

Loose nanofiltration membranes functionalized with in situ-synthesized metal organic framework for water treatment

*Original*

Loose nanofiltration membranes functionalized with in situ-synthesized metal organic framework for water treatment / Mohammad Nejad, S.; Seyedpour, S. F.; Aghapour Aktij, S.; Dadashi Firouzjaei, M.; Elliott, M.; Tiraferri, A.; Sadrzadeh, M.; Rahimpour, A.. - In: MATERIALS TODAY CHEMISTRY. - ISSN 2468-5194. - 24:(2022), p. 100909. [10.1016/j.mtchem.2022.100909]

*Availability:*

This version is available at: 11583/2961955 since: 2022-04-22T12:45:43Z

*Publisher:*

Elsevier

*Published*

DOI:10.1016/j.mtchem.2022.100909

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<http://doi.org/10.1016/j.mtchem.2022.100909>

(Article begins on next page)

1 **Loose Nanofiltration Membranes Functionalized With in Situ-Synthesized**  
2 **Metal Organic Framework for Water Treatment**

3  
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29 **Abstract**

30 In this study, modified loose nanofiltration membranes were prepared by in-situ decoration  
31 with ZIF-7 on the surface of porous polyethersulfone substrates functionalized with co-deposited  
32 sulfobetaine methacrylate zwitterion (ZW) and polydopamine (PDA). By the aid of ZW/PDA  
33 active layer co-deposition under mild conditions, ZIF-7 metal organic framework nanocrystals  
34 were successfully formed and anchored onto the membrane surface via both non-covalent and  
35 covalent bonds, to simultaneously achieve the desired selectivity and productivity of the loose  
36 nanofiltration membranes. The results of characterization confirmed the successful deposition of  
37 the ZW/PDA active layer and the consequent decoration with ZIF-7 nanocrystals. The average  
38 water contact angle decreased notably from 81.4 to 51.43 degrees upon formation of ZIF-7. This  
39 membrane showed high rejection (~99.9%) of either methyl blue and Congo red dyes, and high  
40 water flux with dye solutions (around  $40 \text{ L m}^{-2}\text{h}^{-1}$ ) at very low applied pressure of 1.5 bar.  
41 Moreover, the filtration experiments revealed that functionalized membrane exhibited significant  
42 reduction in fouling and biofouling propensity.

43

44 **Keywords:** Functionalized membrane, SBMA zwitterion, Co-deposition, dye removal,  
45 antifouling, ZIF-7.

46

## 47 **Introduction**

48 Dyes are toxic, carcinogenic, and teratogenic substances causing health problems, such as  
49 allergy, skin irritation, hard breathing, as well as kidney and liver dysfunction <sup>1</sup>. Dye  
50 contaminated wastewaters are a threat to human health and the environment <sup>2</sup> and must be  
51 properly treated before discharge into water streams or reuse. Nanofiltration (NF) is desirable in  
52 meeting wastewater treatment requirements due to its simple operation, high removal efficiency,  
53 low cost and energy consumption <sup>3</sup>. However, fouling is still a severe challenge, resulting in  
54 reduced performance and membrane lifetime <sup>4</sup>. For this reason, one of the key ways to  
55 successfully deploy NF for wastewater treatment and reuse is the fabrication of membranes with  
56 high permeation, rejection, and, importantly, low fouling tendency <sup>5</sup>.

57 Surface modification by hydrophilic polymers, such as polydopamine (PDA), can  
58 effectively mitigate fouling <sup>6</sup>. Regarded as a bio-inspired glue, PDA strongly attaches to any  
59 surface via in-situ self-polymerization of dopamine, forming a highly stable coating <sup>7</sup>.  
60 Furthermore, the catechol, quinone, and the amine functional groups on the PDA layer, offer  
61 secondary reaction sites for attaching other nanostructures and achieve further functionalization<sup>8</sup>.  
62 Membrane surface can thus inherit even higher antifouling properties by additional modification  
63 with compounds, such as zwitterions (ZW) and metal-organic frameworks (MOF) <sup>9, 10</sup>. ZW have  
64 superior antifouling properties especially capable of reducing protein or bacterial adhesion <sup>11, 12</sup>.  
65 The hydration layer formed by ZWs is typically dense, and this feature offers consistent  
66 hydrophilicity and fouling control <sup>4</sup>. Furthermore, as a class of MOFs, zeolitic imidazolate  
67 frameworks (ZIFs) have outstanding chemical stability and biocidal activity <sup>13</sup>. Considering the  
68 hydrophilic nature of both ZWs and ZIFs, their co-deposition with PDA may be a simple method  
69 to achieve functionalized antifouling surfaces.

70        Herein, we develop a method for PDA and sulfobetaine methacrylate (SBMA) co-deposition  
71 on porous PES supports under mild conditions. The presence of functional groups on the surface  
72 of PDA and ZW is anticipated to enhance dye rejection via electrostatic interaction. Besides,  
73 PDA coating provides abundant active sites for the nucleation and growth of ZIF-7 crystals to  
74 further functionalize the membrane surface and achieve further antifouling properties, herein  
75 investigated. All the membranes are comprehensively characterized, and their performance is  
76 evaluated under loose NF conditions for the removal of methyl blue (MB) and Congo red (CR)  
77 from aqueous solutions.

