 3A, section 2.5 of supplementary materials). The pH in the anolyte, for the
163 low HMO loading experiments, declined to 3.3 over the duration of the experiment, and the flux
164 remained fairly constant as compared to that using a high-loading HMO-CEM. The lower flux
165 for the low-loading HMO-CEM highlights the importance of the embedded HMO NPs in
166 enabling phosphate transport across the CEM.

167

168 *Membrane selectivity towards phosphate*

169 Membrane selectivity experiments revealed superior selectivity of the HMO-CEM in
170 transporting phosphate over other competing anions (Figure 3B). The experiments were
171 conducted under electro-dialysis conditions with a mixture of electrolytes, all at an initial
172 concentration of 1 mM, in the catholyte and DI water as the anolyte. For the unmodified CEM,
173 extremely low transport of all anions was observed with a slight preference for Cl^- transport over
174 other species. (Figure 3C). This result is attributed to the large concentration of negatively

175 charged sites on the CEM. We also tested the selectivity of an anion exchange membrane
176 (AEM). The AEM showed high transport rate for all anions, with little selectivity of phosphate
177 over other anions (Figure S3A). The separation factor of phosphate over other anions was
178 determined to be 1 (for chloride), 5 (for sulfate), 1.5 (for nitrate) (Figure S3B). In contrast to
179 both, the HMO-CEM enabled phosphate to pass through the membrane (with a flux of $11.9\text{E-}8$
180 $\text{mol/m}^2/\text{s}$), while still rejecting all other anion species (Figure 3D). While the unmodified CEM
181 shows a gradual increase in Cl^- concentration over time, the HMO-CEM shows an increase in Cl^-
182 concentration only in the first hour followed by a much lower Cl^- transport rate. This initial
183 increase in Cl^- concentration for HMO-CEM is attributed to the chloride ions added into the
184 matrix as a result of using NaOCl during membrane preparation. Moreover, the drop in Cl^-
185 transport rate across the HMO-CEM as compared to the unmodified CEM could be due to the
186 decrease in the intergel (the region of the CEM that allows co-ion transport) volume upon
187 introduction of HMO NPs.^{32,33} Based on the fluxes of the different anions measured in these
188 experiments, the separation factor of phosphate over chloride, nitrate, and sulfate was determined
189 to be 20, 100 and 47, respectively. The large standard deviation in separation factors for the
190 competing anions are due to the low concentrations of these ions (near the detection limit of the
191 IC), resulting in large variability in concentration measurement, as shown in Figure S4.



193
 194 Figure 3: A) Phosphate concentration and pH in the receiving chamber for an unmodified CEM,
 195 high-loading HMO-CEM, and low-loading HMO-CEM in the presence and absence of an
 196 applied potential. The feed solution was composed of 0.1 M NaH_2PO_4 , while 0.05M Na_2SO_4 was
 197 used as the receiving solution. A potential of 0.8 V vs. Ag/AgCl (2V cell potential) was applied
 198 across two Pt wires used as electrodes in the feed (cathode) and permeate (anode) chambers. (B)
 199 Phosphate selectivity over competing anions (Cl^- , SO_4^{2-} , and NO_3^-) for an unmodified and HMO-
 200 CEM. Phosphate concentration in the receiving chamber for the (C) unmodified CEM, and (D)
 201 HMO-CEM for an equimolar solution (1mM) of NaCl , Na_2SO_4 , NaNO_3 , and NaH_2PO_4 as the
 202 feed solution, and 18M Ω de-ionized water as the permeate; a potential of 0.8V Vs Ag/AgCl (2V
 203 cell potential) was applied across two Pt wires used as electrodes in the feed (cathode) and
 204 permeate (anode) chambers. Error bars represent standard deviations.

