

1 **Heat-treated optimized polysulfone electrospun nanofibrous membranes for high**  
2 **performance wastewater microfiltration**

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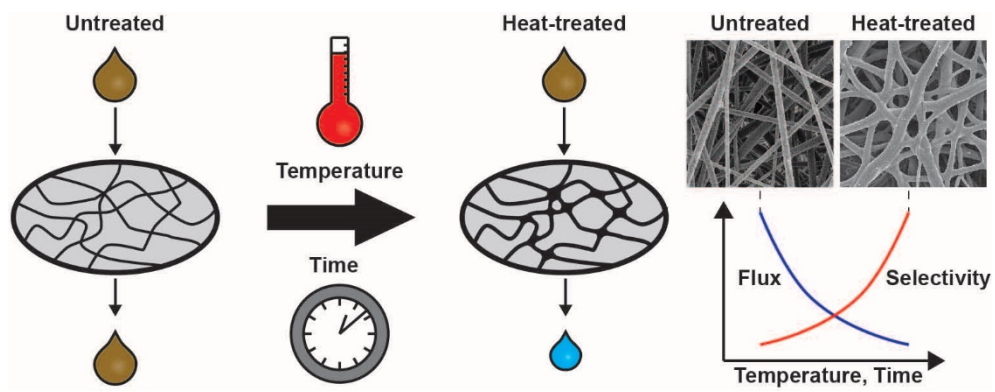
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20 **Graphical Abstract**



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23

24 **Abstract**

25 The structure and morphology of self-sustained electrospun nanofibrous membranes  
26 (ENMs) are key factors determining membrane performance for filtration applications.  
27 In this study, heat post-treatment (HPT) method was applied to modify the structural and  
28 morphological properties of polysulfone (PSU) ENMs, to improve their filtration  
29 performance and to obtain membranes suitable for wastewater treatment. The influence  
30 of the HPT temperature and time on the morphological structure of the PSU ENMs as  
31 well as on fouling and filtration performance was investigated. Microfiltration (MF) tests  
32 were conducted using humic acid model solutions with a concentration of 15 mg/L at pH  
33 11. Increasing the HPT temperature or time, led to an increase of the mean nanofiber  
34 diameter along with a decrease of the mean size of the inter-fiber space, the void volume  
35 fraction and the water contact angle. ENMs treated with a higher HPT temperature and a  
36 longer time exhibited higher nanofibers interconnectivity and a more compact structure  
37 with a smaller size of inter-fiber spaces. Under the same MF operating conditions, a  
38 commercial polyethersulfone (PES) MF membrane (HPWP, Millipore) had lower  
39 filtration performance (i.e. lower performance index, *PI*, 82 kg/m<sup>2</sup>.h) than the treated-  
40 optimized PSU ENMs (i.e. 147 and 133 kg/m<sup>2</sup>.h for ENMs 9 and 10, respectively). The  
41 obtained results confirm the good performance of the developed PSU ENMs for MF  
42 applications.

43

44 **Keywords:** Nanofiber; Heat post-treatment; Electrospun membrane; Humic acid;  
45 Microfiltration.

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## 50 **1. Introduction**

51       The development of efficient membrane filtration technologies is especially  
52 important as water shortage has become a growing global problem in recent years [1].  
53 The improved compactness, low cost operation, high energy efficiency and high  
54 throughput enable membrane separation processes to compete successfully with  
55 conventional separation processes. In fact, membranes are an environmentally-friendly  
56 method highly utilized in waste treatment, water purification and in clarification and  
57 concentration processes [2]. However, the fabrication of adequately designed membranes  
58 for a specific application is challenging [3]. Electrospinning is an attractive and efficient  
59 technique for polymer solution processing that provides a simple and versatile way to  
60 prepare ultrafine polymeric fibers with micro- to nano-scale diameters, ranging from 50  
61 nm to 10  $\mu\text{m}$  thickness [4, 5]. Electrospun fibers are typically collected in the form of a  
62 non-woven mesh, which is of importance for a variety of applications including semi-  
63 permeable membranes, filters, composite reinforcement and scaffolding used in tissue  
64 engineering [6]. Electrospun nanofibrous membranes (ENMs) have a great potential for  
65 membrane filtration due to their attractive structural features, such as high porosity and  
66 interconnected open pore structure, micro-scale interstitial space, controllable thickness  
67 and a large surface area to volume ratio [7]. In ENMs the pores are induced by the  
68 entanglement of interconnected nanofibers (i.e. inter-fiber space). The mean pore size of  
69 ENMs correlates with the nanofiber diameter [8]. Thus, the pore size of ENMs can be  
70 tuned to meet different filtration requirements by changing the nanofiber diameter.