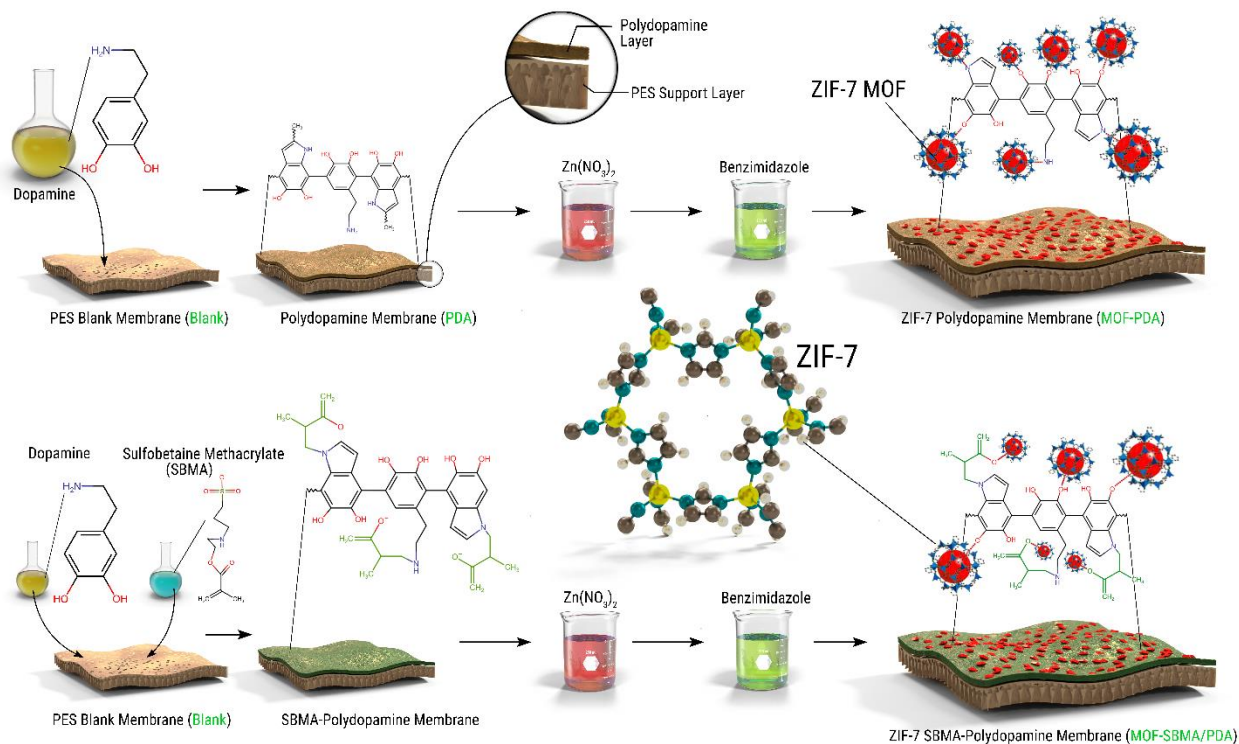
78

## 79 **Materials and Methods**

80        **Reagents.** Polyethersulfone (PES, Ultrason E6020P,  $M_w = 58,000$  g/mol) as polymer, N,N-  
81 dimethylformamide (DMF, 99.5%, Scharlau) as solvent, Triton X-100 (Merck) and polyvinyl  
82 pyrrolidone (PVP,  $M_w = 25,000$  g/mol, Merck) as pore formers, were used for preparation of  
83 porous substrate casting solutions. Dopamine hydrochloride (DP, 98%, Merck), Trizma  
84 hydrochloride (Trizma-HCl, Merck), sulfobetaine methacrylate (SBMA,  $M_w = 279.36$  g/mol,  
85 Merck), and phosphate-buffered saline (PBS) were purchased from Sigma Aldrich.  
86  $Zn(NO_3)_2 \cdot 6H_2O$  ( $\geq 98.0$  %, Merck) and benzimidazole ( $\geq 98.0$  %, Merck) were used for the  
87 synthesis of ZIF-7 crystals. Methyl blue (MB, Merck) and Congo red (CR, Merck) were selected  
88 as model anionic dyes. Sodium alginate was purchased from Sigma-Aldrich. Potassium  
89 dihydrogen phosphate ( $KH_2PO_4$ , 99.5%), glucose monohydrate, magnesium sulfate  
90 ( $MgSO_4 \cdot 6H_2O$ , 99%), sodium bicarbonate ( $NaHCO_3$ , 99.5%), calcium chloride ( $CaCl_2$ , 96%),  
91 and ammonium chloride ( $NH_4Cl$ , 99.5%) purchased from Merck were used for the preparation of  
92 the synthetic wastewater.

93        **Fabrication of ZIF-7 Functionalized NF Membranes.** The porous PES support membrane  
94 was fabricated via non-solvent induced phase inversion by immersion precipitation technique  
95 (denoted as blank membrane hereafter).<sup>14</sup> The PDA self-polymerization on the membrane  
96 surface was performed by preparing 2.0 g/L DA in Tris (pH = 8.5, 0.089 M). The fixed blank  
97 membrane was soaked in DA solution with the active side facing the solution for 2 h at room  
98 temperature while shaking to provide sufficient oxygen for PDA formation. The PDA coated  
99 membranes were thoroughly rinsed with deionized (DI) water and stored overnight in DI water  
100 to remove unattached monomers (denoted as PDA membrane). To form ZIF-7 in-situ, the PDA  
101 membrane was immersed in a metallic aqueous solution containing 0.446 g of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in  
102 100 mL deionized water for 45 min. After removing the excess metallic solution, the Zn  
103 anchored membrane was soaked in the benzimidazole solution containing 0.354 g in 100 mL of  
104 ethanol for 30 min at ambient temperature. Finally, this ZIF-7 functionalized membrane (denoted  
105 as MOF-PDA membrane) was washed with DI water and dried at room temperature. Both  
106 metallic and linker solutions were sonicated for 5 min before use to remove any aggregation.

107        To tailor the functionalization of ZIF-7, other membranes (labeled as MOF-SBMA/PDA)  
108 were obtained via co-deposition of PDA/SBMA on the PES support layer. Specifically, 1 g/L  
109 SBMA was incorporated into the 1 g/L DA solution and all the steps for fabrication of PDA  
110 membrane were repeated. Then, the SBMA/PDA coated membrane was subjected to the same  
111 sequential steps of ZIF-7 functionalization described above for the MOF-PDA membrane.  
112 Therefore, the membranes investigated in this study include: (i) blank membrane (PES porous  
113 support); (ii) PDA membrane; (iii) MOF-PDA membrane; and (iv) MOF-SBMA/PDA  
114 membrane. **Figure 1** illustrates the step-by-step procedures of membrane functionalization.



115  
 116 **Figure 1.** Illustration of membrane functionalization procedures including: blank membrane; PDA coated  
 117 membrane (PDA membrane); MOF deposition on PDA coated membrane (MOF-PDA membrane);  
 118 MOF deposition on SBMA/PDA coated membrane (MOF-SBMA/PDA membrane).

119 **Membrane Surface Characterization.** Field emission scanning electron microscopy (FE-  
 120 SEM, MIRA3 TESCAN) coupled with energy-dispersive X-ray Spectrometer (EDX) was used to  
 121 characterize both the membrane top surface and the membrane cross-sectional morphologies.  
 122 The cross-section morphology was further investigated by transmission electron microscopy  
 123 (TEM, JEOL JEM-ARM200CF), operated at 20 kV. Atomic force microscopy (AFM, EasyScan  
 124 II, Swiss) was applied to determine the surface roughness of membrane samples. To minimize  
 125 the experimental error, the surface roughness was determined for three separate samples of each  
 126 membrane type. Fourier transform infrared spectroscopy (FTIR, Thermo Scientific USA) was  
 127 used to identify the functional groups of the anchored membrane. The surface electric potential  
 128 of all membranes was evaluated with an Anton Paar SurPASS electrokinetic solid surface  
 129 potential analyzer (Anton Paar USA, Ashland, VA). All the streaming potential measurements

130 were conducted in a background electrolyte solution composed of 1 mM KCl at 25 °C, over a pH  
131 4–9 range. The zeta potentials were calculated based on the Helmholtz-Smoluchowski equation.  
132 Two separate samples for each membrane type were assessed to assess repeatability. The  
133 membrane surface hydrophilicity was evaluated by means of contact angle (CA) measurements  
134 (Dataphysics, OCA 15 plus), where an average value of five random positions were probed to  
135 calculate a meaningful average. The elemental composition and chemical features of the  
136 membrane surfaces were evaluated with X-ray photoelectron spectroscopy (XPS, Bestec,  
137 Germany).

