1	In-situ surface modification of a reverse osmosis membrane with acrylic
2	polymers: transport and retention of a small neutral organic
3	micropollutant
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28 Abstract

29 Highly selective in-situ surface grafting approaches were designed to improve the rejection 30 of 1H-benzotriazole (BTA) by a reverse osmosis (RO) membrane. A commercial FT30 31 membrane was grafted in-situ for the first time with 2-(diethylamino)ethyl methacrylate 32 (DEAEMA) and 3-(trimethoxysilyl)propyl methacrylate (TMSPMA), respectively, and 33 compared with the state-of-the-art polydopamine (PDA) modification method. The TMSPMA 34 grafting enhanced the BTA rejection from 88.4% to 98.4%, with a minor drop in water 35 permeability (0.3%) compared to the pristine membrane. The FT30-TMSPMA membrane 36 performed considerably better than the FT30-DEAEMA and FT30-PDA membranes. The 37 improved rejection after TMSPMA modification can be ascribed to enhanced steric exclusion 38 and hydrophobic interactions. The boosted hydrophobicity of the FT30-TMSPMA membranes 39 is the result of the hydrophobic nature of the propyl/methyl groups present in TMSPMA, 40 resulting in an 11.3% and 8.8% higher selectivity of BTA compared to the pristine FT30 and 41 FT30-PDA membrane, respectively. The A/B ratio (which indicates the membrane selectivity 42 to water against the solute) of the FT30-TMSPMA membrane increased by 714%, which is the 43 highest enhancement compared to other modified materials reported in the literature until now. 44 This new modification approach is thus highly promising for membrane functionalization to improve the rejection of small neutral organic micropollutants. 45

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Keywords: Reverse osmosis membrane, In-situ surface modification, Organic micropollutants,
Rejection, Permeability

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51 **1. Introduction**

52 Organic micropollutants (OMPs), including personal care products, pharmaceuticals, and 53 pesticides, have become one of the world's emerging challenges for water systems. Several 54 OMPs are bio-accumulative and persistent [1, 2] despite their low concentration levels in the 55 water environment, ranging from ng/L to µg/L. Long-term exposure to OMPs has raised 56 concerns regarding environmental and health impacts [3]. For example, some pesticides (such 57 as atrazine and diuron) were detected in the UK's groundwaters over a significant period [4]. 58 Lapworth et al. (2012) reported the maximum OMPs concentrations (9.26~1890 ng/L) detected 59 in different regions, including Europe, the USA, England, and Wales [5]. Moreover, OMPs 60 have also been reported in the surface water of the Yangtze River in China, where poly- and 61 perfluoroalkyl substances (PFASs) were detected in the drinking water [6]. One of the main 62 routes for OMPs to enter the water bodies is through effluent discharge from wastewater treatment plants. Due to the inadequate removal of OMPs by wastewater treatment plants, the 63 64 concentration of OMPs in water environments is considerably high, thus, there is a necessity to 65 remove them during drinking water treatment.

Reverse osmosis (RO) is the most robust membrane-based technology for removing OMPs 66 67 in drinking water treatments [7, 8]. However, RO is inefficient in removing neutral (i.e., the charge is determined by the pKa value of the solute), smaller (i.e., expressed by the molecular 68 69 weight-MW), and polar OMPs, such as 1H-benzotriazole, paracetamol and tolyltriazole, which 70 hinders the membranes' applications [9]. For instance, Fujioka et al. (2020) reported that the 71 rejection of N-nitrosodimethylamine (MW=74 g/mol) by an RO membrane was considerably 72 low (i.e., only 15%) [10]. Similarly, a pilot-scale study conducted by this group also showed 73 low retention of N-nitrosodimethylamine (i.e., 25%) under 20% system recovery [11]. 74 Albergamo et al. (2019) noted that the passage of uncharged 1H-benzotriazole (MW=119.05 75 g/mol) through RO membranes can be up to 25% with a water recovery of 15% [12]. To 76 improve the retention of small molecular OMPs by RO membrane technologies, membrane 77 modification has attracted increasing attention in recent years. In-situ membrane surface 78 modification (i.e., defined as the process of modifying the properties of the membrane surface 79 by introducing monomers and/or polymers during filtration with an active layer facing the feed 80 and without dismantling the cells and removing or replacing the membranes) is a promising 81 modification strategy for OMPs removal [13]. The same concept of "in-situ membrane surface 82 modification" is used in the current manuscript. There are also some studies that used the term in-situ modification to refer to the same method as in the current investigation. For instance, 83

84 Fujioka et al. (2020) modified RO membranes by in-situ surface coating with amines, amides, 85 and epoxides of different chain lengths for N-nitrosodimethylamine removal [14]. Li et al. 86 (2018) found that bisphenol A permeability decreased after the NF90 membrane was in-situ 87 coated with polydopamine/polyethyleneimine [15]. Zhang et al. (2021) investgated the 88 retention of aflatoxin B1 after tannic acid-3-aminopropyltriethoxysilane in-situ modification 89 [16]. Compared to other membrane surface modifications, in-situ modification has the 90 advantage of being an easy and cost-effective technique because it does not require additional 91 equipment and processing steps [13]. It reduces the complex handling of removing/replacing 92 the membrane before and after the modification process. As a result, the modification procedure 93 can be repeated, which allows for better fine-tuning of the membrane permeability for different 94 species. Based on its flexibility, this process can be used to modify membranes in real time to 95 accommodate changing processes.

