

1 **Non-Polyamide Based Nanofiltration Membranes Using Green**
2 **Metal-Organic Coordination Complexes: Implications for the Removal of**
3 **Trace Organic Contaminants**

4 Hao Guo,[†] Lu Elfa Peng,[†] Zhikan Yao,[†] Zhe Yang,[†] Xiaohua Ma,^{†‡} Chuyang Y. Tang*[†]

5

6 [†] Department of Civil Engineering, The University of Hong Kong, Pokfulam, Hong Kong
7 SAR, China

8 [‡] Shanghai Key Laboratory of Multiphase Materials Chemical Engineering, Chemical
9 Engineering Research Center, East China University of Science and Technology, 130 Meilong
10 Road, Shanghai 200237, China

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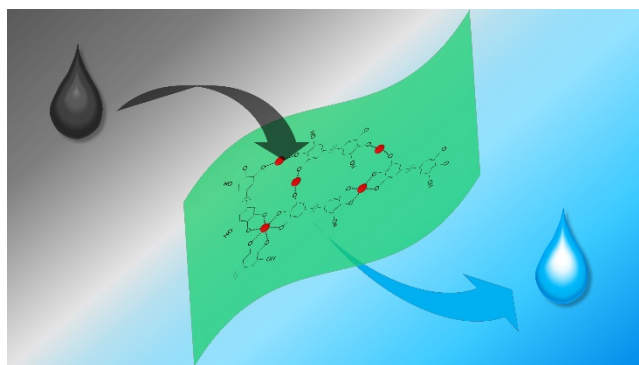
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20 *Corresponding Author: Chuyang Y. Tang, tangc@hku.hk, +852 28591976

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22 **TABLE OF CONTENTS**



23

24 **ABSTRACT**

25 Polyamide-based thin film composite (TFC) membranes are generally optimized for salt
26 rejection but not for the removal of trace organic contaminants (TrOCs). The insufficient
27 rejection of TrOCs such as endocrine disrupting compounds (EDCs) by polyamide
28 membranes can jeopardize product water safety in wastewater reclamation. In this study, we
29 report a novel non-polyamide membrane chemistry using green tannic acid-iron (TA-Fe)
30 complexes to remove TrOCs. The nanofiltration membrane formed at a TA-Fe molar ratio of
31 1:3 (TA-Fe₃) had a continuous thin rejection layer of 10-30 nm in thickness, together with a
32 water permeability of 5.1 Lm⁻²h⁻¹bar⁻¹ and a Na₂SO₄ rejection of 89.7%. Meanwhile, this
33 membrane presented significantly higher rejection of EDCs (up to 99.7%) than that of
34 polyamide membranes (up to 81.8%). Quartz crystal microbalance results revealed that the
35 sorption amount of a model EDC, benzylparbaen, by TA-Fe₃ layer was nearly two orders of
36 magnitude less than that by polyamide, leading to reduced transmission and higher rejection.
37 Further analysis of membrane revealed a much greater water/EDC selectivity of the TA-Fe₃
38 membrane compared to the polyamide membranes.

39

40 INTRODUCTION

41 Modern wastewater reclamation plants generally use thin film composite (TFC) polyamide
42 membranes to retain a wide range of pollutants including dissolved solutes.¹⁻³ Due to their
43 historical roots in desalination, polyamide membranes have been optimized for salts rejection
44 (e.g., rejection of NaCl \geq 99% by reverse osmosis membranes).⁴ Trace organic contaminants
45 (TrOCs) such as antibiotics and endocrine disrupting compounds (EDCs) are ubiquitous in
46 wastewater. Compared to common inorganic salts, TrOCs presents more critical challenges in
47 water reuse.⁵⁻⁸ Many of these contaminants are toxic and harmful to human health and aquatic
48 environment.^{9, 10} Nevertheless, current polyamide-based TFC membranes are often not
49 adequate for the removal of small molecular-weight TrOCs (e.g., < 500 Da), particularly these
50 non-charged and hydrophobic compounds.¹¹ For example, rejection of EDCs \leq 50% have
51 been widely reported for both nanofiltration (NF) and reverse osmosis (RO) membranes of
52 polyamide chemistry,¹²⁻¹⁵ which presents a significant health risk associated with water
53 reuse.¹⁶

54

55 The heterogeneous nature of polyamide layer may be a critical drawback related to the low
56 rejection of TrOCs. It is commonly believed that polyamide layer has nonuniformly
57 distributed functional groups and crosslinking degrees,¹⁷⁻²⁰ which may create a
58 non-homogeneous film containing mixed hydrophobic/hydrophilic and polar/non-polar
59 regions.²¹ Some localized regions can serve as hot spots for the transport of contaminants.
60 For instance, hydrophobic regions allow EDCs to pass more easily as a result of their

61 hydrophobic interactions.²²⁻²⁴ The physicochemical nature of polyamide may also enable
62 supramolecular interactions such as hydrogen bond and π - π stacking between membrane
63 material and EDCs.²⁵ Surface modification and functionalization of polyamide-based
64 membranes have been reported to enhance membrane rejection of TrOCs.^{12, 26-28} Up to date,
65 the use of non-polyamide based membranes for the retention of TrOCs has not been explored.