71       Advantages of using ENMs for water treatment include high permeability, mainly  
72 related to their high void volume fraction (i.e. porosity), and good separation factor due  
73 to the highly tortuous path through the nanofibrous structure and the remaining static

74 charge in the nanofibers after electrospinning, which helps to separate different  
75 contaminants [9-11]. In recent years, Microfiltration (MF) has attracted increasing  
76 attention in the field of wastewater treatment and reclamation as an alternative to  
77 conventional water treatment processes (i.e. coagulation, sedimentation and sand  
78 filtration) [12]. MF offers several advantages including easier control of operation, and  
79 reduced maintenance and sludge production. However, a major factor that limits the use  
80 of membranes in water treatment is membrane fouling, which reduces water production  
81 rates and increases energy consumption [13]. Fouling reduces the effective membrane  
82 surface for filtration leading to a strong decline of permeate flux and worse separation  
83 performance [7, 14, 15]. Given that membrane properties have a high impact on fouling,  
84 it is important to understand their effects well in order to develop adequate membranes  
85 that are capable to mitigate fouling. For instance, it has been demonstrated that membrane  
86 hydrophobicity, roughness, pore size and pore morphology affect membrane-foulant-  
87 interactions and consequently, fouling effects [16].

88         In the literature, there is a large number of studies using nanofibrous scaffolds or  
89 ENMs as pre-filters for particulate removal through MF/UF applications. One of the most  
90 mentioned drawbacks of ENMs is the low mechanical strength and the difficulty of  
91 handling them after electrospinning [17]. Several methods were proposed to overcome  
92 these problems before their application in filtration: plasticization [18]; polymer blending  
93 [19]; solvent induced inter-nanofiber bonding [9]; hot-pressing [20-22]; heat treatment  
94 [5-7, 23-26]; addition of nanoparticles [27, 28]; use of crosslinking agents [29]. One of  
95 the most effective approaches is to enhance the bonding at junction points in the nanofiber  
96 mat by welding the nanofibers together, as for example by applying a heat post-treatment  
97 (HPT) (i.e. heating the mat between the glass transition temperature of the electrospun  
98 polymer and its melting temperature). Compared to plasticizing and polymer blending,

99 an appropriate heat treatment may be more environmental friendly and less energy  
100 consuming. The incorporation of nanoparticles in the membrane matrix, such as titanium  
101 dioxide, usually needs a post-treatment of the membrane (e.g. hydrothermal bath,  
102 annealing), which increases the membrane fabrication costs [27]. Moreover, although  
103 hot-pressing has been reported to increase the structural integrity and mechanical strength  
104 of the ENMs, heat treatment can also induce a change in the molecular structure of the  
105 polymer, leading to a higher degree of nanofibers crystallinity [30] and, consequently, to  
106 a greater elastic modulus of the ENMs [2, 23].

107 In this study, the filtration properties of polysulfone electrospun nanofibrous  
108 membranes (PSU ENMs) were improved by the application of HPT. The effects of the  
109 HPT temperature and the HPT time on the structural and morphological properties of the  
110 membranes (i.e. porosity, pore size and its distribution, wettability, thickness) were  
111 investigated, because these factors affect the membrane filtration performance [2, 31].  
112 The filtration performance index (*PI*) was considered to select the optimum heating  
113 conditions for the application of the ENMs in wastewater treatment by MF.

## 114 **2. Materials and methods**

### 115 **2.1. Materials**

116 The polymer polysulfone (PSU, UDEL P-3500 LCD, Solvay Specialty Polymers; Mw  
117 = 79,000 g/mol;  $\rho = 1.24 \text{ g/cm}^3$ ) and the mixture of solvents N, N-dimethyl formamide  
118 (DMF, Sigma-Aldrich) and tetrahydrofuran (THF, Sigma-Aldrich) were used to prepare  
119 the spinning solution. The organic foulant humic acid (HA, Fluka) with a molecular  
120 weight of 4.1 kDa was utilized to prepare the feed solution for the MF tests. Sodium  
121 hydroxide (NaOH, Panreac) was used to prepare a concentrated HA stock solution of 1  
122 g/L. Hydrochloric acid (HCl, Sigma-Aldrich) was employed to adjust the pH of the  
123 diluted HA feed solutions (15 mg/L) to 11. Isopropyl alcohol (IPA, Sigma-Aldrich) was

124 used to determine the void volume fraction ( $\epsilon$ ) of the PSU ENMs. POREFIL®, a  
125 fluorinated hydrocarbon (chemical nature: pefluoroether; surface tension: 16 mN/m,  
126 vapor pressure: 3.33 Pa; viscosity: 4.4 mPa·s, POROMETER) was used as a wetting  
127 liquid to perform the inter-fiber space measurements.