138 **Membrane Transport and Fouling Evaluation.** The flux and dye rejections of the  
139 membranes were evaluated at an operating pressure of 1.5 bar with a dead-end cell and with an  
140 effective membrane surface area of 30 cm<sup>2</sup>. MB and CR were selected as model anionic dyes<sup>15</sup>.  
141 Further information on the dead-end setup and the performance evaluation are explained in  
142 **SI.1.1.** The **organic** fouling and bio-fouling propensity of the membranes were assessed with  
143 feed solutions containing humic acid and *E. coli* (model bacteria), respectively, guided by  
144 our previous studies (further detail on dynamic fouling experiments is provided in **SI.1.2**).<sup>16</sup>

145 **Metal ion Release Rate.** The release rate of zinc ions from the membranes was evaluated  
146 via batch experiments. Briefly, MOF-PDA and MOF-SBMA/PDA membranes coupons (1 cm<sup>2</sup>)  
147 were separately immersed in 60 mL of DI water and then placed on an orbital shaker (100 rpm)  
148 for several days and the water was replaced every 24 h. Aliquots were taken and acidified using  
149 HNO<sub>3</sub> and then analyzed by inductively coupled plasma optical emission spectrometry to  
150 determine their Zn content.

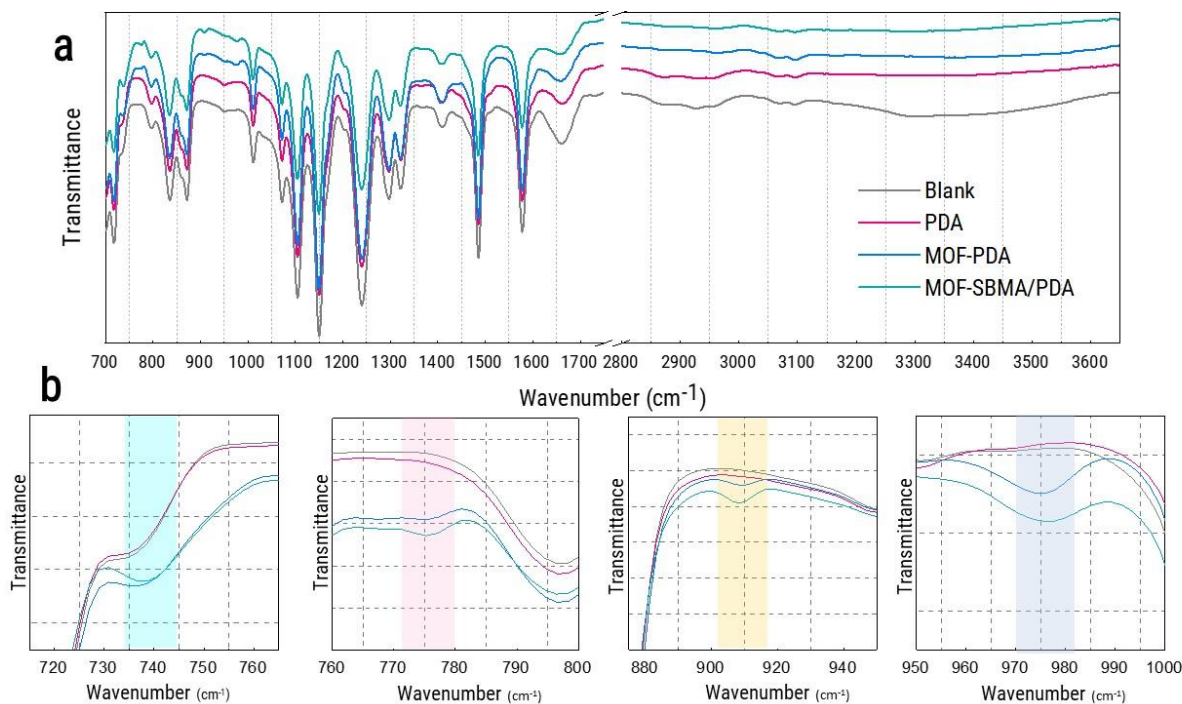


## 151 **Results and Discussions**

152 **Physiochemical properties of the membranes.** The catechol moiety of PDA enhanced the  
153 connection between the PES substrate and grafted SBMA or anchored ZIF-7. As illustrated in  
154 **Figure 1**, a two-step surface modification occurs for MOF-SBMA/PDA membranes, in which (i)  
155 a thin layer of PDA and SMBA was initially co-deposited on the membrane surface, and (ii) ZIF-  
156 7 nanocrystals were in-situ attached on the active sites of this layer. Since SBMA has  
157 methacrylate functional groups, it undergoes an aza-Michael reaction with PDA amine groups.  
158 As a result, the nucleophilic amines of PDA connected to electron-withdrawing  $\alpha$ ,  $\beta$ -unsaturated  
159 carbonyl moieties<sup>17</sup>. Due to the presence of water molecules, hydrogen bonds form, which  
160 promote the aza-Michael reaction by increasing the electrophilic trait of carbon and the  
161 nucleophilic feature of the nitrogen atom in the amine (**Figure SI.1**). Co-deposition of  
162 SBMA/PDA is expected to facilitate post-modification of membrane with ZIF-7 crystals and  
163 improve the stability of the coating. The dopamine monomers act as bio-glue and their amine  
164 groups react with methacrylates moieties of SBMA to attain covalently grafting. Meanwhile,  
165 PDA regulates the nucleation and growth sites and this results in robust coordination interactions  
166 and therefore rapid bio-functionalization of ZIF-7 on the surface.<sup>18</sup> It has been well established  
167 that the catechol groups present on PDA surface chelate various metal ions.<sup>19-23</sup> The ensuing Zn  
168 ions served as seeds that eventually grew into spherical ZIF-7 nanostructures after introducing  
169 the benzimidazole ligand.<sup>24, 25</sup> In other words, the nucleated Zn ions coordinated with the -NH  
170 functional moieties of benzimidazole ligand and formed stable ZIF-7 nanocrystal ZIF-7 on  
171 SBMA/PDA substrate.<sup>26-28</sup>