66
67 A recent study by Ejima et al. reported that tannic acid (TA)-iron (Fe) coordination complexes
68 have the ability to rapidly form a thin film on a variety of substrates.²⁹ TA is a natural
69 polyphenol with a molecular formula $C_{76}H_{52}O_{46}$ (*Supporting Information, Section S1*). It is
70 widely used in medical products and as food additives.³⁰ The coordination structure of TA-Fe
71 has been reported for biomedical capsules, drug delivery, and catalysis.^{29, 31, 32} This chemistry
72 has also been recently explored for membrane surface modification and fouling control.³³
73 Coating a TA-Fe layer onto a commercial polyamide membrane led to significantly improved
74 rejection of EDCs.³⁴ These findings prompt us to hypothesize that a TA-Fe based rejection
75 layer has much higher selectivity against EDCs compared to traditional polyamide
76 membranes.

77
78 In this study, we report the use of non-polyamide TA-Fe assembled membranes for the
79 rejection of TrOCs for the first time. Membrane separation performances including water
80 permeability, rejection of salts, and removal of TrOCs were systematically investigated. The
81 TA-Fe membranes showed significantly high rejection of hydrophobic EDCs. Our findings

82 call for a paradigm shift from designing membranes for salts removal to designing
83 membranes for targeted contaminants removal in membrane-based wastewater reclamation.

84

85 **MATERIALS AND METHODS**

86 **Chemicals.** Unless specified otherwise, all chemicals used were of analytical grade. TA
87 (Tianchem Co., Shanghai) and iron (III) chloride (Dieckmann, Hong Kong) were used for the
88 fabrication of non-polyamide membranes. Sodium chloride (Uni-Chem) and sodium sulfate
89 (Uni-Chem) were used for salt rejection evaluation. Methylparaben, ethylparaben,
90 propylparaben, benzylparaben, sulfadiazine, sulfamethoxazole, sulfamethazine, trimethoprim,
91 norfloxacin, and ofloxacin were bought from Sigma-Aldrich (St. Louis, MO) and used as
92 model TrOCs. In addition, ethylene glycol, diethylene glycol, triethylene glycol, hexaethylene
93 glycol, and sucrose (Dieckmann, Hong Kong), were used as molecular probes to investigate
94 the effect of size exclusion. The physicochemical properties of the TrOCs and molecular
95 probes were summarized in Table S1 (*Supporting Information, Section S2*).

96

97 **Preparation of TA-Fe Membranes.** A polyethersulfone (PES) substrate (SM, Synder
98 Filtration, Inc., CA) was first placed in a custom-designed container with its top surface
99 exposed for membrane casting.¹² According to the manufacturer, the PES substrate has a
100 molecular weight cut-off of 20 kDa. The substrate was rinsed and stored with deionized (DI)
101 water overnight before further using. The substrate was exposed to a 30 mL FeCl₃ solution
102 (0.24, 2.4, 7.2, or 24 mM) at room temperature (25 °C) under moderate shaking for 30 s.

103 Subsequently, a 30 mL TA solution (2.4 mM) was introduced with a contact time of 60 s to
104 form TA-Fe rejection layer. The prepared membranes were rinsed with and stored in DI water
105 for further use. The membranes formed with TA-Fe molar ratio of 1:0.1, 1:1, 1:3, and 1:10
106 were denoted as TA-Fe0.1, TA-Fe1, TA-Fe3, and TA-Fe10, respectively.

107

108 **Membrane Characterization.** Unless specified otherwise, all the membrane samples were
109 vacuum freeze dried for at least 24 h before characterization. Membrane surface morphology
110 was characterized by a field-emission electron microscope (FE-SEM, S-4800, Hitachi). Dried
111 samples were coated with a thin layer of gold using a sputter coater (BAL-TEC SCD 005).
112 The acceleration voltage of SEM was 5.0 kV. Elemental composition of the membrane surface
113 was determined by an X-ray photoelectron spectroscopy (XPS) using an SKL-12
114 spectrometer (Leybold, Shenyang) equipped with a VG CLAM 4 MCD electron energy
115 analyzer. An $K\alpha$ gun (1496.3 eV) was used as X-ray source and operated at 10 kV and 15 mA
116 with a spectra range of 0-1000 eV at a resolution of 0.1 eV. Membrane cross-section was
117 characterized by a transmission electron microscope (TEM, Technai G2 20 S-TWIN, FEI) at
118 an accelerating voltage of 100 kV. An energy-dispersive X-ray spectroscopy (EDX) was used
119 to determine the elemental composition of the cross-section.

