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Atomic layer deposition of TiO₂ on porous polysulfone hollow fibers membranes for water treatment

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Abstract

Numerous membranes devoted to water treatment are made of Polysulfone (PSF) and can suffer from performance deterioration because of the intrinsic hydrophobicity of this material. Modifying membrane surface allows the engineering of its physicochemical properties and can achieve improved permeability and anti-fouling efficiency by tuning the membrane hydrophilicity or porosity. Atomic layer deposition (ALD) is a unique technology that provides highly conformal and uniform coatings layers such as oxides over surfaces of three-dimensional (3D) parts, porous materials and particles. In this work, titanium dioxide (TiO₂) was deposited on polysulfone hollow fibers (HF) membranes via ALD using TiCl₄ and H₂O as precursors. Membranes obtained with increasing number of deposition ALD cycles were tested until the pores were totally blocked. The morphology, structure and mechanical properties of membranes were not altered. The deposition was confirmed by scanning electron microscopy (SEM), Energy-dispersive X-ray spectroscopy (EDX) and X-ray Photoelectron Spectroscopy (XPS) analyses. The deposition of TiO₂ enhanced by 50% the water permeability and by 20% the fouling resistance of the PSF HF membranes until only 20 ALD cycles. This is accompanied by an increase of hydrophilicity and a pores size reduction.

Key words: Membrane, Hollow fibers, Atomic layer deposition, Titanium dioxide, Polysulfone

1. Introduction

During the past few years, fast industrial development and population growth have strongly threatened the ecological environment and human health¹⁻³. As surface and underground water have been more and more contaminated, the availability and safety of drinking water became an ongoing global challenge. One of the solutions to counteract this issue is to reuse wastewater. So far, many water purification processes to separate contaminants from water are developed. Indeed, thanks to their many advantages such as high separation efficiency, easy operation, low energy consumption and their environmentally friendly behaviour⁴, membranes are among the most advanced ones. Pressure-driven separation processes can be divided in four categories such as microfiltration, ultrafiltration, nano-filtration and reverse osmosis depending on the separation properties like water permeability and selectivity. In recent years, hollow fiber (HF) membranes attracted interest due to their larger specific area, excellent scalability and superior flexibility when compared to flat membranes⁵. Among them, water treatment membranes⁶ can be classified, according to their nature, as inorganic membranes when they use ceramics^{7,8}, zeolites^{9,10} or silica materials^{11,12}; or as organic membranes based on synthetic polymers such as polyethylene (PE)¹³, polyethersulfone (PES)¹⁴, polyvinylidene fluoride (PVDF)¹⁵, or polysulfone (PSF)¹⁶. The latter is one of the leading choice for HF membrane fabrication because of its excellent chemical and thermal resistance during membrane washing, and its good mechanical properties suitable for long-term use. However, the main drawback of this polymer is its intrinsic hydrophobicity that affects especially antifouling performances¹⁷. In order to offset this problematic, modifying membrane surface allows the engineering of its physicochemical properties and can achieve improved permeability and anti-fouling efficiency by tuning the membrane

49 hydrophilicity, surface charge or porosity^{18,19}. Several modification techniques are developed like
50 blending, grafting or mixed-matrix. Govardhan *et al.* prepared PES/Polyetherimide HF membranes by
51 blending method and tested the modules in a laboratory membrane unit for water reclamation. They
52 obtained a pure water permeability at 1 bar twice higher than the initial PES HF membrane reaching
53 also a 99 % Bovine Serum Albumin (BSA) rejection²⁰. Cai *et al.* synthesized zwitterionic polymers
54 grafted PES HF membranes for osmotic power generation. They observed that modified membranes
55 exhibited improved fouling resistance to protein and bacterial adhesion without alteration of their
56 morphology. Such systems also achieved higher water flux in pressure retarded osmosis tests
57 compared to initial membrane²⁰. Wan *et al.* prepared PVDF HF membranes with UIO-66 metal organic
58 frameworks for arsenate removal in water. They transformed the initial membrane that could not
59 reject arsenate because of the presence of too large pores, into a hydrophilic mixed matrix membrane
60 able to eliminate arsenate by sorption on UIO-66²¹. Another possibility for surface modification is the
61 use of coating method, which consist in depositing a thin layer of material on the membranes' surface.
62 Different techniques²² can be used, such as sol-gel, physical vapor deposition (PVD), chemical vapor
63 deposition (CVD) or atomic layer deposition (ALD). Dong *et al.* synthesized PVDF/Al₂O₃ hybrid
64 membrane *via* sol-gel process. They obtained a pure water flux increased by 83.4 % between the initial
65 and modified membranes while the BSA rejection was improved from 88.3 to 96.6 %²³. Kowalik-
66 Klimczak *et al.* modified polyamide membranes with copper oxide using PVD techniques. They
67 achieved a stable coating during filtration of demineralized water and the modified membranes
68 showed a strongest bactericidal activity, which allowed eliminating 99% of microorganisms²⁴. Nomura
69 developed silica membranes by CVD method on a porous ceramic substrate with controlled pore sizes
70 and hydrothermally stable for the steam reforming reaction to extract H₂²⁵. All of these methods are
71 interesting and provide promising results but ALD stands out from the crowd thanks to its very high
72 surface conformality. Where PVD concerns only the surface, sol-gel blocks the pores and CVD will not
73 provide a uniform layer all along, the surface-controlled film growth of ALD allows the obtaining of
74 highly uniform coatings over surfaces of three-dimensional (3D) parts, deep trenches, porous materials
75 and particles²⁶. ALD is in fact one of the most recent techniques, a unique technology developed over
76 the last four decades²⁷, which allows the deposition of inorganic coating layers such as oxides; for
77 example iron oxide FeO²⁸, aluminium oxide Al₂O₃²⁹, lanthanum oxide La₂O₃³⁰, silica SiO₂³¹ or tin oxide
78 SnO₂³²; with high uniformity and precise sub-nanometer thickness control.
79 As an environmental-friendly, low-cost and highly hydrophilic oxide, titanium dioxide TiO₂ can be
80 advantageously used for modifying membrane surface properties³³. Hamid *et al.* incorporated TiO₂
81 nanoparticles into PSF HF membranes and observed a diminution of water contact angle (WCA) from
82 75° for raw membranes to 45° for TiO₂ modified membrane. They also proved great antifouling
83 properties against humic acid with a twice higher flux and a better flux recovery from 90 % to 95 %³⁴.
84 Nechifor *et al.* produced polysulfone-silica microfiber grafted with TiO₂ nanoparticles composite
85 membranes. They obtained a 94% retention of BSA and a water permeability increase of 45%, as long
86 as a great anti-bacterial action for PSF/SiO₂ + TiO₂ composite membranes³⁵.
87 Recent studies have shown that ALD is applicable to flexible and temperature-sensitive polymeric
88 membranes^{36,37}, the deposition of an oxide thin layer could increase the membrane hydrophilicity,
89 modify its pore size and reduce the membrane fouling despite sacrificing the water permeability.
90 Actually, some reviews are focused on the sensitization of nominally unreactive membrane materials
91 for subsequent ALD and the use of ALD oxides as a hydrophilization coating on membranes. Yang *et al.*
92 reviewed ALD/ sequential infiltration synthesis (SIS) engineering strategies with realization of efficient
93 water treatment. They laid out a pathway to establish an ALD/SIS-based universal functionalization
94 platform for water treatment, including sensitization strategies.³⁸ Wu *et al.* summarized the most
95 recent advances in molecular engineering to tailor the properties of interfaces in composite
96 membranes. They explained how the performances of membranes can be enhanced by the way of
97 several surface modification techniques.³⁹ Yang *et al.* discussed the application of ALD and related
98 techniques in the design of novel membrane interfaces and explained how ALD can be used for
99 instance to modify the surface chemistry and interfacial properties of membranes and tailor the pore
100 sizes.⁴⁰ Feng *et al.* proceeded ALD of ZnO on carbon nanotubes. For 40 cycles they observed the highest