205 *Molecular Dynamics Simulation*

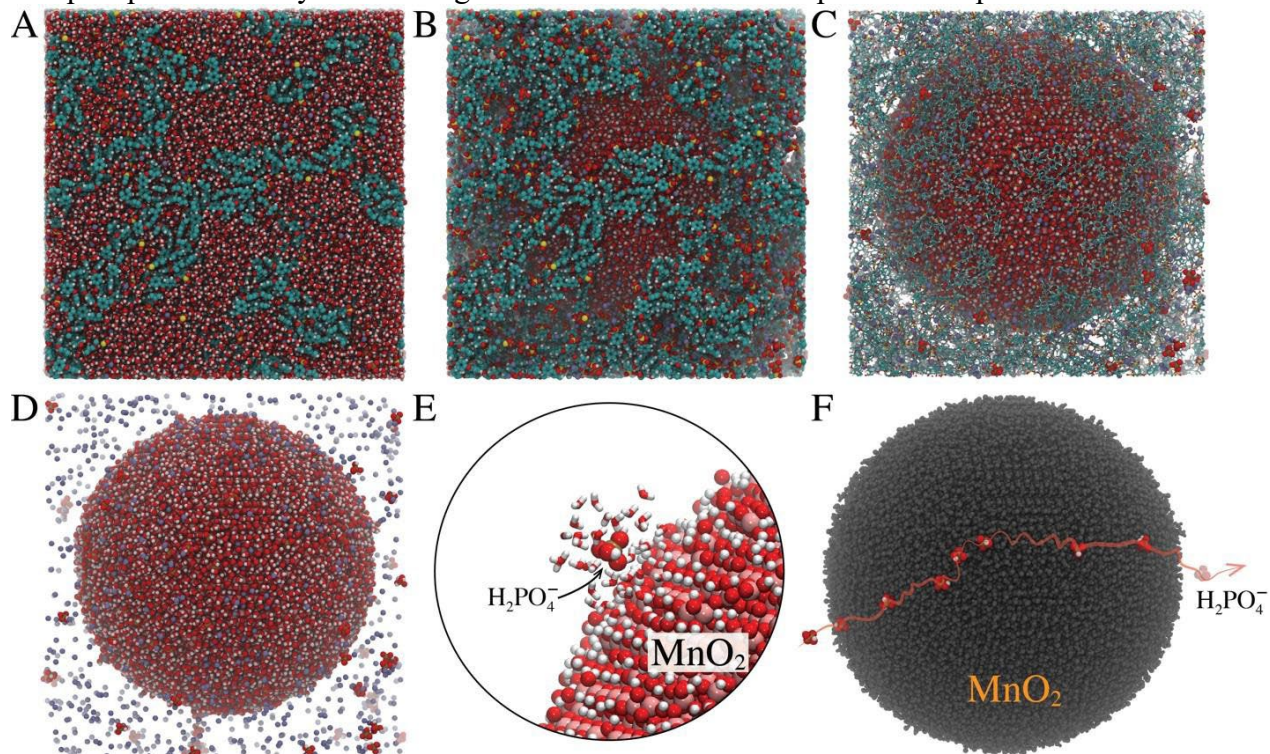
206 To understand the interactions and transport of the ions through the HMO-CEM membrane on
 207 the molecular level, we carried out molecular dynamics simulations of H_2PO_4^- and Na^+ ions in
 208 configurations that resemble the gel and intergel phases of the HMO-CEM (section 2.2 in
 209 supplementary text). The all-atoms simulation protocol imposes a severe restriction on the size of
 210 the simulation cell. Consequently, the size of the embedded HMO particle and pore are scaled

211 down compared to the experimental conditions. Specifically, the diameter of the simulated HMO
212 particle is 10 nm, and the ions can explore the micro- and mesopore spaces of the HMO-CEM
213 composite membrane. In our model, we constrained the size of the HMO particle to 10 nm to
214 minimize the computational load. However, we do not anticipate that the nature of the
215 phosphate-HMO interaction is impacted by the particle size, although we have not verified this.
216 The impact of nanoparticle size is beyond the scope of this paper and is a topic for future studies.
217 The system size is still sufficient to reveal the modes of interactions/complexation by polymer
218 and particle and the molecular mechanism of phosphate transport through the HMO-CEM
219 membrane. In Figure 4A-B, we show molecular snapshots of the HMO-CEM system and the
220 molecular model of the model ion exchange polymer molecule.

221
222 The values of the diffusion coefficients of the H_2PO_4^- and Na^+ ions obtained from the molecular
223 dynamics trajectories are listed in Table S3 (averages over 10 independent simulation runs),
224 where each simulation started from a slightly different initial configuration. The diffusion
225 coefficients for the ions in the aqueous solution are representative of the intergel solution phase,
226 whereas those along the HMO-CEM are representative of the gel phase. As can be seen, the
227 calculated ion diffusivities in the gel phase are approximately three (H_2PO_4^-) and two (Na^+) times
228 lower than their diffusivities inside the intergel solution phase. The presence of the HMO particle
229 increases the mobility of phosphate by about 20%, but has a negligible effect on the mobility of
230 sodium, whose mobility drops by 8% (Table S3). The electric field accelerates the ionic mobility
231 within the gel phase of HMO-CEM by 21% and 27% for phosphate and sodium ions,
232 respectively.