120

121 **Membrane Separation Performance.** Membrane separation performance was evaluated
122 using a lab-scale cross-flow filtration system.¹² Briefly, membrane coupons were placed in
123 three parallel cross-flow filtration cells (CF042, Sterlitech, WA). Water flux was tested using

124 DI water as feed. Salt rejection were measured using a 10 L feed solution containing 10 mM
125 NaCl or 3.4 mM Na₂SO₄ (pH 6.8 ± 0.1). Both feed solutions had an ionic strength of
126 approximately 10 mM, which is in the typical range for water reuse applications.³⁵ The tests
127 were conducted at a pressure of 3 bars and cross-flow velocity of 22.4 cm/s after 12 h
128 pre-compaction at 3 bars. To measure the rejection of TrOCs, stock solutions (1 g/L) of TrOCs
129 were spiked into the feed solution (10 mM NaCl, pH 6.8 ± 0.1) to obtain a concentration of
130 200 µg/L for each compound. The TrOCs rejection tests were performed for a duration of 12 h
131 (excluding membrane pre-compaction time) at 3 bars at room temperature (~25°C). During
132 this testing period, both permeate and retentate were recirculated back to the feed tank. Feed
133 solution and permeate samples were collected for the analysis of TrOCs using an
134 ultra-performance liquid chromatograph with double mass spectra (UPLC-MS/MS).³⁴ The
135 rejection of each molecular probe was determined using a feed solution containing 200 mg/L
136 of the compound. The concentration of the molecular probes was analyzed by a total organic
137 carbon (TOC) analyzer (Shimadzu). The separation performance of one semi-aromatic
138 membrane NF270 and two fully aromatic polyamide membranes of NF90 and XLE^{36, 37} (Dow
139 Chemical Co.) were also investigated for comparison purpose following identical
140 experimental protocol.

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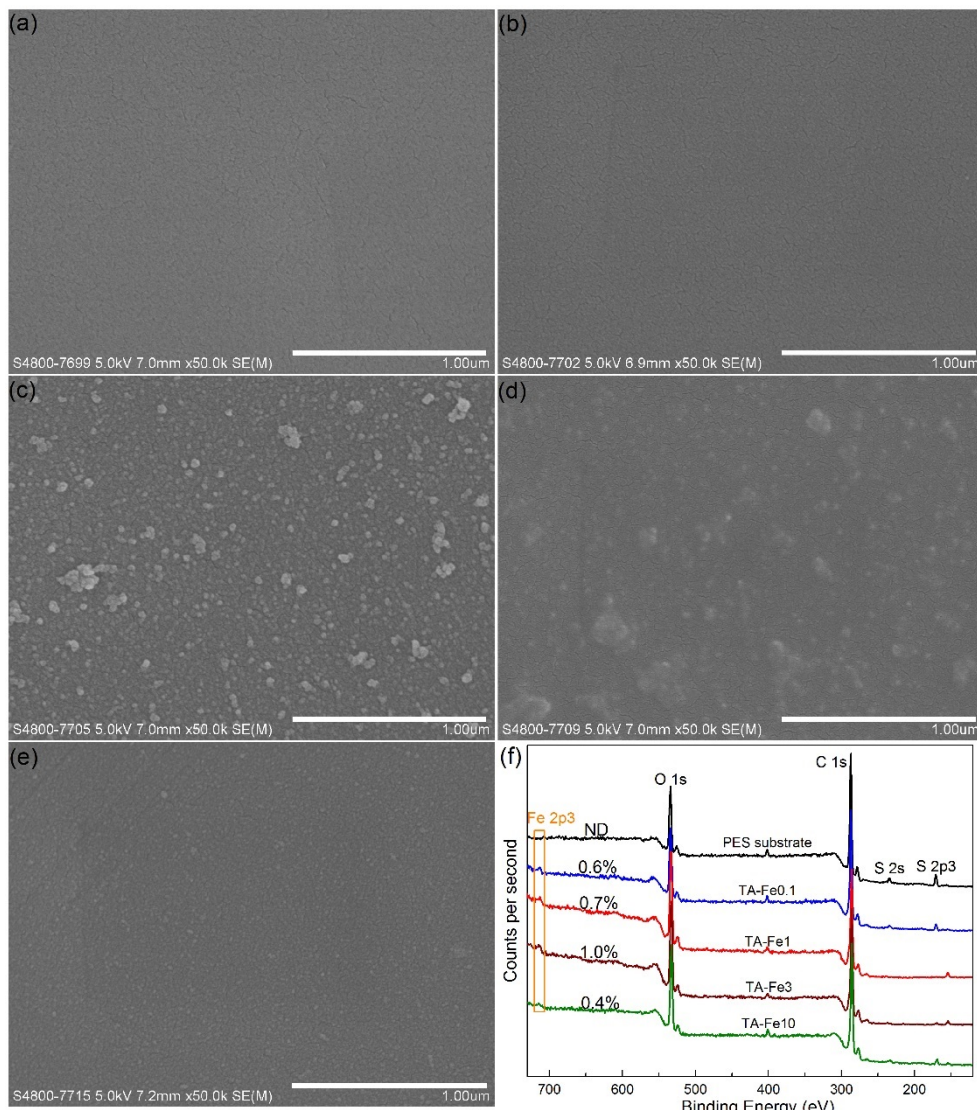
142 **Quartz crystal balance (QCM) analysis.** A QCM (Biolin Scientific) was used to
143 characterize the sorption of a model EDC, benzylparaben, onto different materials, including
144 polyamide, TA-Fe₃ coated polyamide, and bare TA-Fe₃ layer. All the materials were