101 permeability value at $430 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$, a WCA reduced by a third and a six time higher BSA rejection.
102 However, for more than 40 cycles the permeability decreased and the WCA did not change⁴¹. Wang *et al.*
103 deposited polyimide on the surface of nanoporous anodized alumina by ALD. They showed that 50
104 cycles lead to the remarkable upgrade of retention from nearly none for the neat alumina substrate to
105 82 % while the water permeability almost three time lower was still maintained as high as 800
106 $\text{L}/\text{hm}^2\cdot\text{bar}^{42}$. The interest in using ALD technique on polymers is growing for different type of
107 applications such as in barrier materials, protective coatings and gas and liquid filters. The mechanisms
108 and reactions occurring during ALD process on some polymers had been studied by Parsons *et al.* They
109 focused particularly on the common Al_2O_3 reaction sequence using trimethyl aluminum (TMA) and
110 water on different kind of polymers such as polypropylene (PP), polyamide or polyester. They
111 explained that reaction during TMA/ H_2O deposition on polymer materials depends strongly on the
112 starting polymer, the precursor as well as the detailed process conditions. With inert polymer like PP,
113 the TMA diffuses into the near surface region of the polymer and will then react with water during the
114 second half-cycle step to form nuclei beneath or at the polymer surface. On polymers where there is
115 a large density of reactive groups, the ALD reaction can be limited to the top surface of the polymer.
116 Carbonyl site is the most Lewis basic functionality in some polymers, so it is expected to coordinate
117 with the TMA Lewis acid to form an aluminum-oxygen-alkyl unit and to disrupt the hydrogen bonding
118 between neighboring chains, which could act to “open up” the polymer chain network, promoting
119 further TMA diffusion into the subsurface region. Like TMA, TiCl_4 is also a strong Lewis acid, so it may
120 diffuse into the polymer and react with it through similar Lewis acid/base adducts⁴³. To the best of our
121 knowledge, there are several articles that focused on the insertion of TiO_2 onto PSF membranes^{34,44–47}
122 or on the deposition of oxides on polymeric membranes^{48,49} but there is no study focusing on TiO_2 ALD
123 on PSF HF membranes.

124
125 This study focus on the surface modification of PSF HF membranes by TiO_2 using ALD technique and its
126 influence on the fiber properties compared to raw PSF HF membranes. The effect of ALD treatment on
127 the membrane morphology was investigated by scanning electron microscopy (MEB) and in terms of
128 hydrophilicity and pores size. The performances of the HF membranes for water purification
129 application were characterized: water permeability, antifouling using Bovine Serum Albumin (BSA)
130 protein and mechanical properties. The modification of polymeric membranes by ALD requires a
131 preliminary step of conditioning to enable them to withstand vacuum under heat treatment. To the
132 best of our knowledge, there has not yet reported studies in the literature clarifying the conditioning
133 of polymeric membranes for TiO_2 deposition by ALD on PSF HF membranes. So in a first step, we will
134 present the glycerin conditioning of the membrane and then the effect of deposition of 10, 20, 50 and
135 100 cycles TiO_2 on the membrane structure and properties.

136 **2. Materials and methods**

137 **2.1. Materials**

138 PSF HF membranes supplied by Polymem were used as substrates for TiO_2 ALD. The membranes were
139 received after chlorine washing and glycerin conditioning steps. Titanium (IV) chloride (TiCl_4 , 99.9%,
140 CAS: 7550-45-0) and deionized water were served as metallic and oxygen source for the ALD process,
141 respectively. Argon gas was bought from Linde and used as received. Phosphate buffered saline (PBS)
142 (Roth) and bovine serum albumin (BSA) ($M_w=67 \text{ kDa}$, $\geq 96\%$, Sigma-Aldrich) solution were employed
143 to assess the fouling resistance of both raw and modified PSF HF membranes. Dextran (M_w from 6 to
144 2,000 kDa, Sigma-Aldrich) were used for membrane pore size characterization. Deionized water
145 (Millipore Milli-Q) was used in all aqueous solutions.

146

147 **2.2. TiO₂ ALD on PSF HF membranes**

148 The commercial PSF membranes were received conditioned in a water/glycerin mixture. This
 149 processing is usually applied in industry to preserve the porous structure along storage. The glycerin
 150 must then be removed when the membranes are in use. Membranes called P, P-0 and P-10 have been
 151 washed in successive water baths to remove glycerin before experiments. Membranes called P-g-0, P-
 152 g-10, P-g-20, P-g-50 and P-g-100 undergone ALD process as received. After deposition, they were
 153 washed in successive water baths to remove glycerin to determine their functional properties. The
 154 commercial PSF membranes were introduced for a 15 min acclimation in the home-built ALD reactor
 155 under vacuum ($\sim 10^{-2}$ mbar) and preheated at 100°C. The deposition process was achieved using TiCl₄
 156 and H₂O as precursors contained in stainless steel cylinders which lines were heated at 80°C to avoid
 157 condensation. One ALD cycle consisted of 50 ms pulse of TiCl₄, followed by 10 s exposure and 60 s
 158 purge with Ar gas, then H₂O valve was opened for 2 s, followed by an exposure of 10 s and purge for
 159 60 s. Several cycles were applied 10, 20, 50 and 100 that correspond respectively to 1, 2, 5 and 10 nm
 160 thick deposit according to a previous study conducted in this ALD chamber and using these operating
 161 conditions⁵⁰.

162 Table 1 presents the nomenclature of the PSF HF membranes that have undergone the different tests
 163 of this study.

164 **Table 1:** Membranes nomenclature (All membranes, except from P and P-g, were introduced in ALD
 165 chamber for a 15 min vacuum acclimation at 100°C)

Fiber's name	Description
P	PSF industrial fiber reference washed to remove glycerin
P-0	PSF industrial fiber washed and placed in the ALD chamber under vacuum and at 100°C during 25 min without deposition
P-g	PSF industrial fiber reference conditioned with a water/glycerin mixture
P-g-0	PSF industrial fiber conditioned with glycerin placed in the ALD chamber under vacuum and at 100 °C during 25 min without deposition
P-10	PSF industrial fiber placed in the ALD chamber under vacuum and at 100 °C during 25 min for TiO ₂ deposition (10 cycles corresponding to 1 nm thickness)
P-g-10	PSF industrial fiber conditioned with glycerin placed in the ALD chamber under vacuum and at 100 °C during 25 min for TiO ₂ deposition (10 cycles corresponding to 1 nm thickness)
P-g-20	PSF industrial fiber conditioned with glycerin placed in the ALD chamber under vacuum and at 100 °C during 1 h for TiO ₂ deposition (20 cycles corresponding to 2 nm thickness)

P-g-50	PSF industrial fiber conditioned with glycerin placed in the ALD chamber under vacuum and at 100 °C during 3 h for TiO ₂ deposition (50 cycles corresponding to 5 nm thickness)
P-g-100	PSF industrial fiber conditioned with glycerin placed in the ALD chamber under vacuum and at 100 °C during 8 h for TiO ₂ deposition (100 cycles corresponding to 10 nm thickness)