96 The rationale of the membrane modification technique is to modify the surface of the 97 membrane to improve the OMPs rejection based on the mechanisms of steric exclusion, 98 electrostatic interaction, and hydrophobic interaction [17]. For example, Gur-Reznik et al. 99 (2011) reported that the main mechanism for removing hydrophilic OMPs with high MW is 100 through steric exclusion, which was confirmed by the different molecular weight cut-offs 101 (MWCO) of the membranes [18]. Regarding negatively charged OMPs, the retention by 102 negatively charged membranes is relatively high due to electrostatic repulsion compared to that 103 of neutral and positively charged OMPs [19, 20]. This was supported by Huang et al. (2021), 104 who reported that positively charged OMPs can pass more easily through negatively charged 105 membranes [3]. In terms of adsorptive interactions, membrane hydrophilicity plays a significant 106 role in the removal of OMPs. For example, Alonso et al. (2024) demonstrated that the rejection 107 of hydrophobic estrone was higher (99.4%) than that of hydrophilic acetaminophen (98.4%) by 108 hydrophilic RO membrane since estrone is more hydrophobic than acetaminophen [21]. These 109 findings reveal that hydrophobic interactions govern the retention and transport of OMPs. Many 110 studies on membrane surface modification with polydopamine (PDA) appeared in recent years 111 due to its hydrophilic properties. For instance, Guo et al. (2016) coated a membrane with PDA 112 that showed an improved rejection of hydrophobic OMPs (i.e., 29% to 42% enhancement) while 113 sacrificing water permeability (i.e., 5% to 45% reduction) [22], due to the reduced hydrophobic 114 adsorption effects. However, up till now, very little is known about the transport and retention 115 of small molecular, hydrophilic, and neutral compounds using in-situ membrane surface 116 modification.

117 In the current study, the effects of two novel in-situ modification polymers on the transport 118 of a small and neutral OMP, as well as NaCl, were investigated. 1H-Benzotriazole (BTA), the 119 selected model OMP since it is widely known and regularly detected in aquatic environments 120 [23], is an organic compound widely used as a corrosion inhibitor in industrial applications, 121 such as antifreeze, metalworking fluids, and ultraviolet light stabilizer [24-26]. 2-122 (diethylamino)ethyl methacrylate (DEAEMA) and 3-(trimethoxysilyl)propyl methacrylate 123 (TMSPMA) were selected for RO membrane modification. DEAEMA and TMSPMA are 124 versatile monomers polymerized via radical graft polymerization [27-29], making them suitable 125 for a variety of applications. The performance of these two in-situ modified membranes was 126 compared with that of PDA, which was used as a control method. The thin film composite 127 aromatic polyamide (TFC PA) FT30 RO membrane, which is commonly used in the field of 128 water research, was targeted for modification by using a lab-scale system. The morphology, 129 chemistry, and surface hydrophilicity of the membranes were systematically characterized. 130 Moreover, the effects of the surface modification on the water permeability, transport, and 131 rejection of BTA and NaCl were investigated. Finally, the underlying OMP transport and 132 retention mechanism after membrane modification was elucidated. To the best of our 133 understanding and knowledge, this is the first investigation on the transport of smaller and 134 neutral OMPs in RO membrane functionalized with DEAEMA and TMSPMA; therefore, there 135 is no previous literature on these monomers for grafting processes.

136 **2. Materials and methods**

137 **2.1. Chemical reagents and membranes**

Flat-sheet RO FT30 TFC membranes were provided by DuPont FilmTec. 2-(diethylamino)ethyl methacrylate (DEAEMA), 3-(trimethoxysilyl)propyl methacrylate (TMSPMA), dopamine hydrochloride (DA), aluminum oxide (activated, basic), tris-base (\geq 99.8%), potassium persulfate (K₂S₂O₈), potassium metabisulfite (K₂S₂O₅), ethylene glycol, diethylene glycol, pentaerythritol, and D-(+)-Glucose, and 1H-benzotriazole (99%) were purchased from Sigma Aldrich. The physicochemical properties of the three monomers and BTA are presented in Table S1 and Table S2, respectively.

145 **2.2. OMPs filtration protocol**

An in-house built crossflow membrane cell was used to recirculate the retentate and permeate back into the feed tank of 5 L. The dimensions of the channel were 25 cm in length, 5 cm in width, and 1 mm in height, while the cell houses an active membrane area of 124 cm².

149 A diagram of the bench-scale RO system is depicted in Fig. S1. Membrane coupons were 150 soaked in deionized (DI) water overnight prior to the experiments to remove preservatives from the membrane surface. Before filtration, an RO membrane with an effective area of 124 cm² 151 was placed into the filtration cell and pre-compacted with DI water at 13 bar and 25±1°C until 152 153 there were no significant flux changes (i.e., the variation of water flux collected over the last 10 samples should be less than 0.1 L m⁻² h⁻¹). The system was operated hereafter with a 2 g L⁻¹ 154 NaCl solution at 10 bar and a crossflow velocity of 0.2 m s^{-1} at $25 \pm 1^{\circ}$ C. The water permeability 155 156 and NaCl rejection were measured subsequently. Afterwards, a 2 L feed concentration of 20 mg L-1 1H-benzotriazole solution was filtered for 4 days. The concentration of 1H-157 158 benzotriazole was set above the typical levels observed in water sources because of the 159 limitations of the applied analytical methods, which exhibit diminished accuracy below 1 mg L⁻¹. All the experiments were performed in triplicate. The 1H-benzotriazole concentration in 160 161 the collected samples was determined using UV-spectrophotometry (WPA lightwave II, 80-162 3003-72) at a specific wavelength of 259 nm.