145 embedded on gold-coated quartz wafers using a custom-designed cell (*Supporting*
146 *Information, Section S3*). The coated wafers were placed in three parallel flow cells
147 individually, and ultrapure water was pumped into the cell to rinse the system for a duration of
148 10 min. Subsequently, 1 g/L benzylparaben water solution was introduced into the system to
149 investigate its sorption behavior on three materials. The frequency change of the three wafers
150 were monitored and transformed into quantity using the Sauerbrey equation.³⁸

151

152 **RESULTS AND DISCUSSION**

153 **Microscopic Characterization.** Figure 1 presents the SEM surface morphology and XPS
154 elemental composition of both the substrate and the TA-Fe membranes. Membranes formed
155 with TA-Fe molar ratio of 1:1 and 1:3 (i.e., TA-Fe1 and TA-Fe3, respectively, Figure 1c-d)
156 had some particle-like deposition on the surface compared to the smooth surface of substrate
157 (Figure 1a). According to our previous work,³⁴ a TA-Fe molar ratio of 1:3 is optimal for
158 forming TA-Fe coordination complexes. XPS analysis (Figure 1f) showed a maximum Fe
159 content of 1.0% for TA-Fe3 membrane. In comparison, TA-Fe0.1 and TA-Fe10, with lower Fe
160 content (0.6-0.7%), show no significant change on surface morphology (Figure 1a, e). These
161 results are consistent with a prior study that TA-Fe layer is formed as a result of the strong
162 binding between Fe and the galloyl groups in TA (see *Supporting Information, Section S1*).
163 According to Ejima et al.,²⁹ each Fe³⁺ ion can react with up to three galloyl groups, which
164 leads to an optional molar ratio in the range of 1:1 to 1:3. A molar ratio outside this optimal
165 range (e.g., 1:0.1 and 1:10 in this study) could result reduced TA-Fe coating and thus lower Fe



167
 168 **Figure 1. SEM micrographs of top surface of (a) substrate, (b) TA-Fe0.1, (c) TA-Fe1, (d) TA-Fe3, and**
 169 **(e) TA-Fe10, as well as (f) XPS spectra of top surface of various membranes.**

170
 171 The TEM micrograph of the TA-Fe3 cross-section further confirmed the formation of a
 172 continuous thin rejection layer of 10-30 nm in thickness (Figure S3, *Supporting Information*,
 173 *Section S4*). The EDX elemental mapping showed a strong signal of Fe in this rejection layer
 174 (Figure S3, green part), implying the successful loading of TA-Fe. The presence of sulfur was
 175 attributed to the PES substrate membrane. Compared to conventional TFC polyamide

176 chemistry, the simple and green TA-Fe chemistry can be potentially more cost-effective and
177 environmentally-friendly.²⁹

178

179 **Water and salt transport properties.** Water and salt transport properties of various
180 membranes are presented in Table 1. The formation of TA-Fe thin layer on the substrate
181 significantly reduced membrane water permeability from $A = 82.9 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$ for substrate
182 to $A = 5.5\text{-}40.0 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$ for the TA-Fe membranes. Due to the poor formation of TA-Fe
183 coordination complexes for TA-Fe0.1 and TA-Fe10, these membranes presented higher water
184 permeability and lower salts rejection. In comparison, TA-Fe1 and TA-Fe3 showed better
185 separation performance which can be attributed to the optimal formation of TA-Fe thin film
186 with molar ratio from 1:1 to 1:3.²⁹ The TA-Fe3 membrane exhibited nanofiltration-like
187 properties with a NaCl rejection of 53.1% (Table 1) and Na₂SO₄ rejection of 89.7% (Table S2,
188 *Supporting Information, Section S5*). These rejection properties are slightly lower than the
189 commercially available semi-aromatic nanofiltration membrane NF270 (Table 1). In
190 comparison, fully aromatic polyamide membranes (e.g., NF90 and XLE) show significantly
191 higher rejection of salts (Table 1 and S2).

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198

199 Table 1. Water and salt transport properties of PES substrate membrane, TA-Fe
 200 non-polyamide membranes, and commercially available polyamide membranes.