166

167 2.3. Characterizations

168 The morphology of the membrane, both cross-section and surface, was observed using a Hitachi S4800
 169 scanning electron microscopy system (SEM) after previous nitrogen cold-cutting. Energy-dispersive X-
 170 ray spectroscopy analysis (EDX) was performed with a Zeiss EVO HD15 microscope coupled with an
 171 Oxford X-MaxN EDX detector. To investigate the changes in chemical structure and to confirm the
 172 successful deposition of TiO₂ between the raw and the modified PSF HF membranes, Fourier Transform
 173 Infrared (FTIR) spectra were acquired using FTIR spectrometer NEXUS instrument equipped with an
 174 attenuated total reflection (ATR) accessory in the frequency range of 600–4000 cm⁻¹. The ATR-FTIR
 175 spectra were recorded with a resolution of 4 cm⁻¹, and the signals were averaged from 64 scans. The
 176 mechanical properties of the raw and modified PSF HF membranes were characterized using a dynamic
 177 mechanical analysis device (Z005, 5 kN Proline, Zwick Roell). A 10N sensor and a tensile testing speed
 178 of 0.4 mm·min⁻¹ were applied. The Young's modulus of the membranes was calculated directly from
 179 the device. Water contact angles (WCA) were measured using a tensiometer/goniometer ILMs GBX,
 180 equipped with an optic telecentric F55 double focal monochrome and a GBX software. For each
 181 sample, about 0.5 μL of ultrapure water was deposited on the membranes using a needle.
 182 Furthermore, X-ray Photoelectron Spectroscopy (XPS) was carried out with a Kratos AXIS NOVA
 183 spectrometer (Kratos Analytical Ltd., Manchester, UK) using a monochromatized Al Kα X-ray source
 184 (1486.6 eV) operating at a power of 150 W (10 mA, 15 kV). Survey and high-resolution spectra were
 185 acquired at 160 and 20 eV pass energies, respectively. Mean pore diameter of raw HF membrane had
 186 been kindly determined by Porometer using the liquid-liquid porometry on a POROLIQ 1000ML.

187

188 2.4. Filtration experiments

189 A U-tube shaped hollow fiber bundle which consisted of 10 wet fibers measuring each 40 cm long
 190 (equivalent to 90 ± 5 cm² effective membrane area) was prepared using a homemade polyvinyl chloride
 191 (PVC) housing module. Epoxy resin was used to seal the module. The pure water flux (J_w) was measured
 192 for each membrane by circulating pure water through the membrane system using an applied pressure
 193 range of 0.5–1.5 bar. Each point was obtained measuring the flow passing through the membrane
 194 during 60 s. The pure water flux, J_w (L·h⁻¹·m⁻²), was calculated using the following formula:

$$195 \quad J_w = \frac{Q}{A} \text{ (L} \cdot \text{h}^{-1} \cdot \text{m}^{-2}\text{)} \quad (1)$$

196 where Q (L·h⁻¹) is the amount of water that passed through the membrane and A (m²) is the membrane
 197 area. The permeability was determined from the slope of the linear variation of J_w versus the applied
 198 pressure.

199 Rejection experiments were conducted to estimate the pore size and their reduction after ALD using 1
 200 g/L aqueous solutions of Dextran solutes with M_w going from 6 to 2,000 kDa. A U-tube shaped hollow
 201 fiber bundle was prepared like described above. Dextran contents in the feed (C_f) and in the permeate
 202 (C_p) solutions were determined by flow injection analysis using refractometer 2414 (Waters
 203 Corporation). The solute rejection (R) was calculated using the following formula:

$$204 \quad R = 1 - \frac{C_p}{C_f} \times 100 \text{ (\%)} \quad (2)$$

205 The membrane was first conditioned by applying a pressure of 1.5 bar with distilled water for 30
 206 minutes. External-internal solute filtration of the membrane was then carried out for 20 min at 0.5 bar.
 207 The hydrodynamic radius values, r_p in Å, of the various Dextran molecules used in these experiments
 208 were estimated from the following equation⁵¹:

$$209 \quad r_p = 0.488 M_w^{0.437} \quad (3)$$

210 where M_w is the molecular weight of the Dextran.

211 Static protein adsorption was performed to estimate the anti-fouling properties of the TiO₂-deposited
 212 PSF HF membranes and the raw PSF HF membrane was used as reference. An I-shaped hollow fiber
 213 bundle, consisting of 10 wet fibers measuring each 27 cm long (equivalent to an effective membrane
 214 area of 63.28 cm²), was prepared using a polyvinyl chloride (PVC) module and an epoxy resin as sealing
 215 agent. The protein solution was prepared by dissolving 2 g of BSA in 2 L of PBS solution at pH 7.4. The
 216 membrane was first conditioned by applying a pressure of 1.5 bar with distilled water for 30 minutes.
 217 Initial external-internal water filtration of the membrane is then carried out for 20 min at 0.5 bar and
 218 the steady pure water flux was recorded (J_{w_0}) using a balance and data acquisition software. The tank
 219 was then filled with the BSA solution and filtration was carried out at 0.5 bar for 2 hours and foulant
 220 flux was recorded (J_{w_f}). The BSA was removed by mechanical agitation and then backwashing with
 221 water applying a pressure of 1.5 bar internally-externally for 5 min. Finally, a last external-internal
 222 filtration cycle with water for 20 min at 0.5 bar was performed and the steady flux was recorded (J_{w_1}).
 223 The total fouling ratio (R_t), flux recovery ratio (FRR), the reversible fouling ratio (R_r) and the irreversible
 224 fouling ratio (R_{ir}) were estimated using equations (2)–(5), respectively⁵²:

$$225 \quad R_t = \frac{J_{w_0} - J_{w_f}}{J_{w_0}} \times 100 \text{ (\%)} \quad (4)$$

$$226 \quad FRR = \frac{J_{w_1}}{J_{w_0}} \times 100 \text{ (\%)} \quad (5)$$

$$227 \quad R_r = \frac{J_{w_1} - J_{w_f}}{J_{w_0}} \times 100 \text{ (\%)} \quad (6)$$

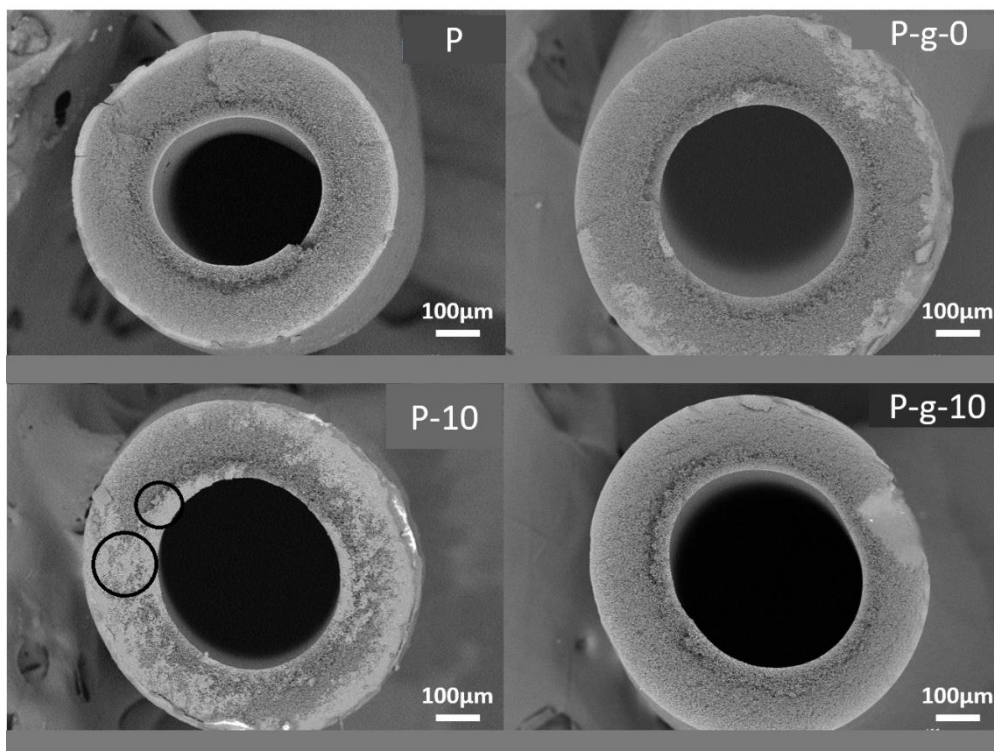
$$228 \quad R_{ir} = \frac{J_{w_0} - J_{w_1}}{J_{w_0}} \times 100 \text{ (\%)} \quad (7)$$

229 The feed BSA solution, BSA retentate and permeate concentrations are calculated from Beer Lambert's
 230 Law using the constant $k = 0.6439$ L/g and an ultraviolet (UV) spectrometer on the absorbance at 280
 231 nm (Uviline Connect Series 940). The rejection of protein was obtained from equation (2) where C_p and
 232 C_f are the protein concentrations of BSA in permeate and feed.