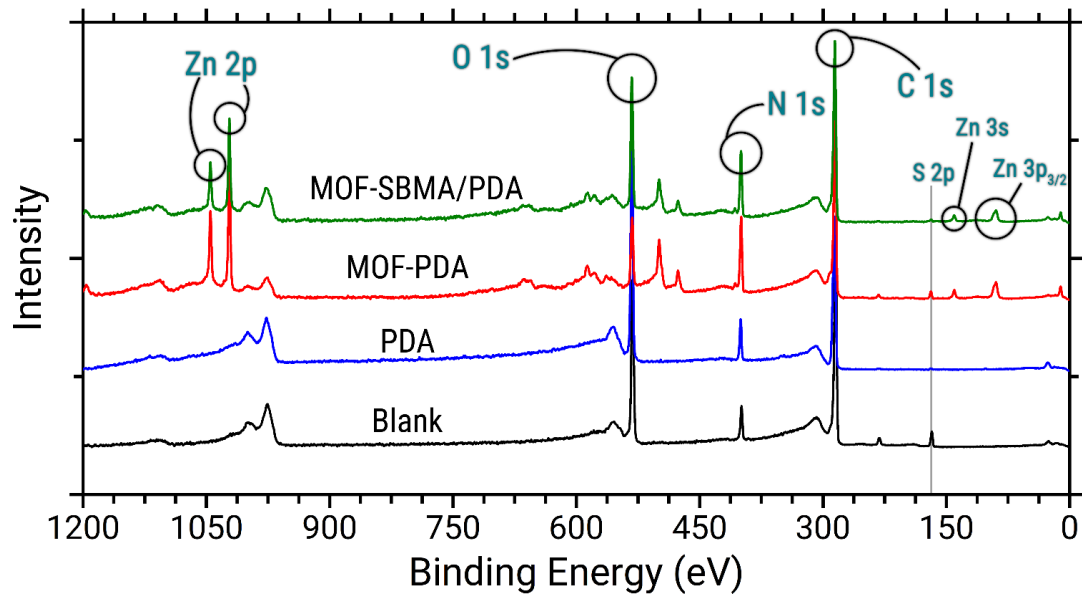
172 The FTIR spectroscopy was conducted to distinguish the functional groups of membrane  
173 surface and to confirm the successful deposition of PDA and ZIF-7 nanocrystal on the substrate

174 **(Figure 2)**. Peaks appeared at around 1150 and 1240  $\text{cm}^{-1}$ , corresponding to the symmetric  
175 O=S=O stretching vibration of the sulfone group and asymmetric C–O–C stretching vibration of  
176 the aryl ether group of the blank membrane, respectively.<sup>29</sup> The peaks observed at around 1300,  
177 and 1320  $\text{cm}^{-1}$  may be assigned to the doublet from the asymmetric O=S=O stretching  
178 vibration.<sup>29</sup> The band at around 1485  $\text{cm}^{-1}$  corresponds to the C–C stretching vibrations in the  
179 aromatic ring.<sup>30, 31</sup> Furthermore, the absorption band observed at about 740  $\text{cm}^{-1}$  may be  
180 attributed to the out-of-plane C–H bending vibration of ortho-disubstituted benzene present in  
181 benzimidazole ligand of the ZIF-7, which is in accordance with previously reported studies.<sup>32</sup>  
182 Comparing the spectra of all membranes, a new peak emerged at 759  $\text{cm}^{-1}$  for MOF-PDA and  
183 MOF-SBMA/PDA membranes, which corresponds to the ZIF-7, corroborating the formation of  
184 the ZIF-7 nanocrystals on the membranes surface.<sup>5</sup> The benzimidazole ligand displays several N-  
185 H signals between 3300 and 2500  $\text{cm}^{-1}$  (Aldrich Library of FTIR spectra, ed II, vol. 3), however,  
186 many of these peaks disappeared after the coordination with Zn atoms, representative of ZIF-7  
187 formation.<sup>33, 34</sup> The stretching vibrations of MOF-PDA and MOF-SBMA/PDA membranes at  
188 around 916  $\text{cm}^{-1}$  may be ascribed to the Zn–OH bond, confirming the decoration of Zn atoms on  
189 the catechol groups of PDA.<sup>8, 9</sup> Meanwhile, a peak at around 997  $\text{cm}^{-1}$  may be attributed to the  
190 C-N stretching vibration of the ZIF-7 structure.<sup>10</sup>



191  
192 **Figure 2** FTIR spectra of blank and modified membranes: (a) survey, and (b) high-resolution spectra.

193 The elemental composition and chemical structure of blank and modified membranes were  
 194 evaluated by XPS analysis with results shown in **Figure 3**. The survey spectra of all membranes  
 195 mainly comprise the energy peaks of carbon (C), nitrogen (N), oxygen (O), and sulfur (S) atoms,  
 196 located at 284.5, 399, 532, and 168.6 eV, respectively. However, appearance of two new Zn  
 197 signals located at 1021.3 and 1044.4 eV (attributed to Zn 2p<sub>3/2</sub> and 2p<sub>1/2</sub>, respectively) indicate  
 198 the presence of ZIF-7 nanocrystals on the surface of both ZIF-7 decorated membranes (MOF-  
 199 PDA and MOF-SBMA/PDA).<sup>38, 39</sup> The elemental compositions of blank and modified  
 200 membranes are presented in **Table 1**. N atoms on the blank membrane are attributed to the  
 201 presence of PVP in the support layer. After PDA deposition, the content of N atoms decreased  
 202 slightly and then increased significantly after ZIF-7 decoration.<sup>40</sup> The negligible reduction of N  
 203 and slight increment of S atoms in MOF-SBMA/PDA membrane can be referred to the  
 204 incorporation of SBMA to the PDA structure.



205  
206 **Figure 3.** The XPS survey spectra of blank and modified membranes.

207 **Table 1.** Elemental compositions of blank and modified membranes.

Membrane	Atomic concentration (%)				
	C(1s)	O(1s)	N(1s)	Zn(2p)	S(2p)
Blank	60.2	30.30	6.80	-	2.70
PDA	69.9	22.00	5.90	-	2.20
MOF-PDA	70.90	9.30	13.20	5.50	1.10
MOF-SBMA/PDA	66.50	16.90	12.00	3.30	1.30

208  
209 Further information on the chemical structure of membranes and coordination of the ZIF-7  
210 nanocrystals was obtained by the deconvolution of the C1s and N1s high-resolution spectra  
211 (**Figure SI.2**). Regarding the blank membrane containing PVP as additive, the de-convoluted  
212 spectrum of C 1s reveals C=C, C–C/C–H, C–N/C–O/C–S, and O=C–NH bonds located at binding  
213 energies of 284.5, 285.9, 287.4, and 288.2 eV, respectively.<sup>39</sup> Due to presence of PVP as  
214 additive, the de-convoluted N 1s spectrum represents the –NH– and N<sup>+</sup> bonds at 400.6 and 401.9  
215 eV. The de-convoluted C 1s spectrum of PDA and MOF-PDA membranes showed three main  
216 peaks, including C–C/C–H, C–N/C–O, and C=O bonds located at binding energies of 284.5,