Membrane	Water permeability, A ($\text{L m}^{-2} \text{h}^{-1} \text{bar}^{-1}$)	NaCl rejection (%)	NaCl permeability, B_{NaCl} ($\text{L m}^{-2} \text{h}^{-1}$)	A/B_{NaCl} (bar^{-1})
PES substrate	82.9 ± 8.7	1.7 ± 0.4	16030 ± 3920	0.01 ± 0.00
TA-Fe0.1	40.0 ± 4.3	5.0 ± 3.2	4170 ± 3090	0.02 ± 0.01
TA-Fe1	7.0 ± 2.5	48.3 ± 2.4	15.3 ± 1.1	0.46 ± 0.03
TA-Fe3	5.5 ± 1.2	53.1 ± 9.6	10.0 ± 3.8	0.40 ± 0.26
TA-Fe10	19.3 ± 6.17	15.0 ± 7.6	437 ± 390	0.09 ± 0.07
NF270 ^a	13.4 ± 1.7	61.1 ± 7.7	90.9 ± 37.7	0.17 ± 0.06
NF90 ^b	7.1 ± 0.7	83.5 ± 2.9	11.3 ± 2.3	0.63 ± 0.14
XLE	6.0 ± 0.6	85.8 ± 1.8	2.8 ± 0.2	2.17 ± 0.12

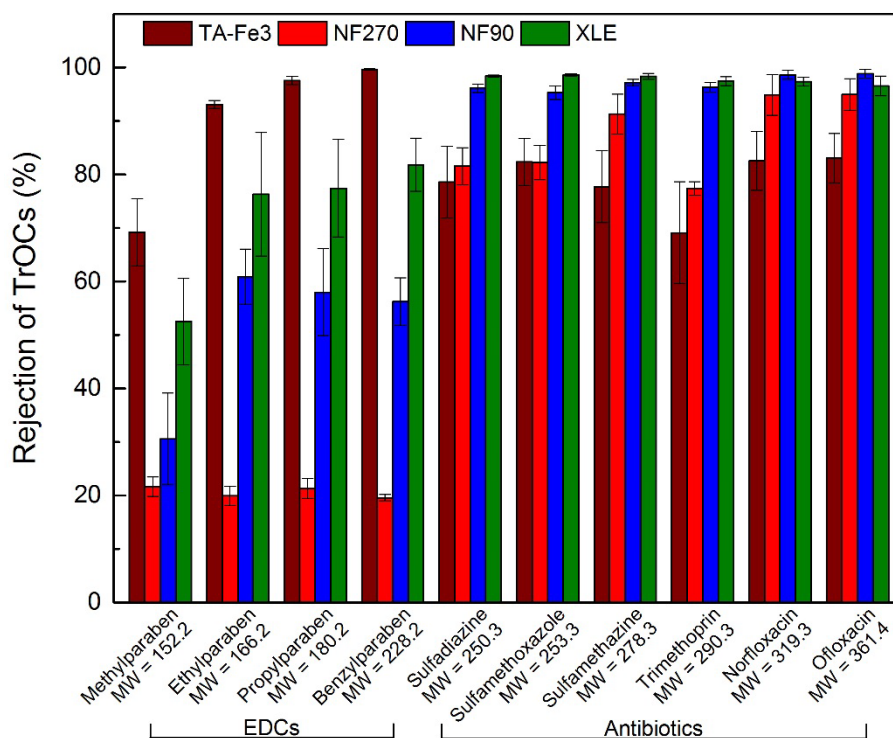
201 a. The data were obtained from reference 18.³⁴

202 b. The data were obtained from reference 22.²⁶

203

204 **Rejection of TrOCs and molecular probes.** Figure 2 presents the rejection of TrOCs by
 205 TA-Fe3, NF270, NF90, and XLE membranes. The non-polyamide TA-Fe3 membrane showed
 206 significantly higher rejection of hydrophobic EDCs than all the polyamide-based NF270,
 207 NF90, and XLE. The rejection rates of methylparaben, ethylparaben, propylparaben, and
 208 benzylparaben by TA-Fe3 were 69.2%, 93.1%, 97.6%, and 99.7%, respectively. These
 209 rejection values were significantly better compared to the best-performing polyamide
 210 membrane XLE (52.5%, 76.3%, 77.4%, and 81.8%, respectively). On the other hand, the
 211 polyamide membranes showed overall better rejection of hydrophilic antibiotics than the
 212 TA-Fe3 membrane.