163 The water permeability coefficient (A, expressed in L $m^{-2} h^{-1} bar^{-1}$ or LMH bar^{-1}) was 164 calculated by the following equation:

$$165 \qquad \mathbf{A} = \frac{V}{A_m \Delta \mathsf{Pt}} \tag{1}$$

where V is the permeate volume (L), A_m is the membrane filtration area (0.0124 m²), ΔP is the transmembrane pressure (bar), and t is the filtration time (h).

The solute permeability coefficient (B, expressed in L m⁻² h⁻¹ or LMH) was calculated as
 follows:

170
$$B = \frac{J_w C_p}{C_f - C_p}$$
(2)

171 where J_w is the permeate flux (L m⁻² h⁻¹), and C_p (mg L⁻¹) and C_f (mg L⁻¹) are the concentrations 172 in the permeate and the feed water, respectively.

173 The solute rejection (R, expressed in %) of the RO membranes was calculated using the174 following equation:

175
$$R = \left(1 - \frac{c_p}{c_f}\right) * 100\%$$
 (3)

176 **2.3. Membrane modification**

177 The RO membrane was first immersed in 1% $Na_2S_2O_5$ to remove possible protective 178 coatings or preservatives, then cut into 75 mm \times 280 mm coupons, and finally stored in DI

water at 4°C in the dark before usage for modification. The flat-sheet RO membrane coupon 179 180 was placed in a crossflow cell with only the active layer of the membrane modified. Subsequently, the different modification solutions (2 g L⁻¹ DA in 500 mL 10 mM Tris-HCl 181 solution at pH 8.5 [30], 2 g L⁻¹ DEAEMA with the initiators (0.01 M K₂S₂O₈ and 0.01 M 182 $K_2S_2O_5$), and 2 g L⁻¹ TMSPMA with 0.01 M $K_2S_2O_8$ and 0.01 M $K_2S_2O_5$) were respectively 183 184 pumped into the operation cell in recirculation for in-situ membrane modification with the 185 crossflow velocity, transmembrane pressure, temperature and exposure time set at 0.2 m s⁻¹, 10 bar, $25 \pm 1^{\circ}$ C and 1 h, respectively. Hereafter, the modified membranes were rinsed with DI 186 187 water until the pH and conductivity were the same as that of DI water. The membrane samples are denoted in the following as FT30-PDA, FT30-TMSPMA, and FT30-DEAEMA after PDA, 188 189 TMSPMA, and DEAEMA modification, respectively. Fig. 1 displays the scheme of the grafting 190 polymerization of (a) TMSPMA and (b) DEAEMA onto the FT30 membrane surface.

(a)



195 **2.4. Membrane surface characterization**

196 **2.4.1. Scanning electron microscopy (SEM)**

SEM (JSM-6010PLUS, JEOL) was applied to analyze the membrane surface morphology. In addition, cross-sections of the membranes were also examined using SEM after cutting the membranes while preventing membrane damage using liquid nitrogen. Prior to the SEM measurements, dry membranes were sputter-coated with gold using a JFC-130 coater (JEOL). SEM images were obtained with an accelerating voltage of 7 kV and measured at magnifications of 5000 × and 10000 ×, respectively.

203 2.4.2. Atomic force microscopy (AFM)

The membrane surface roughness was studied by means of AFM (XE-70, Park Systems). A silicon cantilever (NanosensorsTM PPPNCHR) was used to record a scan of a $5 \times 5 \ \mu m^2$ area. Three different random spots were selected on each sample to measure the root-mean-square (RMS) roughness and root-average roughness (R_a) values. The recorded images were analyzed after flattening via XEI software [31].

209 2.4.3. X-ray photoelectron spectroscopy (XPS)

210 XPS measurements were conducted on a PHI 5000 Versa probe II spectrometer (ULVAC-211 Physical Electronics) to investigate the membrane surface chemical properties using 212 monochromatic Al K_{α} as an X-ray source (hv = 1486.6 eV) at a power of 25 W (beam size of 213 100 μ m). The pressure of the main XPS chamber was constantly kept below 10⁻⁶ Pa during the 214 measurements. The emitted photoelectrons were detected with a hemispherical analyzer placed 215 at an angle of 45° relative to the plane of the samples. Survey scans and high-resolution C1s 216 spectra were recorded at pass energies of 187.85 eV (0.8 eV step size) and 23.5 eV (0.1 eV step 217 size), respectively. Survey and high-resolution C1s scans were obtained on four randomly 218 selected locations for each sample. The acquired survey scans (0–1100 eV) were then analyzed 219 via Multipak software (version 9.6) to determine and quantify the present surface elements after 220 applying a Shirley background subtraction with the relative sensitivity factors provided by the 221 manufacturer of the instrument. Curve fitting of the high-resolution C1s spectra was also 222 conducted using the same Multipak software. Gaussian-Lorentzian curve shapes (80-100% 223 Gaussian) with a full width at half maximum set below 1.5 eV for each line shape were applied 224 for the deconvolution of the peaks. All spectra were charge-corrected based on the C-C 225 constituent of the C1s peak located at 285.0 eV.

226 **2.4.4.** Fourier-transform infrared spectroscopy (FT-IR)

FT-IR analysis was conducted on a Bruker Tensor 27 spectrometer equipped with a single reflection attenuated total reflectance (ATR) accessory (germanium crystal, MIRacle, PIKE technologies) and a mercury cadmium telluride (MCT) detector. FT-IR spectra were acquired in the spectral region 4000-700 cm⁻¹ by averaging 64 scans (resolution 4 cm⁻¹). OPUS 6 software was used to analyze the spectra and for atmospheric vapor compensation to correct for the occurring absorptions of water vapor and carbon dioxide present in the ambient environment.