233 **3. Results and discussion**

234 **3.1. Glycerin conditioning**

235 The successful deposition of TiO₂ by ALD on HF membranes is challenging because of the temperature
236 and pressure sensitivity of the polymers. A first study was carried out to observe the influence of
237 glycerin conditioning on the morphology and water permeability of membranes after the deposition
238 of TiO₂. It is necessary to know whether the glycerin brings a protective effect to the polymeric
239 membranes that underwent ALD process. The internal and external diameters of the membranes as
240 well as their lengths were measured before and after ALD treatment. It can be seen that the diameters
241 and lengths are not affected by vacuum ($\sim 10^{-2}$ mbar), temperature (100°C) and TiO₂ deposition as the
242 values before and after are nearly identical. SEM images of the PSF HF membranes cross sections are
243 presented in Fig. 1. All fibers present a sponge-like asymmetric structure characteristic of HF
244 membranes.



245
246 **Figure 1.** SEM pictures of raw PSf HF (P), PSf HF with 10 ALD cycles (P-10) and PSf HF conditioned with
247 glycerin and with 10 ALD cycles (P-g-10)

248 In the case of P-10 (without glycerin), SEM images show that most of the pores have collapsed during
249 the deposition, which some are pointed out by the circles, whereas for P-g-10 (sample with glycerin) it
250 is not possible to distinguish any significant change comparing to the raw PSf HF membrane. We
251 assume that glycerin originating from conditioning and settled in the pores of the fiber allows
252 protecting the structure during the preheating (100 °C) and under vacuum acclimation ($\sim 10^{-2}$ mbar).
253 Without glycerin, the HF structure is damaged by temperature and vacuum. No other difference was
254 noticeable between raw and TiO₂ deposited membranes on SEM images. The mean pore diameter of
255 the raw PSf HF membrane was determined by liquid-liquid porometry to be 25 nm. It was believed
256 that ALD deposition may reduce the pore size⁴⁸ which was not possible to quantify *via* this technique

257 as they are too small. Pore size reduction will be evaluated in the last part of this paper using dextran
 258 rejection.

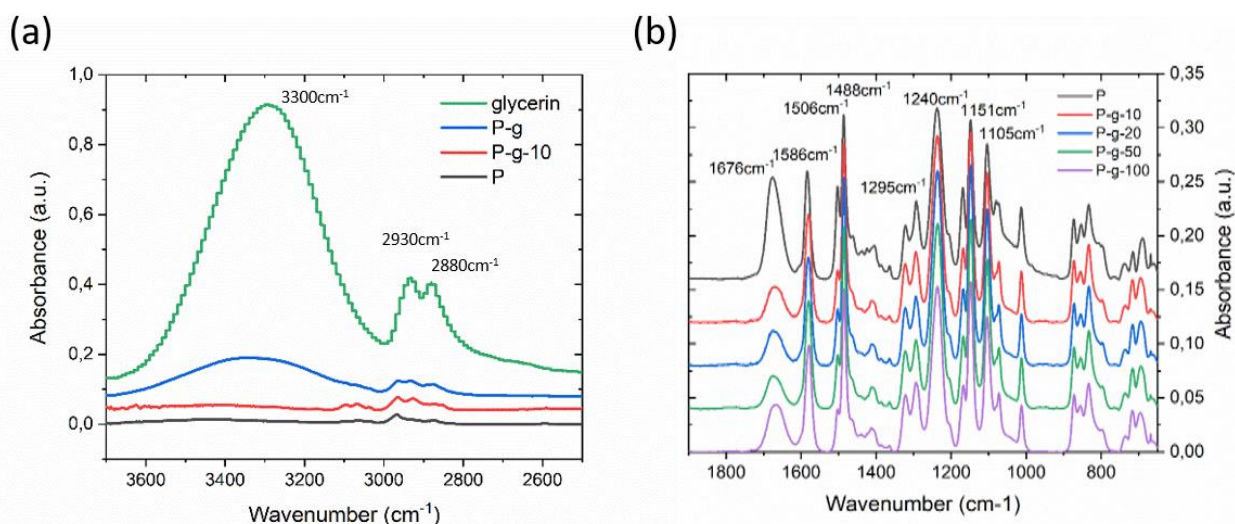
259 The necessity of glycerin conditioning was also evidenced by the results of permeability measurements
 260 presented in Table 2. On one hand, membranes without glycerin conditioning P-0 and P-10 display a
 261 very low permeability (5 ± 1 and 4 ± 1 L/h⁻¹m⁻²bar⁻¹ respectively) after ALD process. In accordance with
 262 SEM images, the deposition damaged the structure of the membrane leading to the collapse of the
 263 pores and thus the diminution of water permeability. On the other hand, the glycerin allowed P-g-10
 264 to show a 26 % higher permeability around 170 L/hm²bar against 135 L/hm²bar for raw membrane P.
 265 The 27 L/hm²bar permeability of P-g-0 pointed out that glycerin is no longer able to prevent the pore
 266 collapsing during the whole vacuum time residence. In fact, as presented in Table 2, P-0 and P-g-0
 267 membranes spent the most time in the ALD chamber under vacuum: 40 min against 15 min for P-10
 268 and P-g-10. So during the fifteen first minutes, the glycerin managed to counteract the pore reduction
 269 under vacuum at 100°C, then it is fully evaporated and the membrane structure is altered for the
 270 twenty-five other minutes. This explains the drop in permeability for P-g-0. For P-g-10, after the 15 min
 271 vacuum acclimation at 100°C, the deposition started and vacuum was stopped.

272 **Table 1** : Water permeability values of P, P-0, P-g-0, P-10 and P-g-10 membranes (the error referred to
 273 standard deviation of 3 samples)

Fiber's name	Residence time under vacuum (min)	Residence time with TiO ₂ deposit (min)	Permeability (L/h ⁻¹ m ⁻² bar ⁻¹)
P	0	0	135 ± 14
P-0	40	0	5 ± 1
P-g-0	40	0	27 ± 4
P-10	15	25	4 ± 1
P-g-10	15	25	170 ± 17

274
 275 According to SEM pictures and water permeability measurements, the efficiency of glycerin
 276 conditioning has been clearly proved. Moreover, the acclimation period before ALD cycles process was
 277 a key parameter to allow a good TiO₂ deposition. Several tests have been performed and it was
 278 observed that, even for HF with glycerin, an acclimation time superior to 15 minutes deteriorate the
 279 HF membrane. After more than 15 minutes in the ALD chamber under vacuum at 100°C, the HF was
 280 totally dried and the result is a water permeability close to zero. This proved that glycerin conditioning
 281 is efficient only coupled with an acclimation no longer than 15 minutes. Indeed, the boiling
 282 temperature of glycerin was reduced from 290°C at atmospheric pressure to 96°C at the pressure
 283 applied during deposition (10^{-2} mbar)⁵³. We can propose that all the glycerin available on the HF surface
 284 is evaporated and only a few amount bounded onto the pores maintain the internal morphology at
 285 the end of acclimation at 100°C. The evaporation of glycerin was proved in Fig. 2 (a) with FTIR analysis.
 286 Indeed, pure glycerin showed two signals between 2800 and 3000 cm⁻¹ corresponding to C-H stretching
 287 and one broad and intense band around 3300 cm⁻¹ corresponding to O-H stretching. Three fibers were
 288 analyzed, the PSF industrial fiber reference conditioned with glycerin P-g, the PSF industrial fiber
 289 conditioned with glycerin placed in the ALD chamber under vacuum and at 100°C during 10 cycles for
 290 TiO₂ deposition P-g-10 and the PSF industrial fiber reference washed after conditioning. The band

291 around 3300 cm^{-1} also corresponds to water but the three fibers have been placed in a 60°C oven
 292 overnight before analysis, which lead to water evaporation as shown by the P spectrum (washed
 293 membrane containing no glycerin). The absorption band at 3300 cm^{-1} is not visible anymore. P-g
 294 spectrum presents the same O-H pic than glycerin but less intense whereas P-g-10 did not show any
 295 pic in this area. Therefore, it can be concluded that 15 min acclimation in the ALD chamber at 100°C
 296 under vacuum eliminate all the glycerin by evaporation as the IR characteristic signals of glycerin have
 297 disappeared of the sample after deposition. When the TiO_2 deposition started, TiCl_4 reacted directly
 298 with PSf support.