233
234 The ions have the lowest mobility in the system composed of electrolyte solution in contact with
235 the HMO particle (Table S3). Both sodium and phosphate adsorb at the HMO particle surface,
236 forming outer-sphere complexes (Figure 4D). The presence of the negatively charged polymeric
237 matrix accelerates ion transport due to disruption of the weak electrical double layer formed
238 around the HMO particle. Because the negatively charged polymeric matrix attracts Na^+ and
239 repels H_2PO_4^- ions, the Na^+ ions are pulled away from the HMO vicinity, and H_2PO_4^- ions are
240 pushed away from the polymer. Critically, H_2PO_4^- ion interaction with the particle weakens due
241 to the depletion of Na^+ ions around the HMO particle, and electrostatic attraction between
242 H_2PO_4^- and Na^+ ions accumulated near negatively charged groups in the ion exchange polymer.
243 As a result, the mobility of H_2PO_4^- increases nonlinearly in the gel phase of HMO-CEM
244 compared to the cases of CEM or HMO-only systems (Table S3). This nonlinearity is due to the
245 complexity of the ion pathways across the HMO-CEM matrix. First, ion fluxes through the micro
246 and mesopores differ due to the variation in the solvent properties, different proximity of the
247 polymer chains and particle surfaces, and pore-size-dependent permeability. Second, an ion's
248 ability to diffuse against the field or in the direction perpendicular to the field decreases with
249 increasing voltage. As the strength of the field increases, the thermal motion of ions diminishes,
250 and the translation along the field lines dominates their dynamics. If the ion reaches the HMO
251 surface, it can diffuse around it as an outer-sphere complex. However, if the ion becomes trapped
252 in the dense polymer pocket with no exit channel, it will not escape by diffusing against the
253 electric field lines. The voltage-dependent diffusivities (Figure 4C) capture this phenomenon,
254 showing subtle deviation from the expected exponential dependence. While the diffusivities of
255 the individual phosphate ions vary in any given simulation, the simulation shows that the slowest
256 ions are moving through the polymeric channels while the fastest move through the intergel

257 solution phase or near the HMO particles. The molecular dynamics simulations provide a
 258 molecular-level understanding of phosphate transport through the HMO-CEM membrane.
 259 Simulations confirm experimental observations (section 2.2 in supplementary text) that H_2PO_4^-
 260 ions are forming only outer-sphere complexes with HMO, enabling their uptake onto the HMO-
 261 CEM material, and facilitating their diffusion across the membrane. This transport is driven by
 262 an electric field or concentration gradient across the membrane. The simulations also confirm
 263 that phosphate mobility is much higher in the HMO-CEM compared to the pure CEM.



264
 265 Figure 4: Example of the simulation cell used in the molecular dynamics simulations: A) all
 266 atoms shown as vdW-spheres, B) water molecules are hidden, C) water molecules hidden and
 267 polymer represented by the ball-and-stick model, D) only HMO particles and ions are shown,
 268 E) example of the H_2PO_4^- ion with its hydration water in the outer-sphere complex geometry, F)
 269 illustration of the diffusion pathway of adsorbed H_2PO_4^- .

270 *Phosphate transport model*

271 Using our experimental observations, a model describing ion transport across the HMO-CEM
 272 was developed based on the microheterogeneous model for ion exchange membranes (section
 273 2.1 in supplementary text).^{34,35} The model was used to predict the flux and transport number for
 274 phosphate, and was then used to estimate the HMO loading needed to increase phosphate
 275 transport across the membrane. Phosphate flux and transport number were calculated using
 276 equations S9- S25, with the concentration profile for the ions throughout the membrane given by
 277 equation eq. S26. The parameter, n , in equation S26, and the structural parameter, α , in equations
 278 S11 & S22, were treated as adjustable parameters and fit to the model. The value of n (Eq. S26)
 279 defines the concentration profile across the membrane thickness; an $n = 1$ value corresponds to a
 280 linear concentration profile, with increasing n values corresponding to a more rapid, exponential
 281 decline (Figure S5).³⁶ The value of α can vary from -1 to 1 , and represents the connectivity of
 282 the gel and intergel phases of the microheterogeneous model, with $\alpha = -1$ referring to the phases