233 **2.4.5.** Water contact angle (WCA) analysis

The hydrophilicity of the membranes was characterized by static WCA measurements via an optical contact angle goniometer (Krüss, DSA25). Four 5 µL droplets of DI water were randomly deposited on a single membrane sample to ensure accuracy. The corresponding WCA values were determined by applying Laplace-Young curve fittings to the observed water drop profiles.

- 239 **3. Results and discussion**
- 240 **3.1. Membrane characterization**

241 **3.1.1. Membrane morphology**

242 The surface and cross-section morphologies of the pristine and modified FT30 membranes were analyzed by SEM at different magnifications (Fig. 2). As seen from Fig. 2, differences in 243 244 surface morphology were observed after membrane modification (Fig. 2 d, e, g, h, j, k) compared to the pristine FT30 membrane (Fig. 2 a, b). The surface of the FT30-PDA, FT30-245 246 TMSPMA, and FT30-DEAEMA membranes showed rough and also distinguishable regions of 247 clumped polymers, verified by the higher magnification images (Fig. 2 e, h, k), while the surface 248 of the pristine membrane was relatively smooth (Fig. 2 b). However, it is important to note that 249 the membrane morphology was more altered upon PDA and TMSPMA modification than the 250 DEAEMA grafting approach. On the other hand, the cross-section images showed no clear 251 differences between the pristine and treated membranes due to the very small features induced 252 (at the applied magnification of $10000\times$) by the specific in-situ surface grafting method.

In addition, AFM was used to further explore the differences in surface topography and roughness of the pristine and modified membranes. Three-dimensional (3D) AFM images of the pristine, FT30-PDA, FT30-TMSPMA, and FT30-DEAEMA membranes were shown in Fig. S2 (a-d), whereas the surface-relevant roughness parameters (RMS and R_a) were listed in Table 1. As observable in Fig. S2, all AFM images presented ridge and valley structures on the plane 258 [32]. The ridge structures on the FT30-PDA, FT30-TMSPMA, and FT30-DEAEMA 259 membranes increased compared to the pristine sample, which is in agreement with the 260 previously discussed SEM surface images. The roughness values presented in Table 1 were in 261 close agreement with the AFM images as the RMS and Ra roughness values increased after 262 PDA and TMSPMA modification compared to the pristine membrane; it can thus be concluded 263 that the PDA and TMSPMA functionalization clearly alter the membrane surface morphology. 264 On the other hand, these roughness values remained almost unchanged after DEAEMA 265 modification, which is in agreement with the previously presented SEM results. They also 266 showed only minor changes in surface morphology upon DEAEMA modification.





Fig. 2 SEM images of the surface and cross-section of pristine (a-c) and modified FT30 membranes with (d-f)
 PDA, (g-i) TMSPMA, and (j-l) DEAEMA.

 Membrane	RMS (nm)	R _a (nm)
 FT30	56.1 ± 4.6	44.8 ± 3.5
FT30-PDA	150.8 ± 17.2	120.7 ± 5.4
FT30-TMSPMA	89.8 ± 12.1	67.6 ± 8.4
FT30-DEAEMA	56.6 ± 2.9	44.9 ± 2.1

Table 1 Roughness values in terms of Ra and RMS for pristine and modified FT30 membranes

271 **3.1.2. Membrane chemistry**

272 The membrane surface chemistry was investigated by FT-IR and XPS. As shown in Fig. 3, 273 the FT-IR spectrum of the pristine FT30 membrane contained numerous absorption peaks, of 274 which the most important ones to describe were the peaks located in the regions 3600-3100 cm⁻ 275 ¹ and 1700-1450 cm⁻¹. The very broad absorption peak in the region 3600-3100 cm⁻¹ can be attributed to OH stretching and NH stretching of carboxylic acids and amides, respectively [33, 276 277 34]. Bands located at the wavenumbers 1660, 1610, and 1540 cm⁻¹ correspond to C=O 278 stretching (amide I), N-H deformation vibration and/or C=C ring stretching vibration in aromatic amides, and C-N stretching and/or NH in-plane bending (amide II) respectively, all 279 280 associated with the presence of amides [35, 36]. A relatively weaker band observed at the 1450 cm-1 wavelength corresponds to C-O stretching/OH bending associated with carboxylic acid 281 282 groups [35]. The measured FT-IR spectrum is thus in close agreement with the chemical 283 structure of the FT30 aromatic polyamide membrane. Fig. 3 also revealed no observable 284 changes in the FT-IR spectrum of FT30-PDA, FT30-TMSPMA, and FT30-DEAEMA 285 compared to the pristine FT30 membrane, suggesting that the performed surface modifications 286 might not have been successful. However, it is more likely that no differences between all 287 samples are present because of the large penetration depth of FT-IR (up to µm's). If the surface 288 modification occurs at the top surface (order of nanometers), these chemical alterations cannot 289 be detected by FT-IR, as already previously observed in the case of top surface modification 290 [37]. To examine whether this assumption is correct, XPS analysis was also performed in this 291 study, of which the results will be described hereafter.