299
 300 **Figure 2.** (a) Comparison of ATR-FTIR spectrum of glycerin with those of PSf membrane with glycerin
 301 (P-g), washed PSf membrane (P) and PSf membrane with glycerin after 10 ALD cycles and (b) Raw
 302 and ALD modified PSF membranes ATR-FTIR spectra

303 Based on these observations, glycerin conditioning and 15 min acclimation were applied for all the
 304 following ALD tests.

305
 306 **3.2 Influence of ALD cycles on membrane properties**

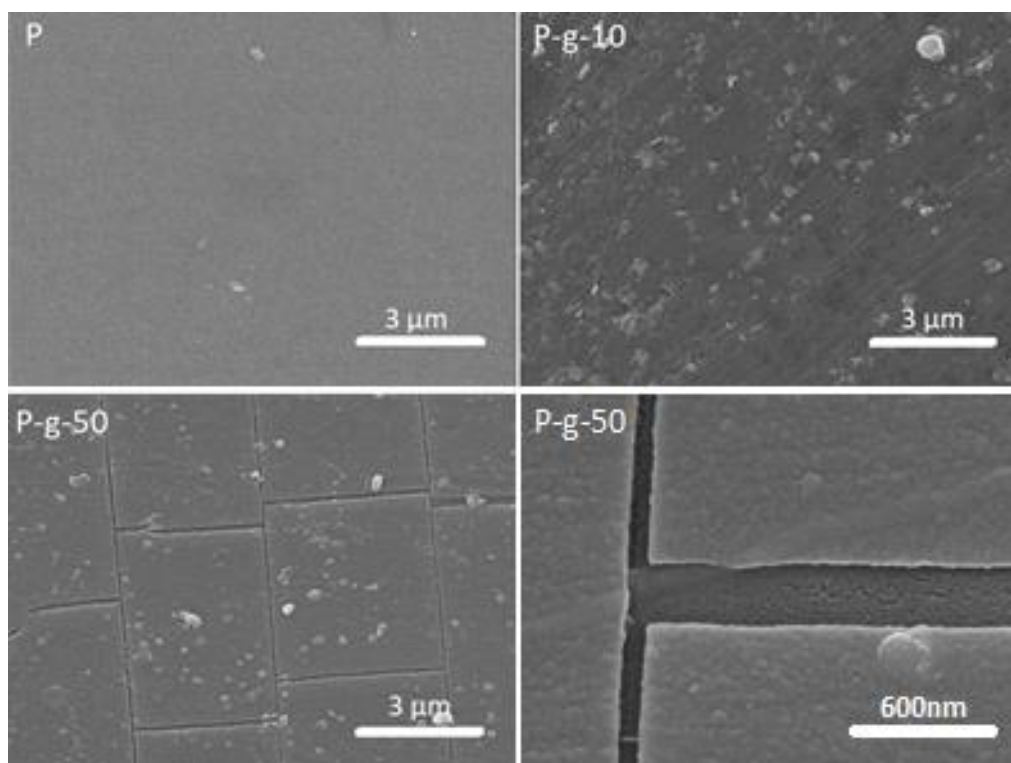
307 **3.2.1 Structural and physico-chemical characterizations**

308
 309 The formation of TiO_2 layers on the PSf HF membranes was investigated by ATR-FTIR spectroscopy. In
 310 Fig. 2 (b), the characteristic IR peaks of PSf are visible in raw and modified membranes. Signals
 311 observed at 1105, 1488, 1506 and 1586 cm^{-1} correspond to the vibrations of PSf aromatic ring (C=C
 312 stretching). Bands at 1151 cm^{-1} and 1240 cm^{-1} were attributed to the $-\text{O}-\text{S}-\text{O}-$ symmetric and aromatic
 313 ether bond ($-\text{C}-\text{O}-\text{C}-$), respectively. The peak at 1295 cm^{-1} was related to SO_2 group stretching
 314 vibration⁵⁴. Additionally, absorbance peak at 1676 cm^{-1} could be attributed either to the C=O stretching
 315 vibration of NMP or PVP that might remain on the membrane surface. Any new peaks could be
 316 observed for the ALD modified membranes in the investigated frequency range. Thus we can assume
 317 that the amount of TiO_2 is too low to be detected *via* this technique, as a consequence of a low number
 318 of ALD cycles. Actually, Jia *et al.* studied the deposition of Al_2O_3 on porous polypropylene HF by ALD
 319 technique, and they only noticed a new absorption peak after more than 100 deposition cycles⁴⁹.

320 Moreover, Wang *et al.* studied the deposition of TiO₂ by ALD on PVDF membranes and they suggested
321 that the pic intensity was similar under 100 deposition cycles and began to drop after, as the number
322 of ALD cycles increased. The TiO₂ coating layer may reduce the depth that the light beam can reach in
323 the material, thus the detected IR signal of the PVDF membrane is weaker.⁴⁸ The same trend is
324 observed for our samples, the intensity of the peaks decreases when increasing the number of ALD
325 cycles. Any evidence of the deposition of TiO₂ on the PSF HF membranes using ALD technique was
326 found by ATR-FTIR spectroscopy technique. In addition, Waldman *et al.* focused on the SIS of Al₂O₃ in
327 PES membranes and were able to understand the molecular interactions during ALD process through
328 FTIR experiments. They explored in situ FTIR of TMA in-diffusion and out-diffusion to elucidate the
329 nature and kinetics of an attractive interaction between the TMA and the PES moieties. All their FTIR
330 measurements allowed them to confirm that TMA associates with the sulfonyl and aryl ether groups
331 of the PES polymer in a qualitatively similar way to the association with the carbonyl and ester groups
332 of PMMA.⁵⁵ This study could help us understanding the molecular interactions that took place in our
333 ALD process supposing that TiO₂ may react with sulfonyl and ether groups of the PSF membrane.

334
335 SEM analyses performed on the top surface of raw PSF HF membrane P, and modified PSF HF
336 membranes are presented in Fig. 3. They showed that for raw PSF HF membrane P and the membrane
337 that undergone 10 cycles ALD no change was observed on the surface, which supposed a thin and
338 uniform coating. However, for the PSF HF membrane with 50 ALD cycles, P-g-50, a geometric and
339 regular structure on surface was observed most likely corresponding to the TiO₂ thicker layer that may
340 have cracked. Similar micrographs were obtained for P-g-100.

341



342

343

344 **Figure 3.** SEM Images of raw (P) and ALD modified membranes surface (10 and 50 cycles)

345

346 In order to quantify the amount of TiO₂ deposited on membranes, EDX of all raw and ALD modified PSF
 347 HF membranes was performed. The measured atomic percentages of C, O and Ti are presented in
 348 Table 3. The detected atomic percentages of Ti were very low for P-g-10 and P-g-20 samples (≤ 0.1)
 349 due to small layer thicknesses of TiO₂ (1 and 2 nm respectively), but the Ti atomic percentage increases
 350 for P-g-50 and P-g-100 following the increasing number of ALD cycles. These results are in good
 351 agreement with SEM observations which allow the observation of the deposit starting from 50 ALD
 352 cycles. Moreover, we can add from EDX cross-sectioned mapping in Fig. S1 and Fig. S2 that TiO₂ was
 353 uniformly deposited onto the membrane network.