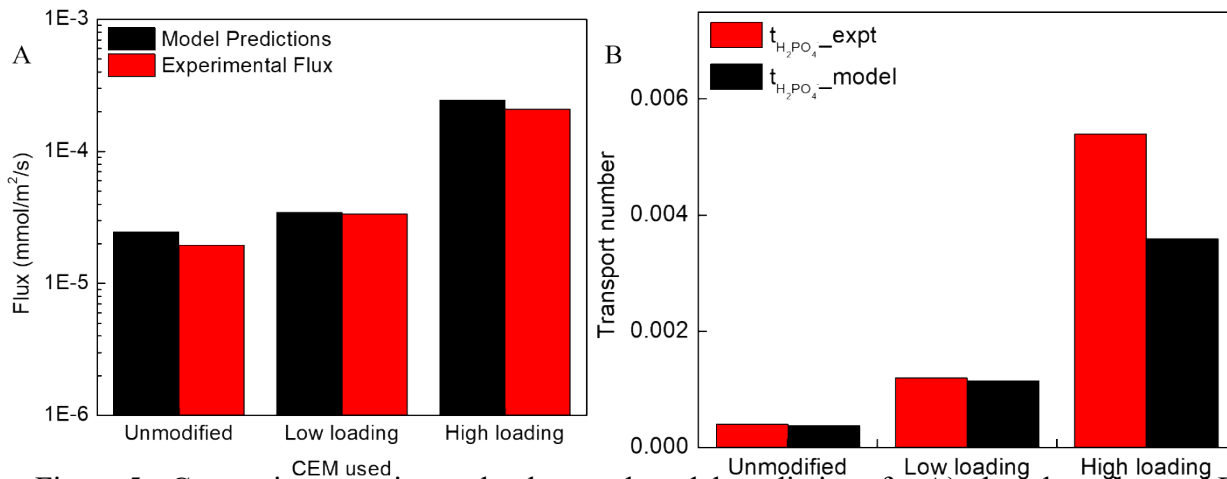
283 connected in a series, while an $\alpha = 1$ refers to a parallel connection.³⁴ We obtained the lowest
284 root mean square error values for the transport number and flux of the unmodified and low-
285 loading HMO-CEM with $n = 10$ and $\alpha = 0.3$, compared to our experimentally-determined values
286 (Table S3); the predicted vs. observed phosphate flux values can be seen in Figure 5A. Although
287 the flux predictions for the unmodified and low-loading HMO-CEM are within 30% of the
288 experimental results, the predicted flux for the high-loading HMO-CEM, using the same n and α
289 values, is almost 2 times lower than the experimental flux (data not shown). However, since
290 hydration of a polymeric membrane leads to the formation of micro and meso-pores, which swell
291 strongly as water intercalates between the polymeric chains within the membrane,³⁷ it is possible
292 that the modification of the membrane by the *in situ* growth of HMO NPs affects the internal
293 membrane structure and changes the α parameter, and by extension, the concentration profile of
294 co-ions within the membrane (the n -parameter). By adjusting the parameters n and α to 5 and
295 0.7, respectively, the predicted flux had an error of about 7% (Figure 5A). Physically, $n = 5$
296 implies that the concentration decline of the phosphate anion across the high-loading HMO-CEM
297 is more gradual compared to that of an unmodified membrane, where an $n = 10$ value yielded the
298 best fit (Figure 5A). This implies that the high concentration of ion-exchange groups in an
299 unmodified membrane limit the presence of co-ions within the membrane, which are thus present
300 primarily near the feed/membrane interface leading to an exponential decline across the
301 membrane thickness (i.e., higher n values). In contrast, in the HMO-CEM, due to phosphate's
302 ability to form outer-sphere complexes with HMO NPs (section 2.6 in SI), phosphate
303 concentrations throughout the material are higher resulting in a linear decline in concentration as
304 one moves away from the membrane/feed interface. Similarly, introduction of a large quantity of
305 HMO NPs alters the internal structure of the membrane; an increased value of α ($\alpha = 0.7$)
306 represents a more parallel orientation of the gel and intergel phases in relation to the transport
307 axis (perpendicular to the membrane surface) as compared to that of an unmodified membrane.