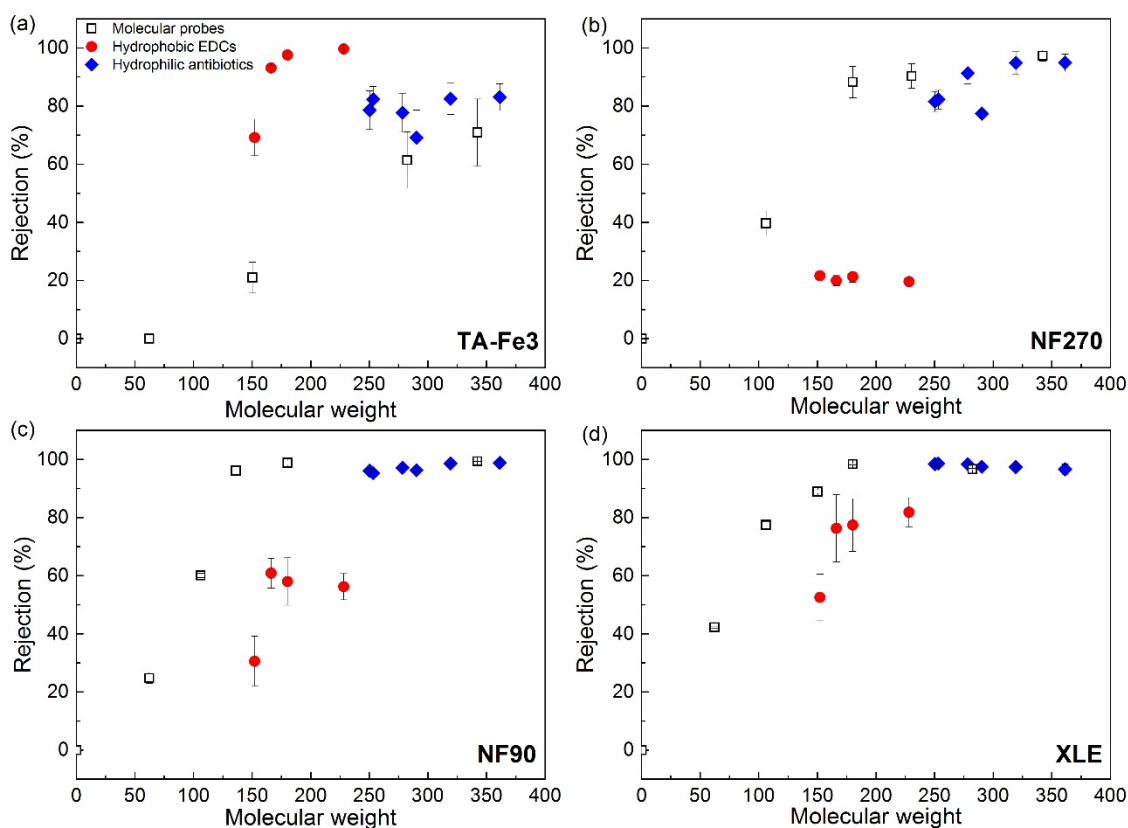
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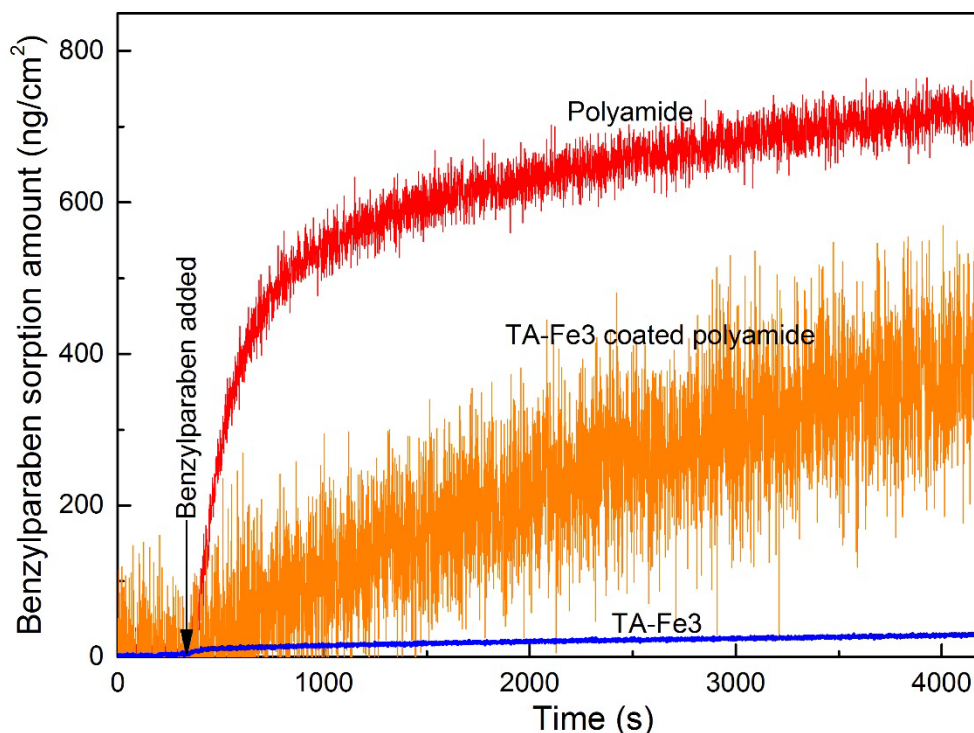
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 215 **Figure 2. The rejection of TrOCs by non-polyamide based TA-Fe3, polyamide-based NF270, NF90,**
 216 **and XLE. The selected TrOCs were classified to two groups, hydrophobic EDCs and hydrophilic**
 217 **antibiotics. Within each group, the compounds were sorted with ascending order of their molecular**
 218 **weight. The error bars represented the standard deviation of the results of at least three independent**
 219 **tests. The data of NF270 was obtained from our previous work.³⁴**