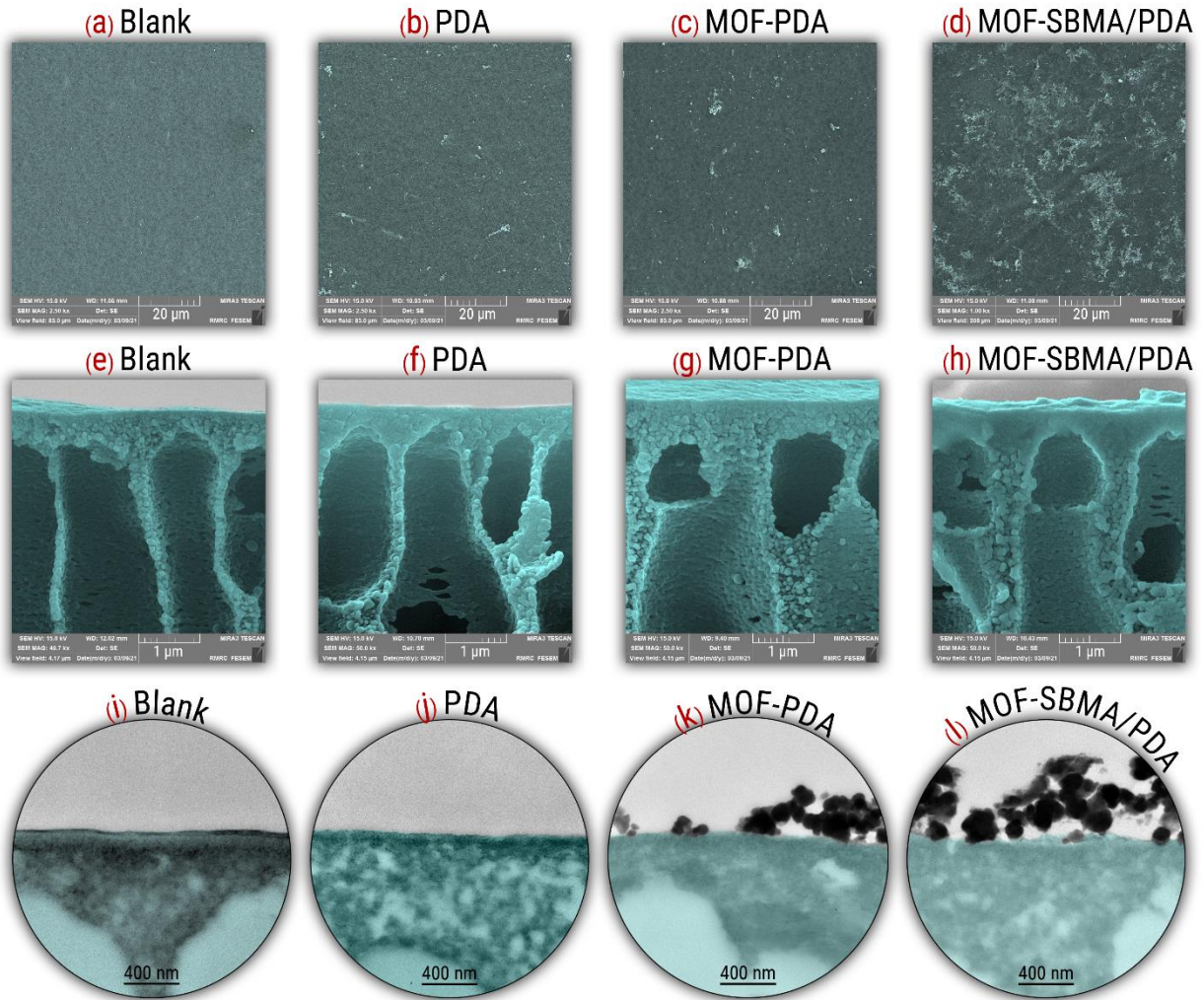
217 285.7, and 287.1 eV, respectively.<sup>18,41</sup> Besides, the de-convoluted N 1s spectrum of PDA coated  
218 membrane showed the =N–C, C–N–C, and N–C bonds located at 398.8, 399.9, and 400.7 eV,  
219 respectively. The de-convoluted C 1s spectrum of MOF-SBMA/PDA membrane revealed C=C,  
220 C–C/C–H, C–N/C–O/C–S, and C=N/C=O bonds located at binding energies of 284.5, 285.7,  
221 287.3 eV, and 287.9 eV respectively.<sup>39</sup> In case of both ZIF-7 modified membranes, owing to the  
222 presence of benzimidazole ligand, three kinds of N-containing functional groups can be observed  
223 in the deconvoluted spectrum of N1s, including pyridinic (=N– bond), pyrrolic (–NH– bond), and  
224 quaternary N centers, located at 398.5, 399, and 400.4 eV, respectively.<sup>34, 42</sup> After reacting with  
225 Zn atoms, signal appears that may be associated to the protonated N atoms coordinated with  
226 Zn.<sup>42, 43</sup>

227 The surface and cross section morphologies of all membranes were assessed by FE-SEM  
228 and TEM (**Figure 4**). SEM micrographs show relatively smooth surfaces for the PDA  
229 membrane, while all the ZIF-7 decorated membranes were characterized by a rougher surface,  
230 comprising some PDA aggregates and ZIF-7 nanocrystals on the surface. PDA catechol  
231 functional groups can provide anchor sites to react with positively charged Zn ions of ZIF-7  
232 nanocrystals. For this reason, some semi-spherical ZIF-7 nanocrystals were formed on the  
233 surface in both cases, for MOF-PDA and MOF-SBMA/PDA membranes.<sup>25</sup> Compared to the  
234 MOF-PDA membrane, the quantity of ZIF-7 increased significantly on the MOF-SBMA/PDA  
235 membrane, although the surface distribution seems to be heterogeneous in both cases.

236 A thicker active layer can be observed on the surface of PDA coated membranes, together  
237 with a denser upper portion of the support, compared to the blank membrane (**Figure 4 f-h**).  
238 Other than forming a surface PDA layer, it is likely that dopamine monomers penetrated into the  
239 surface and partly blocked the pores upon polymerization.<sup>37</sup> The SEM micrographs (Figure 4g

240 vs. 4h) suggest that the clogging degree of the MOF-SBMA/PDA membrane was higher than  
241 PDA and MOF-PDA membranes. This phenomenon may be attributed to the co-deposition of  
242 PDA/SBMA, which would produce a denser structure as chain entanglement occurs. When a  
243 denser structure forms on the surface, it also offers more active sites and functional groups for  
244 further functionalization, thus allowing a larger quantity of ZIF-7 nanocrystals to form on the  
245 surface, as indicated by the SEM micrographs (Figure 4c vs. 4d).