292

293

Fig. 3 FT-IR spectra of FT30, FT30-PDA, FT30-TMSPMA, and FT30-DEAEMA membranes

294 The surface elemental composition of the pristine and modified membranes was shown in 295 Table S3. The pristine FT30 membrane showed 71.4 at. % C, 22.1 at. % O and 6.3 at. % N, 296 which is consistent with the elemental composition of a previously investigated FT30 297 membrane [38]. After PDA functionalization, the relative carbon concentration decreased to 298 70.7 at. %, while the oxygen and nitrogen content slightly increased to 22.3 and 7.0 at. %, 299 respectively. The slightly increased oxygen and nitrogen content can be attributed to the PDA 300 coating on the top membrane surface. In the case of the FT30-TMSPMA membrane, both the 301 carbon and nitrogen concentrations decreased to 67.9 and 4.4 at. % respectively, while the 302 oxygen content considerably increased to 26.1 at. %. In addition, a small amount of Si was also 303 detected on the membrane surface, proving, in combination with the increased oxygen content, 304 the successful grafting of TMSPMA. As TMSPMA did not contain nitrogen, it is also logical 305 that the surface nitrogen content decreased after TMSPMA grafting as the XPS signal coming 306 from the underlying FT30 membrane containing nitrogen was less intense after the grafting 307 procedure. Lastly, after DEAEMA grafting, the carbon content again decreased to 68.3 at. %, 308 while the oxygen concentration considerably increased to 25.7 at. %. No significant change in 309 nitrogen content was observed after DEAEMA grafting, which might be attributed to the fact 310 that the grafting of additional nitrogen atoms to the surface is counterbalanced by the loss in 311 nitrogen signal from the underlying FT30 membrane, resulting in an unchanged overall nitrogen 312 amount. The previously described elemental composition results thus already prove that our

313 previously mentioned assumption is correct in that surface modification does occur, but only at314 the top surface of the membrane.

315 High-resolution C1s spectra were also obtained and deconvoluted to obtain more 316 information about the carbon-containing functional groups present on the FT30 and the 317 modified membranes. The peak fitting results were shown in Fig. 4a, Fig. 4b, Fig. 4c, and Fig. 318 4d for the pristine FT30, FT30-PDA, FT30-TMSPMA, and FT30-DEAEMA membranes, 319 respectively, while the relative concentrations of the different carbon-containing groups were 320 presented in Table 2. The high-resolution C1s spectrum of the original FT30 membrane was 321 decomposed into 4 separate peaks. The large peak located at 285.0 eV can be assigned to 322 carbons in aliphatic or aromatic C–C/C–H bonds, which are abundantly present in the aromatic 323 polyamide membrane [36, 39]. The moderate peak at 286.5 eV can be attributed to C-O or C-324 N bonds; however, in the case of the pristine membrane, the peak can be fully assigned to C-N 325 groups as C-O bonds were not present in the chemical structure of FT30. The peak located at 326 288.0 eV represents amides (N-C=O groups) [40], while the smallest peak at 289.1 eV can be 327 assigned to O–C=O bonds. The XPS deconvolution results thus clearly confirm the chemical 328 structure of FT30, which is an aromatic polyamide containing both amine and carboxylic acid 329 end groups. After PDA modification, similar peaks were used for the C1s deconvolution, but 330 their relative peak areas changed, as observed from the results presented in Table 2. In this 331 particular case, the relative concentration of the C-O/C-N groups increased compared to the 332 pristine sample at the expense of C-C/C-H bonds, while the amount of amides remains stable. 333 These changes thus confirm the successful coating of PDA on the FT30 membrane, as PDA 334 contained C-O/C-N functional groups. As amides were not present in the chemical structure of 335 PDA, the amide signal was most likely originating from the underlying FT30 substrate, showing 336 that most likely only a very thin layer of PDA is coated on the membrane surface. After 337 TMSPMA modification, besides the 4 previously mentioned peaks, a new peak at 284.5 eV was 338 also present, which is associated with C-Si bonds [41]. Table 2 revealed that after TMSPMA 339 grafting, the relative concentration of the C-C/C-H bonds decreased compared to the pristine 340 FT30 sample, resulting from the incorporation of additional O–C=O, C-N/C-O, and C-Si bonds. 341 As these latter bonds were present in the chemical structure of TMSPMA. Additional 342 information on the surface chemical functionality of FT30-TMSPMA membrane can be 343 observed from the Si 2p peak fitting (Fig. 4e). The Si 2p peak was deconvoluted into two peaks 344 located at 101.2 eV due to Si-C and at 102.7 eV due to Si-O [42], while no silicon peak was 345 detected of other membranes in this study. The high-resolution Si 2p curve-fitting results in 346 Table S4 showed that the relative concentration of the Si-O bonds was higher than Si-C bonds, 347 which is in good agreement with the chemical structure of TMSPMA. Both C-Si and Si-O bonds 348 can prove the occurrence of TMSPMA grafting reaction in this study. XPS analysis thus clearly 349 confirmed the successful membrane surface modification by TMSPMA. Finally, in the case of 350 the DEAEMA functionalization process, all previously mentioned peaks, except for the C-Si 351 peak, were again present in the deconvoluted C1s peak. Similar to the TMSPMA grafting 352 process, the performed functionalization with DEAEMA again led to the incorporation of O-353 C=O and C-N/C-O groups at the expense of C-C/C-H bonds. As DEAEMA has a chemical 354 structure containing O-C=O, C-N and C-O groups, the results thus revealed the successful 355 grafting of DEAEMA on the membrane surface.