308
309 The ion transport numbers predicted by the model were compared to those obtained from the
310 experiments in Figure 5B. Transport numbers describe the fraction of current carried by a
311 particular ion species relative to the overall current passing through the system (eq. S23). For the
312 case of phosphate transport across unmodified and modified CEMs, the model predicts that the
313 addition of HMO to the CEM matrix increases the fraction of current carried by phosphate.
314 Moreover, it also accurately calculates transport numbers for the unmodified and low loading
315 HMO-CEM. Thus, for these membranes, our simplifying assumption that accounts for sodium
316 and proton transport during the experiments (see eq. S23 and S24) is valid. However, the model
317 under-predicts the transport number for the high loading HMO-CEM by ~30%, thus indicating
318 that at higher HMO loadings the simplifying assumption fails to appropriately account of
319 fraction of phosphate transport and thus its transport number.

320
321 The model predicts a higher gel-phase diffusion coefficient for anions over cations, by nearly
322 two orders of magnitude (Table 1). This could be attributed to the electrostatic attraction between
323 cations and the polymeric fixed charges, which the anions/co-ions do not experience.³⁸ While
324 this may seem counter-intuitive (since the flux of cations is much higher than that of anions), the
325 higher flux can be explained by Donnan exclusion, which causes counter ions to partition into
326 the membrane at a higher rate than co-ions, resulting in higher counter ion concentrations within
327 the membrane. Thus, cations are transported across by interaction with the fixed charges in the
328 gel phase of the membrane, while the anions are transported through the electroneutral solution

329 present in the intergel phase and the cation and anion transport are correlated (coupled) to
 330 maintain charge-neutrality of the fluid phase. In the HMO phase, the diffusion coefficient of
 331 phosphate is higher than that of cations. Importantly, the specific interactions of phosphate ions
 332 with the HMO particles enables their partitioning into and diffusion across the HMO-CEM,
 333 resulting in a higher diffusion coefficient for the phosphate anions. As a result, phosphate is
 334 transported across the membrane through the intergel phase by „hopping“ along the HMO NPs.
 335

336 Finally, the model was used to estimate the HMO loading that would yield a phosphate flux
 337 comparable to phosphate flux through an anion exchange membrane. Increasing the HMO
 338 loading of a CEM affects its properties including water uptake, ion exchange capacity, the
 339 diffusion coefficient of salt through the membrane, and the volume fraction occupied by the NPs
 340 within the membrane. However, since most of these values were obtained from experiments and
 341 used as inputs into the model, extrapolating the model to accurately predict phosphate flux at
 342 higher HMO loading is riven with uncertainty. During the formation of HMO NPs within the
 343 CEM (according to the reactions listed in 1.2), Na^+ displaces the Mn on the charged fixed sites,
 344 forming the eventual HMO particles in the vicinity of the gel phase, which could possibly
 345 explain the decrease in ion exchange capacity with increase in the HMO loading (Table S1).
 346 Assuming that the ion exchange capacity decreases and f_{int} (volume fraction of intergel phase in
 347 the membrane) increases linearly with f_p (volume fraction of particles within the membrane), we
 348 can estimate that for $f_p = 0.07$, the flux of phosphate would increase to $1.04 \times 10^{-5} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$,
 349 comparable to the cation flux through CEM and anion flux through an anion exchange
 350 membrane.³⁹⁻⁴¹ It is also possible that NP size could affect the performance of HMO-CEM. We
 351 speculate that a decrease in NP size would lead to decrease in the ion exchange capacity since
 352 the smaller sized NPs would block the fixed charges and decrease their charge exclusion effect
 353 on the co-ion. However, our model does not account for NP size and the experimental work is
 354 beyond the scope of this study.



355
 356 Figure 5: Comparing experimental values and model predictions for A) phosphate flux and B)
 357 phosphate transport number.

358 Table 1: Results from the microheterogenous model

	[mM]	[M]	[m ² /s]	[m ² /s]

Unmodified	0.24	4.49	3.00×10^{-9}	2.65×10^{-11}	0.0004
Low-loading	0.35	3.07	3.01×10^{-9}	3.87×10^{-11}	0.0011
High-loading	0.62	2.91	3.03×10^{-9}	4.06×10^{-11}	0.0036

359 In this study, we successfully synthesized, characterized, and tested a new class of membranes
360 that allow for selective transport of phosphate across a cation exchange membrane. Selective
361 separation is achieved by exploiting the outer-sphere complexation reaction between phosphate
362 and the embedded HMO NPs within the membrane. This technique paves the way towards a
363 novel approach to specific ion recovery, which utilizes similar complexation interactions
364 between the target ions and the embedded extractant groups in ion exchange membranes, while
365 the fixed charges prevent passage of competing co-ions. Other ionic species such as lithium,
366 uranium, gold, and metals that exist as oxy-anions (including arsenic, vanadium, and hexavalent
367 chromium) could possibly be extracted by employing appropriate NPs that complex with the
368 target ion. Thus, these membranes demonstrate an innovative technology desirable from the
369 perspective of both water quality (due to toxicity) and resource recovery.