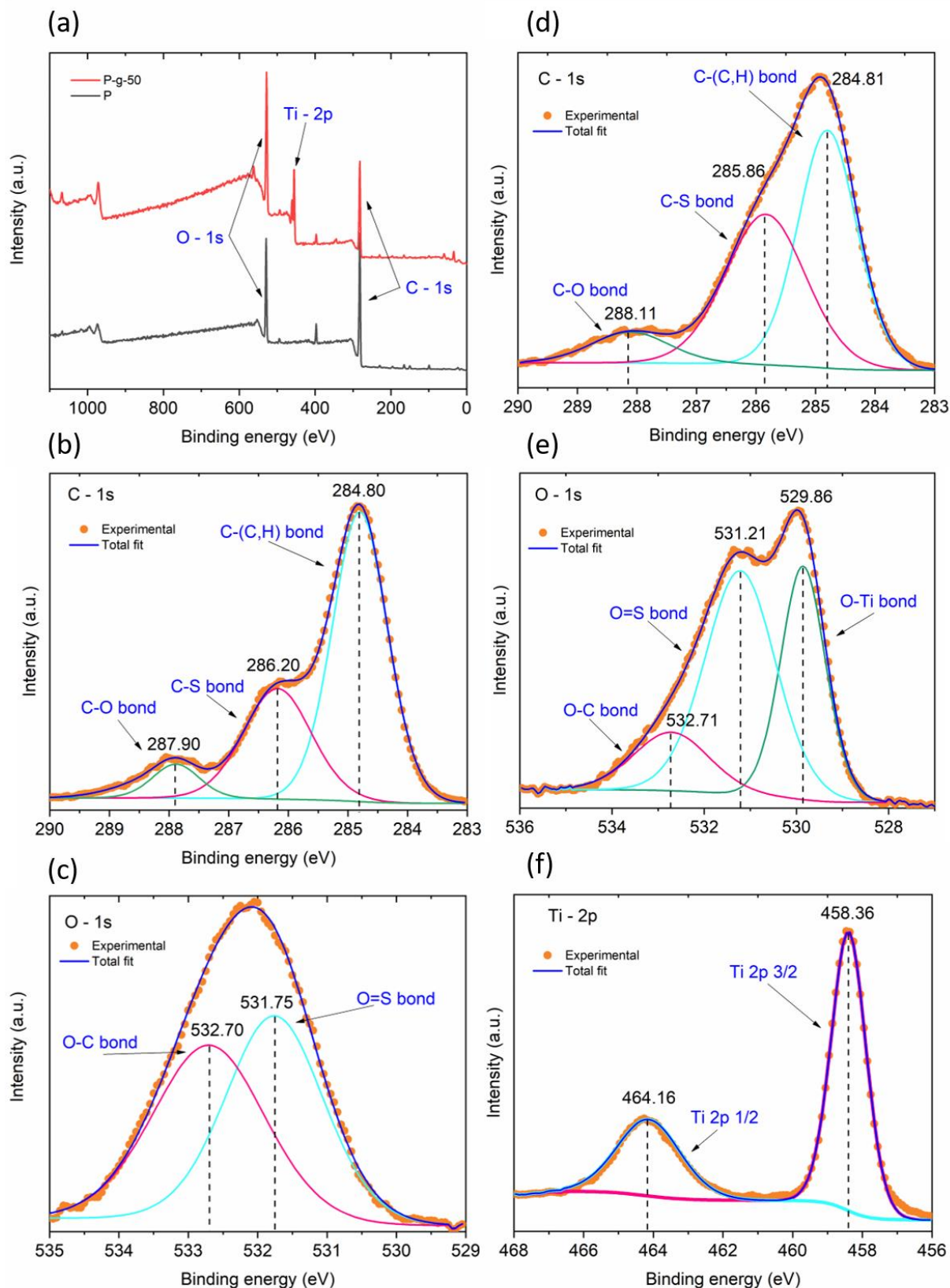
354

355 **Table 2.** EDX data showing the composition of the raw and ALD modified membranes (the error was
 356 calculated based on a 10% EDX measurement uncertainty)

Atomic percentages (%)			
Samples	C	O	Ti
P	86.8 ± 8.6	9.9 ± 0.9	0
P-g-10	86.3 ± 8.6	11.3 ± 1.1	≤ 0.1
P-g-20	87.2 ± 8.7	9.9 ± 0.9	≤ 0.1
P-g-50	76.8 ± 7.7	20.5 ± 2.1	0.8 ± 0.1
P-g-100	74.7 ± 7.5	22.2 ± 2.2	1.2 ± 0.1

357

358 To go further, XPS analyses were performed on raw and modified membranes. No difference was
 359 observed between raw and P-g-10 and P-g-20. We assumed that, according to the other analyses
 360 methods, for 10 and 20 ALD cycles the amount of TiO₂ was too low and under the detection limit. P-g-
 361 50 and P-g-100 presented the same spectra. The survey of C 1s, O 1s and Ti 2p deconvoluted spectra
 362 of P and P-g-50 are presented in Fig. 4. The XPS survey spectra of both membranes (Fig. 4a) consist of
 363 two peaks at the binding energies of 284.85 and 532.05 eV assigned to C and O atoms respectively
 364 with an additional peak around 458.36 eV for P-g-50 assigned to Ti atom. The C signal in the high-
 365 resolution spectra of the raw membrane P could be deconvoluted into three peaks (Fig. 4b): Carbon
 366 atoms attached to hydrogen/carbon, sulfone and ether groups exhibit C 1s core-level binding energies
 367 of 284.80, 286.20 and 287.90 eV respectively. The C 1s spectra of P-g-50 (Fig. 4d) was similar which
 368 supports that the PSf matrix was not damaged during deposition. However, the deconvoluted spectra
 369 of O 1s included two peaks for P (Fig. 4c) at 532.70 and 531.75 eV corresponding to O-C and O=S bonds
 370 respectively while a third peak appeared for P-g-50 (Fig. 4e) at 529.86 eV corresponding to the O-Ti
 371 bond. This confirmed that TiO₂ was well deposited and reacted with the oxygen atoms of the PSf
 372 matrix. For P-g-50, in the deconvoluted Ti 2p spectra (Fig. 4f), two peaks are positioned at 458.36 and
 373 464.16 eV, corresponding to Ti 2p_{3/2} and Ti 2p_{1/2} states indicating that Ti is 4+ valence.



374

375 *Figure 4: Survey XPS spectra (a) and deconvoluted XPS spectra of P C 1s (b) and O 1s (c) and P-g-50 C 1s (d), O 1s (e) and Ti 2p*
 376 *(f)*

377 **3.2.2 Membrane performances**

378 Mechanical tests were performed on raw and modified membranes. Young modulus and the strength
 379 at break values are presented in Table 5. The results showed that ALD-modified membranes displayed
 380 a higher Young modulus around 147 MPa in average compared to raw membrane (132 MPa), which
 381 corresponds to a lower resistance to stress deformation. Any correlation between the increasing
 382 number of ALD cycles and the increase Young modulus has been noticed. Because the ALD modified
 383 membranes were more rigid, the strength applied to break them was lower than for raw PSF HF
 384 membrane decreasing from 2.10 ± 0.02 to in average 1.76 N. However, TiO_2 could act as crosslinker
 385 between the polymer chains, improving consequently the rigidity of the network and therefore, the
 386 mechanical strength⁵⁶. This observation is in accordance with Diez-Pascual *et al.*, who studied the
 387 effect of TiO_2 nanoparticles insertion on the performance of polyphenylsulfone. They observed a
 388 gradually increasing Young's modulus upon raising nanoparticle loading, by up to 62 % at the highest
 389 concentration tested. They attributed this improvement to the effect of the rigid TiO_2 with the
 390 interactions (H-bonding) it established with the membrane matrix. This results in a decrease in polymer
 391 chain motion and in promoting the adhesion between the two phases⁵⁷. In Table 4 are also presented
 392 the permeability values which matched with the SEM observation. In fact, a thin and uniform TiO_2 layer
 393 on the membrane surface for P-g-10 and P-g-20 allowed a 26 to 50 % higher permeability value
 394 compared to raw membrane P. However, starting from 50 cycles when the coating was thicker a drastic
 395 drop in permeability is observed. From these results, 50 and 100 cycles could be discriminated,
 396 supposing that the layer is too thick to allow great performance. For the rest of the study, P-g-100 was
 397 forsaken and P-g-50 was still studied to compare with P-g-10 and P-g-20.