356 Table 2 showed that the relative concentration of O-C=O increased for both FT30-357 TMSPMA and FT30-DEAEMA membranes compared to the pristine FT30 membrane. Thus, 358 the carboxyl groups were the primary characteristic determining the grafting ratio for both 359 modifications. The grafting ratio was calculated after TMSPMA and DEAEMA modifications 360 according to the relative concentration ratio of carboxyl groups of modified membranes to the 361 pristine membrane through XPS analysis. Xu et al. (2013) also calculated the grafting ratio by 362 the ratio of -COOH groups via XPS measurement [43]. The grafting ratio of the FT30-363 TMSPMA membrane was 2.75, and it was 3.50 for the FT30-DEAEMA membrane, as shown 364 in Table S5. The grafting ratio can influence the membrane hydrophilicity due to the carboxyl 365 groups. Although the concentration of carboxyl groups increased after TMSPMA modification, 366 the membrane hydrophilicity still decreased due to the hydrophobic nature of TMSPMA 367 chemical structure (as described below in 3.1.3), leading to a reduction in water flux but not 368 significantly (p > 0.05). The higher grafting ratio of the FT30-DEAEMA membrane showed 369 that the increased presence of O-C=O groups was responsible for the improved surface 370 hydrophilicity, contributing to the enhanced water permeability after DEAEMA modification, 371 which is in agreement with the results of section 3.2.

372 Table 2 3

Table 2 XPS high-resolution C1s peak deconvolution results for the pristine and modified FT30 membranes

Chemical state	Binding energy (eV)	Relative concentration (%)			
		FT30	FT30-PDA	FT30-TMSPMA	FT30-DEAEMA
C–Si	284.5	n.d.	n.d.	1.7±0.5	n.d.
СС/СН	285.0	73.4±3.2	71.5±0.6	70.3±2.1	64.7±3.0
C-O/C-N	286.5	19.5±4.8	22.5±0.8	20.0±3.5	26.3±2.9
N-C=O	288.0	6.3±1.4	6.1±0.2	5.8±1.3	6.2±0.6
0–C=0	289.1	0.8±0.1	n.d.	2.2±0.9	2.8±0.7

373

n.d.—not determined



Fig. 4 XPS high-resolution C1s peak fitting for pristine and modified FT30 membranes with different polymers:
(a) FT30, (b) FT30-PDA, (c) FT30-TMSPMA, and (d) FT30-DEAEMA, and (e) XPS high-resolution Si 2p peak
deconvolution for FT30-TMSPMA membrane.

380 **3.1.3. Membrane hydrophilicity**

The membrane hydrophilicity was determined by WCA measurements for the pristine and modified RO membranes, and the results were shown in Fig. 5a. The pristine membrane showed slightly hydrophilic properties with an average WCA of 45.5°, which is in accordance with previous findings [44]. The three different polymers induced a change in the hydrophilicity of the membrane surface. Upon modification with PDA, the average WCA of the RO membrane increased to 59.2°, thereby leading to a decreased surface hydrophilicity. This result is in 387 agreement with the literature, where WCA values of different PDA-coated substrates were found in the range of 50-70° [45]. After TMSPMA modification, the decrease in surface 388 389 hydrophilicity was even more pronounced, resulting in a WCA value of 67.3°. This increasing 390 hydrophobicity could be assigned to the hydrophobic nature of the propyl/methyl groups 391 present in the chemical structure of TMSPMA [46]. In contrast, after DEAEMA grafting, the 392 average WCA value decreased to 30.8°, thereby thus resulting in increased hydrophilicity. This 393 increasing hydrophilicity was most likely due to the presence of hydrophilic C-N, C-O, and O-394 C=O groups at the membrane surface, as evidenced by the XPS results.



Fig. 5 (a) The WCA of the pristine and modified FT30 membranes with different polymers. Error bars represent
one standard deviation of quadruplicate measurements, (b) Pure DI water permeability (A), (c) NaCl

399 permeability of pristine and modified membranes. The different lowercase letters on the top of the bars indicate a 400 significant difference between the bars at p < 0.05, while the same lowercase letters on the top of the bars are not

401 significantly different (p > 0.05). Error bars represent one standard deviation of triplicate measurements.

402 **3.2.** Intrinsic separation properties of the RO membrane before and after modification

403 Compared to the pristine FT30 membrane, the DI water permeability (A) shown in Fig. 5 404 (b) decreased by 2.4% (p < 0.05) and 0.3% (p > 0.05) after modification with PDA and 405 TMSPMA, respectively. Guo et al. (2017) also found that the water permeability decreased by 406 4.3% after PDA coating on an NF90 membrane due to the additional PDA layer [47]. The 407 observed decrease in water permeability after PDA and TMSPMA modification can be mainly 408 attributed to the reduced surface hydrophilicity of these modified membranes, as observed in 409 Fig. 5a. On the other hand, DEAEMA modification led to a 3.4% increase in water permeability, resulting in the highest obtained water permeability (3.13 LMH bar⁻¹) in this study. Similarly, 410 411 Liu et al. (2011) modified the RO membrane with hydrophilic poly(N-isopropylacrylamide-co-412 acrylamide) (P(NIPAM-co-Am)), and they reported that the water permeability exhibited 413 enhancement with P(NIPAM-co-Am) concentrations below 200 mg L⁻¹ [48]. The improved 414 water permeability resulted from the increased hydrophilicity of the membrane surface after 415 modification, evidenced by a considerable decrease in contact angle. Consequently, water was 416 more prone to transport through the membrane, leading to improved permeability. In this study, 417 as discussed previously, the enhanced water permeability after DEAEMA modification with 418 the DEAEMA concentration of 2 g/L can be explained by the increased surface hydrophilicity 419 attributed to the presence of O-C=O, C-N, and C-O groups on the surface of the FT30-420 DEAEMA membrane.

421 On the other hand, the modified membranes showed a significant (p < 0.05) enhancement 422 in NaCl permeability compared to the pristine membrane (Fig. 5c). More specifically, the NaCl permeability increases from 0.17 L m⁻² h⁻¹ for the FT30 membrane to 0.21, 0.22, and 0.21 L m⁻ 423 ² h⁻¹ after PDA, TMSPMA, and DEAEMA modification, respectively. This observation implies 424 425 that the membranes, after the conducted modifications, do not have the capacity to improve 426 NaCl rejection. The increased NaCl permeability of functionalized membranes may be due to 427 the external concentration polarization (ECP). The improved ECP resulting from the enhanced 428 membrane surface roughness can lead to increased NaCl accumulation at the membrane surface 429 [49].