370 **Methods**

371 **Materials.** A commercial CEM (Fumasep FKS-PET-130, FuelCellStore, College Station, TX)
372 and AEM (Fumasep FAS-PET-130, FuelCellStore, College Station, TX) were used for this study
373 and were either used without further modifications or modified as described below. Manganese
374 chloride tetrahydrate ($\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$, Reagent grade, Sigma Aldrich), manganese (II) sulfate
375 monohydrate ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$, 99%, extra pure, ACROS Organics), sodium hydroxide (NaOH,
376 pellets, certified ACS, Fisher), Sodium hypochlorite (NaOCl, 7.1% available chlorine, Clorox),
377 sodium phosphate monobasic monohydrate ($\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$, 98%, ACS reagent, Sigma Aldrich),
378 sodium sulfate (Na_2SO_4 , Certified ACS, Fisher), sodium nitrate (NaNO_3 , Certified ACS, Fisher),
379 and sodium chloride (NaCl, ACS grade, Fisher) were used as received.

380 **1.2 Preparation of HMO-CEM.** HMO was loaded into the CEM, to form the Mixed Matrix
381 Membrane (MMM) HMO-CEM, by using a three step process, modified from Qing and Pan.^{42,43}
382 First, the CEM in its dry form was immersed in a solution containing 2.5 M $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ and 3
383 M $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ (5.5 M total Mn^{2+} concentration) for either 1 hour or 24 hours (to form a low-
384 loading and high-loading (fully loaded) HMO-CEM, respectively). As a result, Mn^{2+} in solution
385 exchange with H^+ in the membrane:⁴²

386 ()

387 Next, an oxidizing solution was prepared by dissolving NaOH into a sodium hypochlorite
388 solution to prepare a 1M NaOH solution with 7% NaOCl (w/w). The Mn-exchanged membrane
389 was then immersed into the oxidizing solution for either 1 hour or 24 hours, for the low- and
390 high-loading HMO-CEM, respectively, and the Mn^{2+} counter-ions were oxidized to produce
391 HMO (unbalanced):

392 () ()

393 Finally, The HMO-CEM was then washed with copious amounts of deionized (DI) water and
394 vacuum dried at 50 °C for at least 12 hours. The prepared HMO-CEM was immersed in a 0.5 M
395 $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ solution prior to experiments.

396 **1.3 Membrane Characterization.** The surface morphology and cross-sectional structure of the
397 unmodified CEM and HMO-CEM were studied using scanning electron microscopy (SEM)
398 equipped with energy dispersive X-ray spectroscopy (EDX) (ZEISS Supra 40VP SEM), and
399 transmission electron microscopy (TEM; TF20 High Resolution EM, FEI). X-ray photoelectron
400 spectroscopy (XPS; Kratos Axis Ultra DLD spectrometer equipped with a monochromatic Al K α
401 X-ray source) was used to characterize the elemental composition of the membrane surface and
402 the oxidation state of manganese; all binding energies were referenced to the C 1s peak at 284.8
403 eV. Chemical bonds in the membranes were evaluated using Fourier transform infrared
404 spectroscopy (FTIR) operated in transmission mode (Thermo Scientific FTIR iS10 Smart iTR
405 Basic), with a Ge prism as an internal reflection element. FTIR was also used to evaluate
406 possible Mn-P interactions in the phosphate loaded HMO-CEM; for this, the sample was
407 prepared by soaking the membrane in 0.5M NaH₂PO₄·H₂O solution for 24 hours, rinsed with DI
408 water, and dried at 50 °C for 12 hours. To measure the total amount of HMO NPs incorporated,
409 the HMO loaded membranes were weighed before and after placing them in a high temperature
410 furnace. The weight of the ash is subtracted to achieve the weight of HMO nanoparticles. The
411 HMO quantity is normalized to the membrane surface area to calculate HMO loading.

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