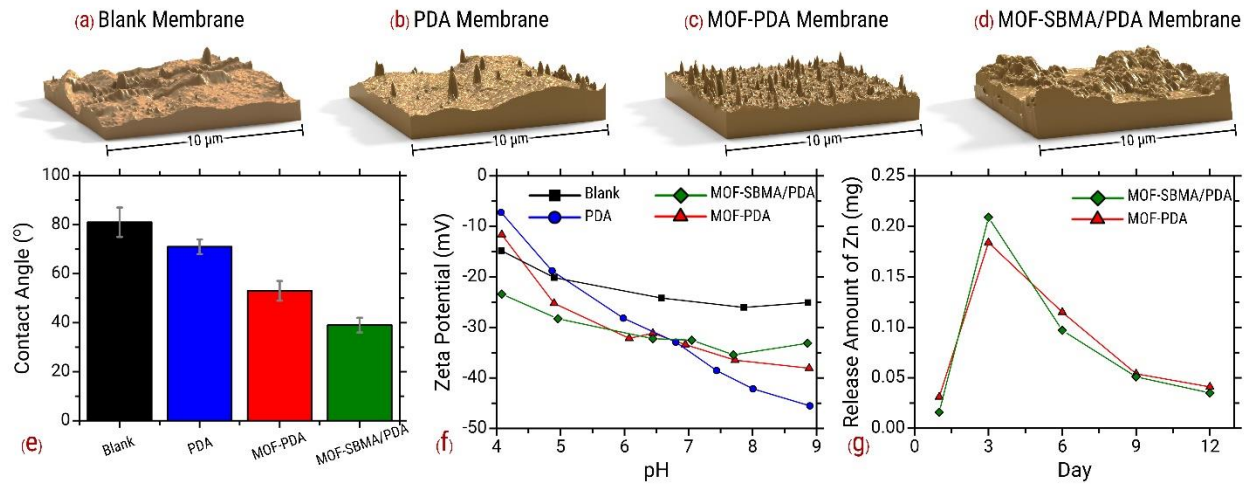
246 The corresponding EDX mapping (**Figure SI.2**) of ZIF-7 decorated membranes indeed  
247 revealed the presence of Zn ions and nitrogen atoms on the surface. The content of Zn increased  
248 on the MOF-SBMA/PDA membrane compared to MOF-PDA, consistent with SEM images.  
249 Supporting the aforementioned statements, TEM images (**Figure 4i-1** and **Figure SI.4 , 4**)  
250 illustrate that the surface of blank membrane was successfully modified as ZIF-7 nanocrystals  
251 formed on the MOF-PDA and, even more importantly, on MOF-SBMA/PDA membrane surface  
252 due to the accessibility of a larger density of functional groups.



253  
 254 **Figure 4.** (a-d) the surface FE-SEM images, (e-h) the cross sectional FE-SEM images and (i-l) TEM  
 255 images of the blank and modified membranes.

256 AFM images of membrane surfaces and their relevant roughness parameters are illustrated  
 257 in **Figure 5a-d and Table 2**, respectively. The average roughness of the membrane decreased  
 258 from 45.32 to 28.81 nm after PDA deposition, indicating appropriate surface coverage. Due to  
 259 formation of some ZIF-7 nanocrystals on the surface of PDA membrane, the surface roughness  
 260 of the MOF-PDA membrane increased to 39.59 nm. However, the MOF-SBMA/PDA membrane  
 261 demonstrated the roughest surface among all membranes as the density and quantity of decorated  
 262 ZIF-7 nanocrystals increased, consistent with both TEM and FE-SEM images. Even though it is

263 generally accepted that a rougher membrane is more inclined to fouling and especially  
 264 biofouling, there is a complex relationship between surface morphological, chemistry and  
 265 hydrophilicity, and fouling tendency.<sup>45</sup>



266  
 267 **Figure 5.** (a-d) surface AFM images, (e) CA, (f) zeta potential and (g) release rate of the blank and  
 268 modified membranes.

269 **Table 2.** Roughness parameters of membranes.

Membrane type	Roughness parameters (nm)	
	Average roughness ( $R_a$ )	Root mean squared roughness ( $R_{rms}$ )
Blank	45.32	58.37
PDA	28.81	38.18
MOF-PDA	39.59	52.65
MOF-SBMA/PDA	238.50	291.50

270  
 271 To evaluate the surface hydrophilicity of the blank and modified membranes, the CA  
 272 analysis was carried out and the results are depicted in **Figure 5e**. The average CA declined  
 273 noticeably from 81.4° for the blank membrane to 71.4°, 56.6°, and 51.43 for PDA, MOF-PDA,  
 274 MOF-SBMA/PDA membranes, respectively. This descending trend indeed suggests enhanced  
 275 surface wettability and higher affinity to water molecules. The hydrophilic functional groups of  
 276 PDA as well as the sulfonate terminals on the SBMA structure (in case of MOF-SBMA/PDA  
 277 membrane), may be regarded as water acceptor sites and could considerably increase the



278 hydrophilicity of modified membranes. Generally speaking, this increased surface hydrophilicity  
279 is expected to hinder foulant attachment and therefore fouling propensity.<sup>46</sup> When a feed solution  
280 contains charged foulants, also surface charge plays an important role in reducing the fouling  
281 propensity.<sup>48,49, 50</sup> As illustrated in **Figure 5f**, all membranes demonstrated negative zeta potential  
282 over the pH range 4–9. Overall, the MOF-SBMA/PDA membrane showed the lowest surface  
283 charge at acidic pH, suggesting the presence of moieties undergoing acid-base reaction at highly  
284 acidic pH, hence the lowest isoelectric potential (although this value was not attained in the range  
285 of pH investigated in this study). The surface potential of this membrane was uniform at basic  
286 pH, a behavior usually observed for hydrophilic surfaces that do not adsorb hydroxyl ions at  
287 increasing pH values. On the other hand, PDA membrane had the higher IEP, a steeper potential  
288 curve as a function of pH and the greatest negative charge among all membranes at basic pH  
289 values. This behavior is indicative of a combination of different functional groups, protonating  
290 and deprotonating at different pH values, consistent with the nature of dopamine monomers.<sup>51,</sup>  
291 <sup>52,53</sup> MOF-PDA membranes showed an intermediate behavior between PDA and MOF-  
292 SBMA/PDA membranes, consistent with their surface nature. Generally, a membrane with  
293 negatively charge surface is less prone to bacterial deposition and hence biofouling in normal pH  
294 ranges<sup>54</sup>, as bacterial cells carry negative charges in a pH ranges of 4–9.<sup>55, 56</sup>

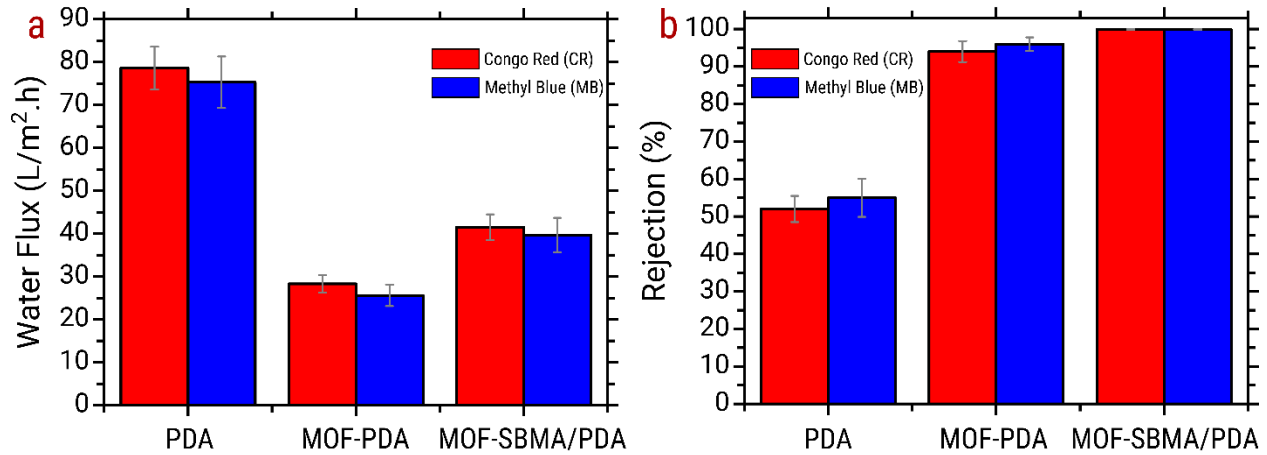
295 Since the stability of decorated ZIF-7 and the controlled release of zinc ions considerably  
296 affects the performance and anti-biofouling properties of the modified membranes, zinc leakage  
297 assessment was conducted. As displayed in **Figure 5g**, both MOF-PDA and MOF-SBMA/PDA  
298 membranes demonstrated the same release trend of zinc ions, which included a rapid rate for the  
299 first 3 days and then gradually lowering rate along the subsequent 3-day periods. The initial  
300 relatively high zinc release may be ascribed to the release of loosely bound zinc from the surface.