430 **3.3. Effect of surface modification on BTA rejection**

The BTA rejection after a 4-day filtration with the pristine and modified FT30 membranes was depicted in Fig. 6 a. In general, the functionalized membranes demonstrated a significant (p < 0.05) increase in BTA rejection compared with the pristine FT30. The BTA rejection was enhanced by 11.3%, 4.3%, and 2.3% by using TMSPMA, DEAEMA, and PDA, respectively.

To gain a comprehensive understanding of the rejection behavior after functionalization, the rejection of four neutral hydrophilic molecules was analyzed, and the results were shown in Fig. 6 c. The modified membranes, especially the FT30-TMSPMA membrane, showed an improvement in the rejection of these 4 molecules compared to the pristine membrane, thereby 439 revealing the increased steric exclusion after membrane functionalization. Guo et al. (2017) 440 also analyzed the rejection of neutral hydrophilic molecules to evaluate the size of the exclusion 441 effect [47]. The FT30-TMSPMA membrane achieved the highest rejection (98.4%) among the 442 examined samples, which can be attributed to (1) the high hydrophobicity of the FT30-443 TMSPMA membrane (Fig. 5a) resulting in increased hydrophobic interactions between this 444 modified membrane and hydrophilic BTA to hinder the passage of BTA across the membrane 445 and (2) the enhanced steric exclusion after TMSPMA modification (Fig. 6 c), as evidenced by 446 the increased four neutral hydrophilic molecules rejection. The synergy of these mechanisms 447 prevents the passage of BTA through the membrane and contributes to its selective separation 448 properties.

449 In the case of DEAEMA modification, a lower BTA rejection of 92.2% was observed 450 compared to the FT30-TMSPMA membrane. Similar to TMSPMA, the molecular probes 451 analysis suggests that an improved steric exclusion can increase BTA rejection. However, the 452 FT30-DEAEMA membrane showed a higher affinity for BTA than the FT30-TMSPMA 453 membrane, resulting in a lower retention of BTA. In the case of the FT30-PDA membrane, the 454 BTA rejection was 90.5% (an increase of only 2.3% compared to the pristine membrane). 455 Clearly, the rejection of the four molecular probes of the FT30-PDA membrane was lower than 456 the other two modifications mentioned above. Although the increased membrane surface 457 hydrophobicity can affect the hydrophobic interactions after PDA coating, steric exclusion may 458 play a more important role in enhancing BTA retention.

459 Further analysis of the A/B ratio of BTA and NaCl, representing the membrane selectivity 460 to water against BTA and NaCl, respectively, was performed for the modified membranes. The 461 results were compared with the pristine FT30 membrane (Fig. 6 b). For BTA, the A/B ratio of 462 the FT30-TMSPMA membrane was approximately 10-fold higher than the pristine FT30. The 463 improved rejection of this compound can be explained by the superior selectivity after 464 TMSPMA modification, which outperforms that of the pristine membrane and the other 465 modified membranes. As previously mentioned, the remarkably improved selectivity can be 466 ascribed to the increased steric exclusion and enhanced hydrophobic interactions for the 467 hydrophilic BTA.

18



470Fig. 6 (a) Rejection of BTA for the pristine and modified membranes, (b) A/B ratio of pristine and modified471membranes to BTA and NaCl, (c) rejection of four neutral hydrophilic molecules for the pristine and modified472membranes. The different lowercase letters on the top of the bars indicate a significant difference between the473bars at p < 0.05, while the same lowercase letters on the top of the bars are not significantly different (p > 0.05).474Error bars represent one standard deviation of triplicate measurements.

475 To the best of our knowledge, no comparative studies on BTA rejection by in-situ RO 476 membrane modification have been reported until now. For this reason, a comparison was 477 conducted with other reported modified materials that have been used for in-situ membrane 478 modification to remove different kinds of small, hydrophilic, and neutral OMPs. A comparison 479 in terms of variation in percentage of water permeability (Fig. 7 a) and A/B ratio was performed 480 (Fig. 7 b). As shown in Fig. 7 a, 80% of the in-situ modified materials reported in literature 481 reduced the water permeability by 3%~66% [14, 50]. The water permeability reduction of the 482 PDA (2.4%) and TMSPMA (0.3%) modified membranes presented in the current work is thus 483 considerably lower compared to the state-of-the-art materials. In contrast, the water 484 permeability of the FT30-DEAEMA membrane increased by 3.4%. This improvement is higher 485 than that of hexanamide (2.9%) and 1,2-epoxydodecane (2.9%) but lower than that of 486 octanamide (8.6%), which indicates that the DEAEMA modification is a promising method for 487 improving water permeability. In Fig. 7 (b), the variation in the percentage of the A/B ratio for 488 in-situ RO-modified membranes was presented for the rejection of small, hydrophilic, and 489 neutral OMPs. The A/B ratio of the materials reported in the literature commonly increased by 490 50%~529%, while an enhancement of 714% was observed for the FT30-TMSPMA membrane 491 in this work. The FT30-TMSPMA membrane is thus promising as it exhibits an excellent BTA 492 removal performance combined with only a minor loss of water permeability.