398

399 **Table 4.** Tensile properties of raw and ALD modified HF membranes (the error referred to standard
 400 deviation of 3 samples)

	Young Modulus (MPa)	Strength at break (N)	Permeability (L/hm ² bar)
P	132 ± 5	2.10 ± 0.02	135 ± 14
P-g-10	153 ± 9	1.72 ± 0.11	170 ± 17
P-g-20	143 ± 6	1.84 ± 0.05	200 ± 20
P-g-50	144 ± 4	1.76 ± 0.06	15 ± 2
P-g-100	150 ± 6	1.71 ± 0.08	< 1

401

402 SEM did not permit to measure the pore size reduction reported in other works⁴⁸. To complete,
 403 different sizes of dextran were filtered through raw and ALD modified PSF HF membranes (P-g-10 and
 404 P-g-20). The evolution of the rejection rate versus molecular weight of dextran molecules is presented
 405 in Fig. 5 (a). The correspondence between the molecular weight and the pore diameter of dextran
 406 molecules was calculated based on Equation (3) and is presented in Table 5. All dextran molecules
 407 were able to pass through the raw PSF HF membrane pores from a rejection rate near zero for the
 408 smallest molecule to 80% rejection for the biggest at 55.3 nm. It can be observed that even if the mean
 409 pore size of raw PSF HF membrane was measured at 25 nm, there is a large distribution that allows
 410 molecules up to 55.3 nm going through the membrane. On the other side, P-g-10 presented already
 411 20% rejection rate for smallest dextran at 4.7 nm, 50% for 10 nm sized molecules and reached 90% for
 412 30.2 nm dextran. P-g-20 follows the same trend. Other works from the literature gathered in Table 6
 413 confirmed a noticeable reduction of pore size and pore size distribution after ALD process. Dextran

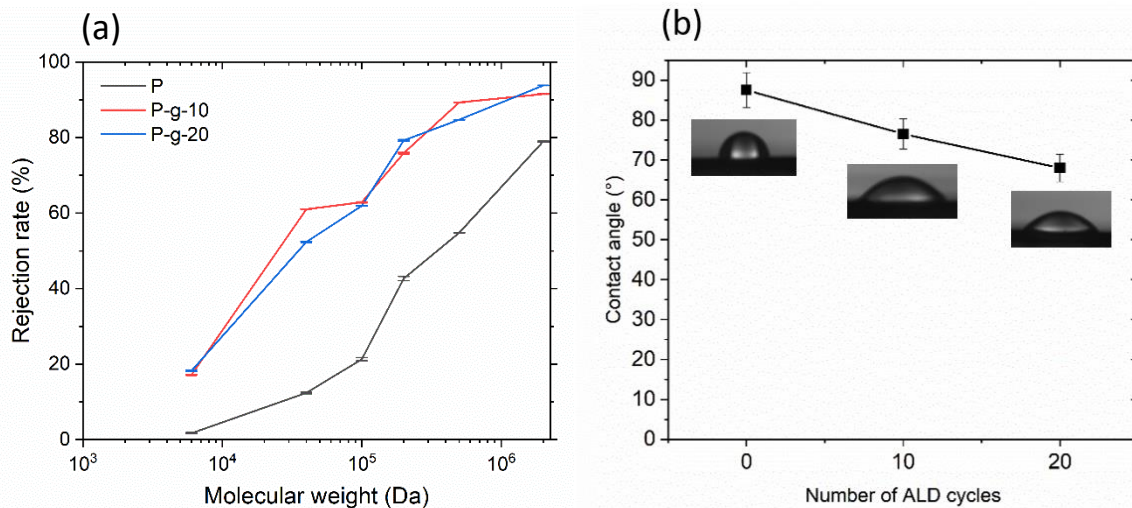
414 rejection rates support SEM observations to evidence the deposition of TiO₂ on all the PSF HF
 415 membrane surface and subsurface.

416

417 **Table 5.** Correspondence between molecular weight and hydrodynamic radius values of dextran
 418 molecules

M _w (Da)	6.10 ³	4.10 ⁴	10 ⁵	2.10 ⁵	5.10 ⁵	2.10 ⁶
r _p (nm)	4.7	10	14.9	20.2	30.2	55.3

419 It is well known that surface hydrophilicity affects the membranes antifouling properties. Membranes'
 420 WCA were measured for P, P-g-10 and P-g-20 and the results are presented on Fig. 5 (b). Initially, the
 421 raw membrane had a WCA of around 90° and this value was gradually reduced down to 70° as the
 422 number of ALD cycles increased. These results are in good agreement with literature as reported in
 423 Table 5. Indeed, Zhang *et al.* prepared PSF hybrid ultrafiltration flat membrane with TiO₂-g-HEMA and
 424 studied its antifouling characteristics. The best hydrophilicity improvement they obtained with a WCA
 425 of 72° was for 2% concentration⁴⁵.



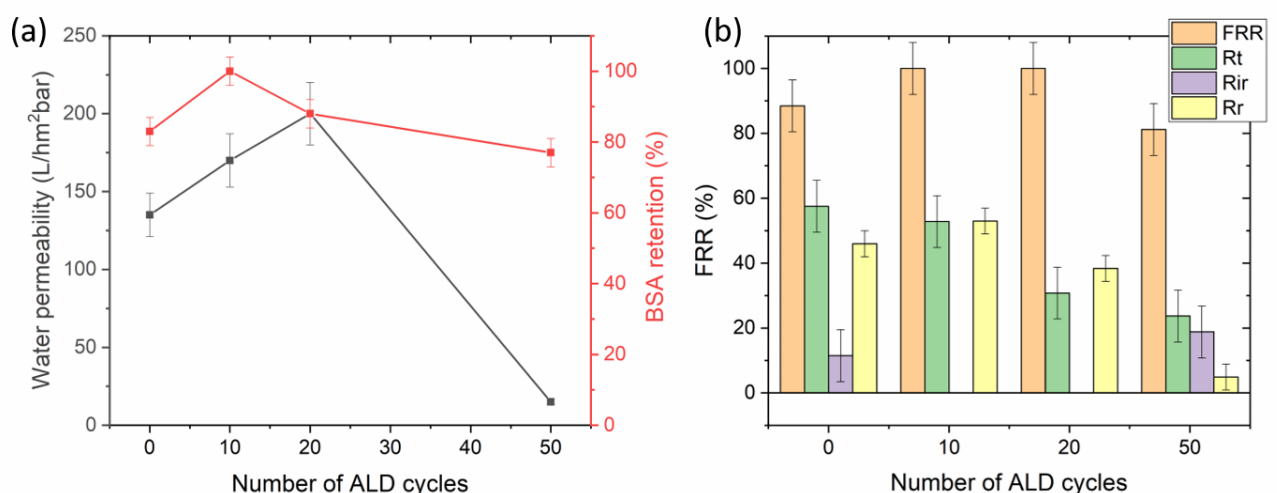
426 **Figure 5.** (a) Different sized dextran rejection rate and (b) WCA of raw and ALD modified membranes
 427 (the error referred to standard deviation of 3 samples)