301 In case of the MOF-SBMA/PDA membranes, the observed slightly higher release rate is  
302 rationalized with the higher density of deposited ZIF-7. The total leakage rate of zinc ion was  
303 low in both membranes and reached a negligible level at the end of the assessing process.<sup>14, 57</sup>

304 **Filtration performance and fouling evaluation of membranes.** The separation  
305 performance of blank and modified membranes in terms of water flux and dye rejection is  
306 presented in **Figure 6**. The water flux of MOF-PDA membrane was significantly lower  
307 compared to that of the PDA membrane, namely, it decreased from 78.6 to 28.3 and from 75.3 to  
308 25.6 LMH for CR and MB solutions, respectively. According to the permeability-selectivity  
309 trade-off, the dye removal rate by the MOF-PDA membrane increased, from 52 to 94% for CR  
310 and from 55 to 96% for MB, respectively. This behavior indicates that an effective selective  
311 layer was formed on the membrane surface via PDA deposition followed by decoration of ZIF-7  
312 nanocrystals.<sup>28</sup> Although the formation of ZIF-7 nanocrystals on the PDA layer sacrificed some  
313 membrane flux, it significantly improved dye rejection.

314 Interestingly, the water permeability of MOF-SBMA/PDA membrane was notably higher  
315 than that observed with the membrane that did not contain zwitterions ((MOF-PDA), with an  
316 increment from 28.3 LMH to 41.5 LMH for the CR solution as a feed. At the same time, the  
317 rejection performance of this membrane also increased remarkably up to 99.9% for both dyes,  
318 attributed to the formation of a denser selective layer, as supported by SEM and TEM images.  
319 Although the formation of ZIF-7 on the surface can diminish the water flux, the combination of  
320 SBMA with PDA appears to have enhanced the permeability to water as well. SBMA can slow  
321 down the PDA polymerization via Michael addition, resulting in a more hydrophilic surface,  
322 therefore facilitating water molecules transport (**Figure 5e**).<sup>28</sup> The functional groups present on  
323 the PDA chain and SBMA structure may improve dye rejection owing to the charge adjustment

324 of the composite surface by multiple interactions.<sup>58</sup> In fact, some hydrogen bond, electrostatic,  
 325 and  $\pi$ - $\pi$  interactions can be formed due to the existence of amino, imine, and catechol moieties  
 326 on PDA chain that can increase the selective adsorption performance of the outmost layer.<sup>59, 60</sup> It  
 327 remains to be determined whether this performance can be maintained also for long term  
 328 filtrations.



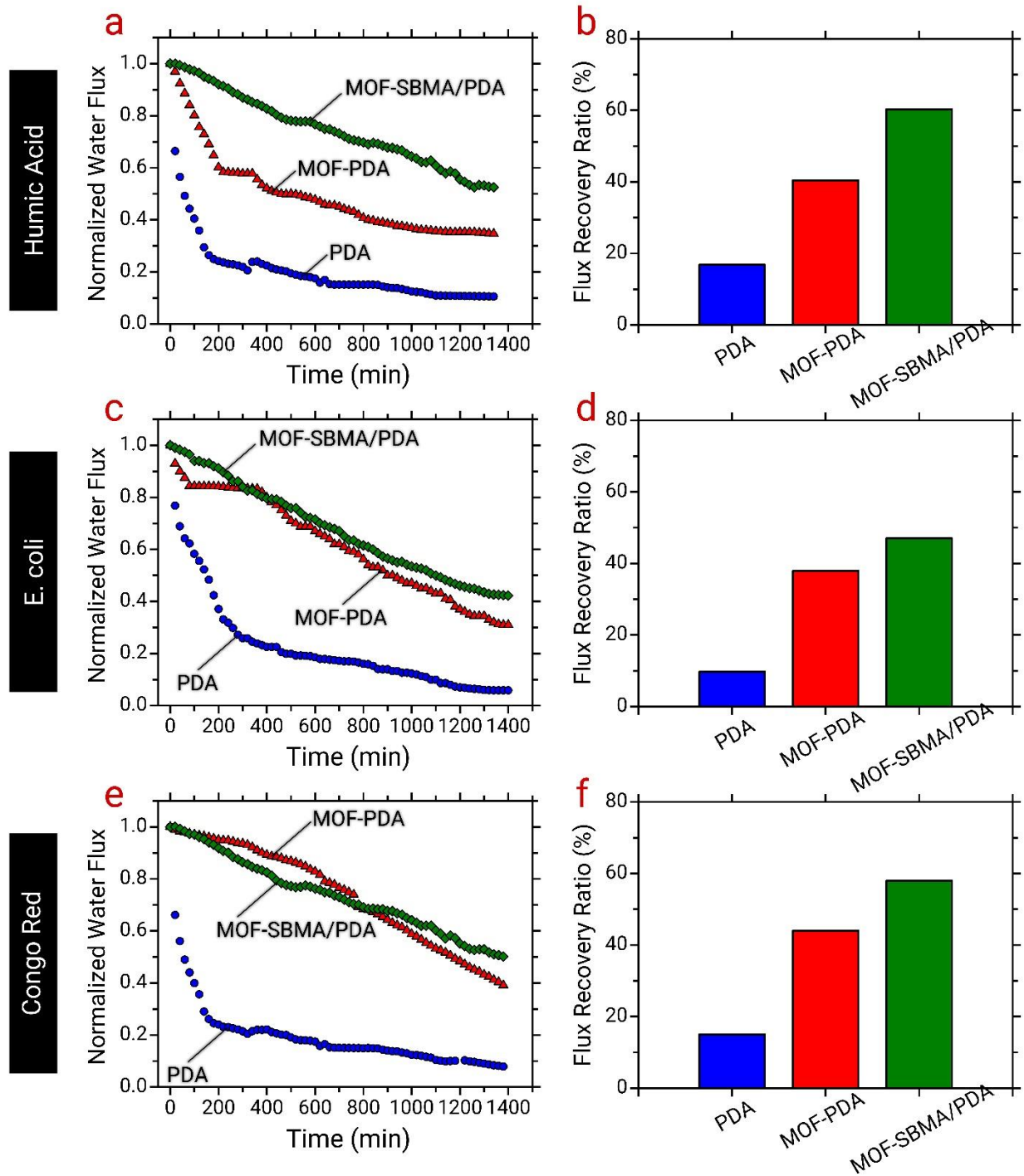
329 **Figure 6.** (a) Water flux and (b) dye rejection of blank and modified membranes ( $\Delta P=1.5$  bar).  
 330