128

## 129 **2.2.Preparation and characterization of the polymer solution**

130 The polymer solution was prepared by mixing DMF (64 wt.%) and THF (16 wt.%)  
131 at room temperature with a magnetic stirrer (IKA, RCT basic) for 2 min at 80 rpm.  
132 Subsequently, 20 wt.% PSU was added to the solvent mixture and the solution was stirred  
133 at 60°C and 80 rpm for 10 h until the PSU was completely dissolved and the resulting  
134 polymer solution homogeneous.

135 The polymer solution was characterized by measuring its surface tension, viscosity  
136 and electrical conductivity. The surface tension of the spinning solution was determined  
137 at room temperature by the pendant drop shape analysis using an Optical Contact Angle  
138 Meter (CAM 200) and a stainless steel needle with an outer diameter of 1.825 mm. The  
139 volume of all drops was maintained constant at  $16.08 \pm 0.82 \mu\text{L}$ . The viscosity of the  
140 spinning solution was measured with a Digital Viscometer (Brookfield, Model DV-I+) in  
141 a cylindrical sample container and using the SC4-31 spindle at 30 rpm and a shear rate of  
142  $10.2 \text{ s}^{-1}$ . The temperature of the spinning solution was maintained constant at 25°C by a  
143 thermostat (Techne, Model TU-16D). The electrical conductivity of polymer solution was  
144 measured at 25°C using a conductivity meter (CyberScan con11 Conductivity/TDS/°C,  
145 Eutech Instruments).

146

147 **2.3. Preparation of PSU ENMs**

148 PSU ENMs were prepared by electrospinning using the polymer solution indicated  
149 in the previous section. The used electrospinning system was described elsewhere [7]. In  
150 this study, all PSU ENMs were prepared under the previously obtained optimum  
151 electrospinning parameter conditions: a polymer solution flow rate of 2.5 mL/h, an  
152 electric voltage of 16 kV, a distance between the needle tip and the collector or air gap of  
153 10 cm and an electrospinning time of 45 min [7]. The ambient conditions during  
154 electrospinning fabrication were a temperature between 20-25°C and a relative humidity  
155 in the range 38-41%.

156

157 **2.4. Heat post-treatment (HPT) of PSU ENMs**

158 The silky, fluffy and loose structure of the PSU ENMs complicated their handling  
159 after the electrospinning step. In addition, it was observed that PSU ENMs without any  
160 HPT were not useful for filtration application as the membranes were not capable to  
161 achieve any separation. Thus, a HPT step was carried out to get membranes with  
162 improved structural integrity and greater filtration performance.

163 The HPT was carried out in a ceramic oven (CWF 13/13, Carbolite®). Before being  
164 placed into the oven, the ENMs deposited on the aluminum foil were attached to a smaller  
165 rounded copper support to avoid shrinkage of the membrane during heating. The samples  
166 were first heated from 70°C to the established HPT temperature (i.e. 190- 250°C) at a rate  
167 of 30°C/min (this process took between 6-8 min, depending on the final temperature) and  
168 then exposed to the HPT temperature for a specific HPT time (i.e. 20-300 min). HPT  
169 temperatures above the boiling point of the used solvents were chosen to guarantee their  
170 complete evaporation from the formed ENMs. To induce good bonding points between  
171 nanofibers (i.e. points in which nanofibers were fused together) the applied temperatures



172 were also higher than the glass transition temperature of the used polymer (185°C for  
173 PSU). After the HPT step, ENMs were wetted with DI water, peeled off from the  
174 aluminum foil, dried at room temperature for 24 h and stored until use.

175 In order to perform a systematic and accurate study on the effect of the HPT on the  
176 morphological structure of PSU ENMs, all membranes were obtained from the same  
177 manufacturing batch, avoiding as many steric dissimilarities (in terms of, for example,  
178 pore size, structure, porosity and surface roughness) between them as possible. In  
179 addition, SEM images of membranes with an initial thickness of  $900 \pm 50 \mu\text{m}$  were used  
180 to select those ENMs with similar initial nanofibrous structure (i.e. uniformity of the  
181 nanofiber web).