428

429 The filtration performances of raw and ALD modified PSF HF membranes are depicted in Fig.6 (a). The
 430 raw membrane exhibited a pure water permeability of 135 L·h⁻¹·m⁻²·bar⁻¹ and a retention of BSA around
 431 80%. However, after the ALD deposition of TiO₂, the permeability increases slightly reaching the higher
 432 value for 20 ALD cycles, then it decreases drastically for P-g-50 which displayed a water permeability
 433 of 15 L·h⁻¹·m⁻²·bar⁻¹. P-g-10 and P-g-20 not only showed an increased water permeability but also a
 434 higher BSA retention compared to raw PSF HF membrane. Wang *et al.* deposited TiO₂ on PVDF
 435 membranes *via* ALD process at 80°C. They observed a decrease of permeability that they attributed to
 436 the pore size diminution which is probably the result of the ALD process. Indeed, in addition to the
 437 surface, the TiCl₄ molecules can also penetrate into the subsurface of the membrane. Water vapors
 438 pulsed into the chamber reacted with the TiCl₄ entrapped in the free volumes between the polymer
 439 chains producing layers of TiO₂. When the number of ALD cycles increases, the TiO₂ keeps growing
 440 inside the membrane pores until they are completely blocked⁴⁸. In our case, a pore size reduction was

441 also noticed from dextran filtration accompanied by an increase in hydrophilicity. These two combined
 442 parameters explain the membrane filtration performances. Hypothetically, during acclimation all the
 443 glycerin was slowly evaporated which prevented the pores from collapsing and maintained the internal
 444 morphology. Above 20 ALD cycles, in accordance to SEM images, the observed TiO_2 layer for P-g-50
 445 and P-g-100 could block the pores on the membranes' surface causing the drop in water permeability.

446 Antifouling performances of the ALD modified membranes were investigated using BSA as a fouling
 447 agent, for that the FRR, R_t , R_r and R_{ir} of the membranes are calculated from equations (4) to (7). All
 448 the calculated values are represented in Fig. 6 (b). FRR is at 100% for P-g-10 and P-g-20 compared to
 449 88% for raw PSF HF membrane. This means that due to TiO_2 addition, ALD modified PSF HF membranes
 450 were recovering all the flux after BSA filtration. Indeed, all ALD modified PSF HF membranes exhibited
 451 lower R_t , furthermore interestingly the R_r decreased with the increase of the number of ALD cycles. A
 452 reducing R_r means that BSA adsorbed reversibly was removed after water backwashing, which is a
 453 good result as membranes lifetime is threatened by fouling and most of all irreversible fouling and
 454 chemical backwashing needed to clean them. R_{ir} initially at 12% for raw membrane was at 0% for both
 455 P-g-10 and P-g-20 and around 19% for P-g-50. P-g-100 was tested but the result was not detectable.
 456 On the one hand, the ALD modified PSF HF membranes demonstrated lower BSA fouling but also a 0%
 457 R_{ir} which means that all the BSA adsorbed can be removed with water backwashing. This shows that
 458 with TiO_2 the PSF HF membranes are less sensitive to BSA fouling and would have a longer lifetime.
 459 They display higher fouling resistance against protein compared to the raw PSF HF membrane. These
 460 results are very interesting since the values are even better than that reported in other studies (Table
 461 6). Yang *et al.*⁴⁶ and Zhang *et al.*⁴⁵ inserted for instance TiO_2 nanoparticles into flat PSF membranes and
 462 obtained respectively 97 and 95% BSA rejection. Jia *et al.*⁴⁹ deposited Al_2O_3 on PP HF membranes and
 463 obtained a maximum of 75% BSA rejection.



464

465 **Figure 6.** (a) Water permeability and BSA retention and (b) Fouling resistance parameters for raw and
 466 ALD modified membranes (the error referred to standard deviation of 3 samples)

467 To go further, BSA hydrodynamic radius is 10 nm and for P-g-10 40 % of corresponding Dextran
 468 molecule ($M_w = 4.10^4$ Da) passed through against 0 % of BSA molecule. This proved that BSA is not
 469 only rejected because of its size but thanks to the higher hydrophilicity of the membrane due to TiO_2
 470 deposit.

471 **Table 6.** Comparison of this study with results reported in literature

472
 473

reference	support	oxide	HF or flat membrane	method	Water permeability ($L.m^{-2}h^{-1}bar^{-1}$)	foulant rejection (%)	Mean pores diameter (nm)	WCA (°)
This study	PSF	TiO_2	HF	ALD 0 cycle	135	83	25	88
				ALD 10 cycles	170	100	Reduction	76
				ALD 20 cycles	200	88	Reduction	68
Hamid <i>et al.</i> ³⁴	PSF	TiO_2	HF	Insertion	78.33 ± 0.52	90 (HA)	47.58 ± 0.14	45
Yang <i>et al.</i> ⁴⁶	PSF	TiO_2	Flat membrane	Insertion 1wt%	400	97 (BSA)	6.9	52.6
Zhang <i>et al.</i> ⁴⁵	PSF	TiO_2	Flat membrane	Insertion 1wt%	90	95 (BSA)	18	78
Kusworo <i>et al.</i> ⁴⁴	PSF	TiO_2	Flat membrane	Insertion 1wt%	0.5	90 (NH_3)	9.05 ± 0.63	44.17
Cheraghi Bidsorkhi <i>et al.</i> ⁴⁷	PSF	TiO_2	Flat membrane	Insertion 1wt%	500	98 (BSA)	/	59.9
Galiano <i>et al.</i> ⁵⁶	PVDF	/	HF	Insertion 0.5wt%	280	/	130 ± 30	78 ± 2
Wang <i>et al.</i> ⁴⁸	PVDF	TiO_2	Flat membrane	ALD 30 cycles	70	85 (BSA)	40.8	65
				ALD 100 cycles	110	90 (BSA)	25.7	45
Jia <i>et al.</i> ⁴⁹	PP	Al_2O_3	HF	ALD 50 cycles	284.9	28 (BSA)	not quantified	
				ALD 200 cycles	180	75 (BSA)		

474

475 4. Conclusion

476 Atomic layer deposition of TiO_2 on PSF HF membranes was studied. The protective effect of glycerin to
 477 prevent pore collapsing during ALD process when the polymeric membrane is exposed under vacuum
 478 at $100^\circ C$ was clearly demonstrated. By this way, TiO_2 deposit onto the surface and the porous
 479 substructure can be achieved to give better performances in terms of permeability and anti-fouling

480 properties with BSA. Moreover, the acclimation duration in the ALD chamber must not be too long
481 because of the drastic reduction of glycerin boiling temperature under 10^{-2} mbar vacuum (98°C against
482 290°C under atmospheric pressure). The duration of the ALD process cannot be much more longer
483 than the glycerin evaporation. Based on these conditions, different number of ALD cycles were tested
484 from 10 to 100 corresponding to thicknesses between 1 and 10 nm. The presence of TiO₂ was proved
485 by EDX analysis. On SEM images, TiO₂ layer was observed only upon 50 ALD cycles. Thanks to XPS
486 analyses, the reaction between TiO₂ and the oxygen groups of PSF membranes was confirmed. Dextran
487 molecules filtration showed a clear pore size and pore size distribution reduction for ALD modified PSF
488 HF membranes compared to raw PSF HF membranes. Hydrophilicity improvement was confirmed by
489 WCA reduction from 90° for raw PSF HF membrane to 70° for 20 ALD cycles modified PSF HF
490 membranes. These two parameters explain the enhanced water filtration and fouling properties
491 results of ALD modified PSF HF membranes. Indeed, the ones with 10 and 20 ALD cycles showed the
492 best results, with water permeability up to 26 % higher compared to raw HF membrane and an
493 optimum 100% FRR and a 0% R_{ir}. All ALD modified PSF HF membranes' mechanical properties were not
494 altered by ALD process. The obtained results are a first step for a more in-depth study on TiO₂ coating
495 by ALD on PSF HF membranes. It would be interesting to open the test in real membrane measurement
496 and for filtration of other contaminants. Finally, to the best of our knowledge, this work is a first report
497 on TiO₂ ALD on PSF HF membranes and may pave the way for further studies.

498

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507

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