331 **Figure 7** illustrates the results of both organic and biofouling assessment of PDA, MOF-  
 332 PDA, and MOF-SBMA/PDA membranes, as well also their correspondent flux recovery ratios.  
 333 The flux declined sharply in the first phase of all fouling experiments, and this phenomenon was  
 334 particularly important for the PDA membrane. The results summarized in **Figure 7a** indicate a  
 335 lower rate of flux decline for the MOF-SBMA/PDA in the presence of humic acid. Moreover, as  
 336 illustrated in **Figure 7b**, after a simple water washing process conducted for 30 min, flux  
 337 recovery ratios (FRR) of 16.8, 40.4, and 60.3% were achieved for PDA, MOF-PDA, and MOF-  
 338 SBMA/PDA membranes, respectively. This interesting antifouling properties of the MOF-  
 339 SBMA/PDA membrane is attributed to the weaker adhesion of humic acid molecules to the  
 340 hydrophilic surface of this membrane.<sup>61</sup> Furthermore, the nitrogen and oxygen atoms of ZIF-7

341 nanocrystals can also attract water molecules as hydrogen acceptors and form a hydration layer to  
342 hamper the humic acid deposition.<sup>62</sup>

343 The results of biofouling experiments are illustrated in **Figure 7c**. The water flux of PDA  
344 membrane declined after introducing of *E. coli* to the feed solution, while the antifouling  
345 tendency of modified MOF-PDA, and MOF-SBMA/PDA membranes improved significantly via  
346 ZIF-7 formation and/or SBMA co-deposition. In addition, after physical cleaning (**Figure 7d**),  
347 FRR of 9.7, 37.9, and 47% were attained for PDA, MOF-PDA, MOF-SBMA/PDA membranes,  
348 respectively. This FRR value are consistent with the antibacterial activity of ZIF-7 nanocrystals,  
349 which hinder biofilm formation. SBMA structures tend to prevent microbial attachment on  
350 membrane surface but they are unsuccessful in deactivating bacteria cells.<sup>65, 66</sup> Therefore, an  
351 integration of passive anti-adhesion (SBMA) and active antibacterial (ZIF-7) strategies can result  
352 in synergetic effects.<sup>67 68</sup> In addition, the protonated amine groups possibly trigger additional  
353 antibacterial property, as they result in cell lysis when in contact with the bacteria<sup>69</sup>.

354 In order to also elucidate the effect of the dye fouling, the flux decline was investigated in  
355 the presence of CR for ~24 h (**Figure 7e**), which again revealed the lower fouling tendency for  
356 both MOF modified membranes compared to PDA membrane. FRR of 15, 44, and 58% were  
357 achieved for PDA, MOF-PDA and MOF-SBMA/PDA membranes, respectively (**Figure 7f**). The  
358 remarkable antifouling properties of both MOF-PDA and MOF-SBMA/PDA compared to that of  
359 the PDA membrane may be attributed to their enhanced hydrophilicity and highly negatively  
360 charged surfaces.



361  
 362 **Figure 7.** Long-term antifouling performance of the PDA, MMOF-PDA, and MOF-SBMA/PDA  
 363 membranes versus time.

364 Table 3 presents a summary comparison between the most performing membrane in this  
 365 study, namely, MOF-SBMA/PDA, and some membranes developed for dye removal reported in

366 the literature. The productivity (normalized by applied pressure) is one of the highest for our  
367 membrane, which showed. comparable separation performance in terms of dye rejection with the  
368 membranes previously discussed in the literature. Notably, the MOF-SBMA/PDA membrane  
369 displayed favorable antifouling behavior associated with a significant ability to recover flux upon  
370 simple physical cleaning. The combination of these two properties is possibly the most  
371 promising feature of the membrane proposed in this study.

Membrane type	Membrane Support layer	Dye type	Dye Carbon number	Modifying agent	Modifying technique	Applied pressure	Membrane flux	Dye removal	Ref
NF	PSF	Anionic (MB)	37	TEOA-TMC-PAA	Interfacial polymerization and physio-chemical	5 bar	40.25 LMH	99.6%	70
TFN	HPAN	Anionic (CR, MB, reactive black5, Direct red 23)	32 37 26 35	PVP-uo-66-NH <sub>2</sub> -PVA-GA	Drop coating	4 bar	52.36 LMH	99.89-100%	71
NF	HPAN	Anionic (CR, MB) Cationic(MB)	32 37 16	Sulfonated Dopamine(SDA)	Interfacial polymerization	6 bar	62.2 LMH	99.9%	72
Composite	PES	Anionic(Reactive black 5, Reactive Green 19)	26 40	MOS <sub>2</sub> -PSBMA	MMM(Phase inversion)	6 bar	108.3 LMH	98.2% 99.3%	73
Loose NF	HPAN	Anionic(CR, MB)	32 37	PEI-GA	Dip Coating	2 bar	51 LMH	97.1% 97.3%	74
Loose NF	PVDF	Anionic(CR)	32	PAA	UV-grafting	4 bar	104 LMH	99.38	75
Composite	PAN	Anionic (CR, Reactive-black-5, reactive orange16)	32 26 20	PDA-PEI/TiO <sub>2</sub> -Ag	Coating and vacuum filtration	2 bar	81.2 LMH	99.6% 99.5% 96.2%	76
Loose NF	PES	Anionic (CR) Cationic (MB)	32 37	MOF-SBMA/PDA	Coating and surface functionalization	1.5 bar	63 LMH	99.9%	This work

**Table 3:** A comparison of the performance of various surface modified membranes developed for dye removal reported in literature.

## Conclusion

In this study, in-situ heterogeneous nucleation and growth of ZIF-7 nano-crystals (MOF) was developed on the functional sites of PDA-assisted coating. Also, the SBMA zwitterion was co-deposited with PDA through the aza-Michael reaction to obtain a dense layer with high dye rejection capability. The zwitterion incorporation into PDA matrix played a favorable role in the performance improvement of the membrane also in terms of ZIF-7 formation and resulting surface density. The results indicated that MOF-SBMA/PDA membrane provided suitable water flux and high dye retention for loose nanofiltration applications. Perhaps most importantly, the membrane demonstrated remarkable antifouling properties due to the presence of hydrophilic SBMA zwitterion. Considering the adaptable surface modification, this functionalization strategy exploiting the aza-Michael addition offers a platform for developing diverse surface modified membranes with promising potential for industrial applications necessitating the separation of aqueous streams from low molecular weight compounds.



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