220
 221 To further analyze the rejection behavior of various membranes for different compounds, the
 222 effect of molecular weight on the rejection of both TrOCs and molecular probes were
 223 evaluated (Figure 3). In this study, we purposely used molecular probes with neutral and
 224 hydrophilic nature, such that their rejections are dominated by size exclusion.¹¹ Generally, the
 225 rejection of hydrophilic antibiotics by all membranes followed the same trend of the
 226 molecular probes, suggesting the critical role of size exclusion on the rejection of antibiotics.
 227 The fully aromatic polyamide NF90 and XLE membranes showed higher rejection of
 228 antibiotics than semi-aromatic NF270 and the non-polyamide TA-Fe3 membrane, which is
 229 ascribed to the stronger size exclusion effects for the former. Indeed, these membranes also

230 had better rejections of the molecular probes (e.g., ethylene glycol, diethylene glycol,
 231 triethylene glycol, hexaethylene glycol, and sucrose) compared to NF270 and TA-Fe₃,
 232 confirming their tight membrane structure. In contrast, the rejection of hydrophobic EDCs
 233 behaved very differently. For the TA-Fe₃ membrane, its rejection of EDCs was much greater
 234 compared to that of molecular probes with similar molecular weights (Figure 3a). On the
 235 other hand, all the polyamide membranes presented much lower rejection of EDCs compared
 236 to that of molecular probes (Figure 3b-d), which can be attributed to the unfavorable
 237 interactions between polyamide and EDCs (e.g., hydrophobic interaction^{12, 15} and π - π
 238 stacking²⁵) that promotes the sorption of EDCs into the polyamide membranes.



239
 240 **Figure 3. The effect of molecular weight on the rejection of TrOCs and molecular probes. The**
 241 **selected molecular probes were ethylene glycol, diethylene glycol, triethylene glycol, glucose,**
 242 **hexaethylene glycol, and sucrose, with molecular weight of 62.1, 106.1, 150.2, 180.2, 282.3, and 342.3,**
 243 **respectively. The error bars represented the standard deviation of the results of at least three**
 244 **independent tests. The rejection data of molecular probes for NF90 and all data for NF270 were**
 245 **obtained from our previous work.^{26, 34}**



246
 247 **Figure 4. The sorption amount of benzylparaben in polyamide, TA-Fe3 coated polyamide, and bare**
 248 **TA-Fe3 using QCM characterization.**

249

250 **Mechanistic insight.** The solution-diffusion theory states that the transport of a solute
 251 through a dense membrane is governed by its sorption and diffusion inside the membrane.³⁹
 252 Enhancing either sorption or diffusion can result in accelerated transmission of a solute (thus
 253 a lower rejection). In our prior study, we reported a strong inverse correlation between the
 254 sorption of EDC and its rejection by the membrane.¹² In order to characterize the sorption
 255 behavior of EDCs into TA-Fe3 and polyamide membranes, we performed QCM
 256 measurements using wafers coated with polyamide, TA-Fe3 or both using benzylparaben as a
 257 model EDC (Figure 4). The bare TA-Fe3 layer showed the least sorption of benzylparaben,
 258 with nearly two orders of magnitude reduction compared to that of polyamide. Polyamide
 259 presented the greatest sorption amount of benzylparaben, which may be attributed to the
 260 strong hydrophobic interaction between the compound and hydrophobic moieties of

261 polyamide.^{15, 40} The significantly higher benzylparaben sorption by polyamide may be
262 attributed to its surface heterogeneity (*Supporting Information, Section S6*). A typical
263 polyamide film presents both charged functional groups ($-\text{COO}^-$ and $-\text{NH}_3^+$) that imparts
264 hydrophilicity to the membrane and non-charged moieties that are hydrophobic.¹⁷⁻²¹ The
265 presence of such hydrophobic “hot spots” promotes the transport of EDCs. In comparison, the
266 TA-Fe₃ layer showed a more homogeneous nature (*Supporting Information, Section S6*),
267 which is beneficial for the rejection of EDCs. In the current study, by coating the polyamide
268 with TA-Fe₃, we observed half reduction of benzylparaben sorption.