182 It was observed that not all the heat post-treatments (HPTs) led to the same  
183 morphology and structure of the membranes. In order to fully understand the influence of  
184 the applied HPT on the morphological and structural changes of PSU ENMs, a  
185 preliminary study with 90 membranes and 30 different HPTs was conducted to determine  
186 the operational working area (i.e. region of interest) of the HPT as shown later on. Then,  
187 a systematic study in this region of interest was conducted and eleven PSU ENMs were  
188 evaluated and compared in terms of their morphological characteristics (i.e. mean  
189 nanofiber diameter, mean size of the inter-fiber space, water contact angle, void volume  
190 fraction, etc.). Moreover, MF tests were carried out with these eleven ENMs to determine  
191 the optimum region of the HPT, in which the treated membranes exhibit the highest  
192 filtration performance indexes.

193

## 194 **2.5. Characterization of PSU ENMs**

195 The thickness of each PSU ENM was measured at 40 different spots on the sample  
196 using a micrometer equipped with a feeler (ISL Isocontrol). The final thickness of each

197 sample was determined as the average value of the measured thicknesses with its  
 198 corresponding standard deviation.

199 The morphology of the surface of the PSU ENMs was evaluated with a field emission  
 200 scanning electron microscope (FESEM, JEOL Model JSM-6335F) operating at 5 kV.  
 201 Before conducting the SEM analysis, a thin gold layer of approximately 5 nm was sputter-  
 202 coated on the membrane surface using an evaporator (EMITECH K550 X) for one minute  
 203 under 25 mA. SEM images were analyzed with the UTHSCSA Image Tool 3.0 software  
 204 to determine the nanofiber diameter. For each membrane, at least 3 SEM images were  
 205 analyzed and the diameters of a total number of 100 nanofibers/per image were measured.  
 206 Statistical analyses were applied to determine the nanofiber diameter distribution (i.e.  
 207 nanofiber diameter histogram). The weighted arithmetic mean of the nanofiber diameters  
 208 ( $\lambda_w$ ) along with its corresponding weighted standard deviation ( $s_w$ ) were evaluated as  
 209 follows:

$$210 \quad \lambda_w = \lambda_0 + \frac{h}{N} \sum_{j=1}^m u_j \cdot FC_j \quad (1)$$

$$211 \quad s_w = \sqrt{\left( \frac{1}{N} \sum_{j=1}^m (u_j^2 \cdot FC_j) - \left( \frac{1}{N} \sum_{j=1}^m (u_j \cdot FC_j) \right)^2 \right) \cdot h^2} \quad (2)$$

212 where  $m$  denotes de number of bins (disjoint categories),  $h$  is the width,  
 213  $h = (\lambda_{max} - \lambda_{min})/m$ ,  $FC$  is the frequency count,  $N$  is the number of samples in the  
 214 statistical set (in our case  $N = 100$ ),  $\lambda_0$  is the dominant characteristic of the statistical set  
 215 that corresponds to the highest peak,  $u$  is a variable defined as  $u = (\lambda_c - \lambda_0)/h$  and  $\lambda_c$  is  
 216 the bin characteristic (or bin center).

217 The final value of the weighted arithmetic mean of the nanofiber diameters ( $\overline{\lambda_w}$ ) with  
 218 its corresponding weighted standard deviation ( $\overline{s_w}$ ) for the PSU ENMs was determined

219 as the arithmetic mean and standard deviation of all SEM samples evaluated for each  
220 membrane.

221 The water contact angle ( $\theta_w$ ) values on the surface of the PSU ENMs were measured  
222 at room temperature using a computerized optical system (CAM100 device, Sb) equipped  
223 with a CCD camera and an image analysis software (Cam200usb). This system enables  
224 the acquisition of photographs of the water drop on the sample surface and to evaluate  
225 the contact angle. A Hamilton stainless steel needle was used to control the volume of the  
226 drops, which was between 12 and 14  $\mu\text{L}$ . Every drop was recorded taking five images  
227 within 4 s. For each ENM sample at least 10 different drops were considered to determine  
228 the final averaged  $\theta_w$  value together with its standard deviation.

229 The void volume fraction (i.e. porosity,  $\varepsilon$ ) is defined as the ratio between the volume  
230 of the inter-fiber space and the total volume of the membrane. The value of  $\varepsilon$  was  
231 determined by measuring the density of the polymer material ( $\rho_{pol}$ ) using isopropyl  
232 alcohol (IPA), which penetrates inside the inter-fiber space, and the density of the  
233 membrane ( $\rho_m$ ) using distilled water, which does not get into the inter-fiber space,  
234 according to equation (3) [32].

$$235 \quad \varepsilon (\%) = \left( 1 - \frac{\rho_m}{\rho_{pol}} \right) \cdot 100 \quad (3)$$