497 4. Cost-benefit analysis

498 To provide an indicative cost of the polymers/materials used for the current in-situ 499 modification approach, the costs for the raw polymers or materials used in this study and 500 reported in the literature on the in-situ membrane coating and grafting methods were provided 501 in Table 3. For clarity purposes, the materials used for surface coating and surface grafting 502 methods were separated and ranked from the lowest to the highest cost. As seen from this table, 503 the modification costs ranged between 0.3 and 1076 €/g for an in-situ coating, whereas the cost 504 for the PDA coating, used as a control method in our study, is 7.9 €/g. The cost ranged between 0.1 and 712 €/g for the in-situ grafting. The TMSPMA and DEAEMA cost 8.9 €/g, which is on 505

506 the relatively low-cost end of the polymer costs found in the literature. Compared to other 507 reported modified materials, the polymers used in our work are thus more cost-effective. In 508 addition, the required amount of material for in-situ modification is also an important factor to 509 take into account, and it may vary from material to material depending on the concentration 510 required. Apart from the material cost, an in-situ modification will require a temporary 511 installation downtime, impacting the overall production cost to be outweighed by the potential 512 benefits (e.g., flux improvement, fouling mitigation, and improved OMPs rejection). 513 Furthermore, the required frequency of in-situ modification will have a consequence on the cost 514 of in-situ modification, but this strongly depends on the water type and pretreatment train, 515 which is difficult to assess. Based on the literature, the modification material cost is the main 516 parameter found and the only one used for comparison. Overall, the material costs summarized 517 in Table 3 provide a first estimate of in-situ membrane modification methods.

518 519

 Table 3 Comparison of the cost estimates of different polymers or materials used for in-situ membrane coating and grafting methods

In-situ	Raw polymers/materials	Raw materials	Ref.	
modification				
methods				
	1,2-Epoxybutane	0.33	Fujioka et al. [14]	
	Tannic acid	0.76	Zhang et al. [16]	
	3-aminopropyltriethoxysilane	0.81		
	Butyramide	1.1	Fujioka et al. [14]	
	1,2-Epoxydodecane	1.86	Fujioka et al. [14]	
	1,2-Epoxyhexane	1.92	Fujioka et al. [14]	
Surface coating	Poly[2-(methacryloyloxy)ethyl-dimethyl-(3- sulfopropyl)] ammonium hydroxide	3.32	Abdelhamid et al. [51]	
	Hexylamine	4.62	Fujioka et al. [14]	
	Octylamine	4.68	Fujioka et al. [14]	
	1,2-Epoxyoctane	6.76	Fujioka et al. [14]	
	PDA	7.86	This study	
	Polydopamine	7.86	Lietal [15]	
	Polyethyleneimine	8.96	21 of all [10]	
	Polyethyleneimine	8.96	Zhou et al. [52]	

	poly(N-isopropylacrylamide-co-acrylamide)	10.57	Liu et al. [48]
	poly(N-isopropylacrylamide-co-acrylamide)	10.57	Yu et al. [53]
	Dodecylamine	12.88	Fujioka et al. [14]
	Decylamine	21.65	Fujioka et al. [14]
	Hexanamide	40	Fujioka et al. [14]
	Dodecanamide	107.6	Fujioka et al. [14]
	Decanamide	584	Fujioka et al. [14]
	Octanamide	1076	Fujioka et al. [14]
	Diethanolamine	0.12	Liu et al. [54]
	Triton	0.86	Baransi-Karkaby et al. [50]
	Piperazine	5.2	Liu et al. [54]
	Amidosulfonic acid	8.4	Liu et al. [54]
	TMSPMA	8.9	This study
	DEAEMA	8.9	This study
	2-hydroxyethyl methacrylate	14.75	Ben-David et al. [55]
Surface grafting	2-hydroxyethyl methacrylate	14.75	Lin et al. [56], Lin et al. [57]
	Glycol ester of methacrylic acid	14.78	Gilron et al. [58]
	2-acrylamido-2-methylpropane sulfonate	14.84	Gilron et al. [58]
	3-sulfopropyl methacrylate	16.41	Ben-David et al. [55]
	3-sulfopropyl methacrylate	16.41	Lin et al. [56], Lin et al. [57]
	3-sulfopropyl methacrylate	16.41	Gilron et al. [58]

Glycidyl methacrylate	712	Baransi-Karkaby et al. [50]
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520 **5. Conclusions**

521 In this study, two novel modification polymers were proposed for the first time to in-situ 522 graft TMSPMA and DEAEMA on an RO membrane surface for enhancing BTA rejection. 523 After TMSPMA and DEAEMA modification, the BTA removal improved from 88.4% to 92.2% 524 and 98.4%, respectively. Compared to PDA modification, it increased by 8.8% and 2.0% for 525 TMSPMA and DEAEMA, respectively. The FT30-TMSPMA membrane presented the highest 526 rejection (98.4%) of the small, neutral, and hydrophilic BTA with only a slight drop in water 527 permeability (0.3%). The increased rejection can be attributed to the improved steric exclusion 528 effect and the reduced surface hydrophilicity. Moreover, the TMSPMA and DEAEMA 529 polymers used in this work were cheaper compared to the other reported polymers applied in 530 in-situ modification approaches. This work provides fundamental insights into in-situ RO 531 membrane surface modification for removing the small, neutral, and hydrophilic BTA molecule. 532 BTA is an important example of a pollutant with properties similar to many other organic 533 contaminants of high importance in water treatment areas. As such, the current study is 534 primarily focused on fundamental aspects and novel properties of modification processes rather 535 than the exploitation study of a large variety of pollutants. Additional studies are required to 536 examine the impact on the retention of different OMPs with the presented new materials and to 537 scale up the in-situ modification strategy using TMSPMA for selected water types.

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