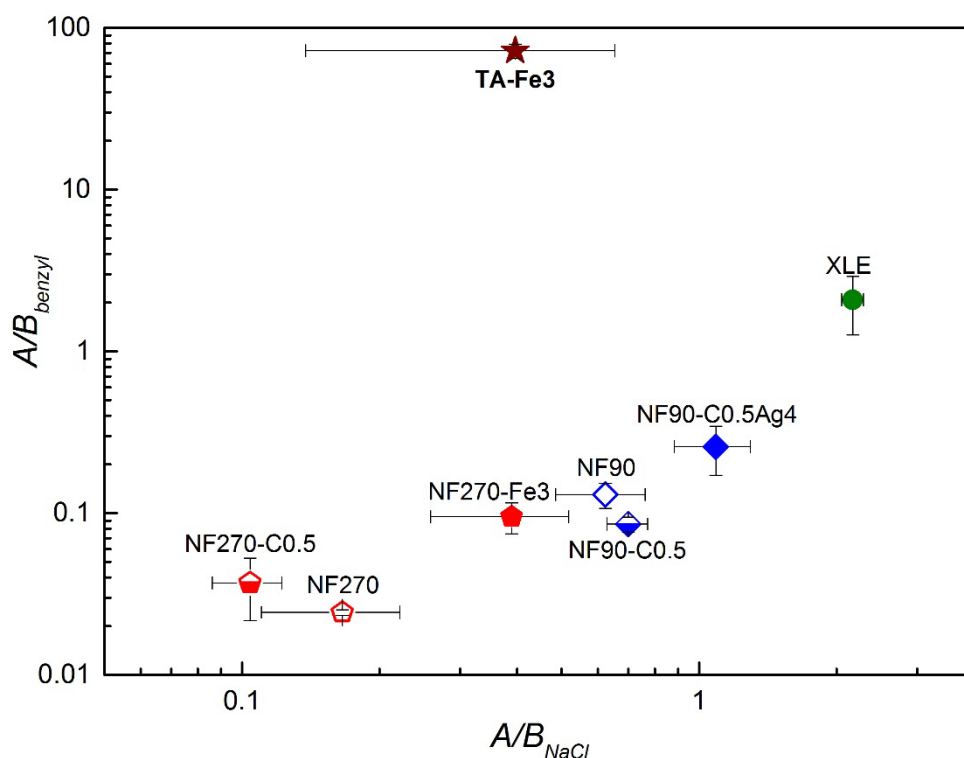
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270 **Implications for wastewater reclamation.** Despite polyamide-based TFC membranes can
271 retain a wide range of solutes including dissolved salts, they often have insufficient rejection
272 of some hydrophobic EDCs.^{15, 41} In the current study, the non-polyamide based TA-Fe₃
273 membrane showed significantly higher rejection of EDCs. This membrane presented nearly
274 two orders of magnitude larger water/EDC selectivity (e.g., A/B_{benzyl}) than traditional
275 polyamide membranes (NF270, NF90, and XLE) and their derivatives (Figure 5). Although
276 many polyamide membranes show high water/salt selectivity (e.g., A/B_{NaCl}) that is beneficial
277 to desalting purpose,^{42, 43} they lack the required selectivity against EDCs that is essential in
278 wastewater reclamation. Together with their good membrane stability and antifouling
279 performance (*Supporting Information, Section S7*), the novel non-polyamide TA-Fe
280 membranes may have a great potential to safeguard harmful TrOCs and control membrane
281 fouling during water recycling. Both TA and Fe are inexpensive (e.g., US\$10-40/kg for TA,

282 *Supporting Information, Section S1*) and non-toxic (approved by U.S. Food and Drug
283 Administration).²⁹ Furthermore, the production of TA-Fe membranes uses water instead of
284 organic chemicals as the solvent. Consequently, TA-Fe membranes can be produced in a green
285 and economical fashion. Existing literature³³ has also demonstrated the feasibility of using the
286 TA-Fe layer as a platform for further functionalization, which provides additional flexibility
287 for enhancing membrane fouling resistance.

288
289 Future studies shall focus on improved mechanistic understanding of TrOCs transport in
290 non-polyamide materials and systematic membrane performance evaluation in complex
291 wastewater matrix. Deeper mechanistic insights would also facilitate the development of
292 alternative novel membrane materials such as carbon-based materials,⁴⁴⁻⁴⁶ covalent organic
293 frameworks,⁴⁷ and aquaporin^{48, 49} with proper tuned physicochemical properties for removing
294 a wide range of contaminants for membrane-based wastewater reclamation. In view of the
295 lower rejection of the TA-Fe membranes towards hydrophilic antibiotic compounds (Figure 3),
296 further attention is needed to tune size exclusion effects in these non-polyamide membranes to
297 achieve high retention of both hydrophobic and hydrophilic TrOCs.

298



299
 300 **Figure 5. Water/sodium chloride selectivity (A/B_{NaCl}) and water/benzylparaben selectivity (A/B_{benzyl})**
 301 **co-relation for TA-Fe3 membrane, coated and/or uncoated NF270, NF90, and XLE membranes. The**
 302 **NF270-C0.5 and NF90-C0.5 represent 0.2 wt% polydopamine coating with a duration of 0.5 h for**
 303 **NF270 and NF90, respectively. The NF270-Fe3 represent the NF270 membrane with a TA-Fe3**
 304 **coating and NF90-C0.5Ag4 represent the NF90 membrane with a 0.5 h polydopamine (0.2 wt%)**
 305 **coating followed by a 4 h silver nanoparticles immobilization. The data of NF270 and NF90 were**
 306 **obtained from our previous works.^{26, 34}**

307

308 SUPPORTING INFORMATION

309 S1. Properties of tannic acid (TA); S2. Physicochemical properties of trace organic
 310 contaminants (TrOCs) and molecular probes; S3. Preparation of polyamide and TA-Fe coated
 311 wafers; S4. TEM cross-section image and EDX mapping; S5. The rejection of Na_2SO_4 for
 312 various membranes; S6. Surface properties of polyamide NF90 membrane and TA-Fe3
 313 membrane; S7. Membrane stability and antifouling. This material is available free of charge
 314 via the Internet at <http://pubs.acs.org>.

315

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324

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