236 The inter-fiber space ( $d_f$ ) of the PSU ENMs was measured with capillary flow  
237 porometry (CFP) using a gas-liquid displacement Porometer (POROLUX™ 100,  
238 Porometer). CFP uses the displacement of a wetting liquid inside a porous network by  
239 means of an inert gas flow to measure  $d_f$ . In this study, POREFIL® (Porometer) was used  
240 as the wetting liquid agent, compressed air was employed as the inert gas and the applied  
241 hydrostatic pressure was varied in the range of 0–0.7 MPa at room temperature ( $\sim 23^\circ\text{C}$ ).  
242 The ENMs were first wetted by the POREFIL® and the gas permeation flow was

243 measured by increasing the transmembrane pressure to obtain the *S* shaped wet curve.  
244 Subsequently, the dry curve was obtained by measuring the gas flow through the dry  
245 sample as a function of the applied pressure. Both, the wet and dry curves were used to  
246 determine the mean size of the inter-fiber space ( $\bar{d}_f$ , which corresponds to the size of the  
247 inter-fiber space at which the wet curve intersects the half-dry curve that corresponds to  
248 50% gas flow through the dry membrane), the inter-fiber space distribution or differential  
249 filter flow (*DF*, which represents the increase in flow rate per unit increase in inter-fiber  
250 space), and the cumulative filter flow distribution (*CF*, i.e. percentage of the total gas  
251 flow that goes through inter-fiber spaces of a certain size and larger) of the PSU EMNs.

252

## 253 **2.6. Filtration experiments**

254 The experimental set up used for MF tests was described elsewhere [7]. The effective  
255 filtration area of the membrane was  $(21.76 \pm 0.01) 10^{-4} \text{ m}^2$ . The feed solution was kept at  
256 room temperature ( $\sim 23^\circ\text{C}$ ) and the feed flow rate was maintained at 1.6-1.8 L/min.

257 To carry out the MF tests, diluted HA feed solutions of 15 mg/L were prepared from  
258 a concentrated HA stock solution of 1 g/L. In our previous study, it was demonstrated  
259 that PSU ENMs were not selective to HA in acidic media ( $\text{pH} = 3$ ), whereas clear HA  
260 separation factors were observed when using alkaline HA solutions ( $\text{pH} = 11$ ) [7]. Thus,  
261 in this study the solution pH was adjusted to 11 by adding 2 M NaOH as needed using a  
262 pH/Ion meter (692, Metrohm). A spectrophotometer (UV/VIS 7315, Jenway) was used  
263 to determine the HA concentration of the permeate, the retentate and the feed samples at  
264 a wavelength of 254 nm.

265 Before carrying out the MF tests, all membranes were pre-compacted by circulating  
266 distilled water at a transmembrane pressure ( $\Delta P$ ) of  $3 \cdot 10^5 \text{ Pa}$  for 3 h. Subsequently, MF  
267 tests were conducted at a transmembrane pressure of  $10^5 \text{ Pa}$  using first distilled water for

268 1 h to determine the pure water permeability ( $PWP$ ), then the aqueous HA feed solution  
 269 for 7 h (i.e. HA test), and finally distilled water again for 1 h. The permeate fluxes of both  
 270 HA solution ( $J_{HA}$ ) and distilled water before ( $J_{w0}$ ) and after ( $J_{wf}$ ) each HA test were  
 271 measured and the irreversible fouling factor ( $FR_W$ ) of the membrane was evaluated as  
 272 follows [33]:

$$273 \quad FR_W(\%) = \frac{J_{w0} - J_{wf}}{J_{w0}} \cdot 100 \quad (4)$$

274 The permeate fluxes were calculated using the weight of the permeate produced  
 275 during a specific time on an electronic balance (AND GF-1200) as follows:

$$276 \quad J \left( \frac{kg}{m^2h} \right) = \frac{m}{A_{ef} \Delta t} \quad (5)$$

277 where  $m$  is the mass of the obtained permeate over a period of time  $\Delta t$  and  $A_{ef}$  is the  
 278 effective filtration membrane area.

279 The separation factor ( $\alpha$ ) of the membranes was evaluated using the following  
 280 equation:

$$281 \quad \alpha (\%) = \left( 1 - \frac{2C_p}{C_r + C_f} \right) \cdot 100 \quad (6)$$

282 where  $C_p$ ,  $C_r$  and  $C_f$  are the HA concentration of the permeate, retentate and feed  
 283 solutions, respectively.

284 The initial HA permeate flux decline ( $FD_0$ ), which relates to the beginning of the  
 285 fouling of the membranes, was determined as follows:

$$286 \quad FD_0 = 1 - \frac{J_{HA0}}{J_{w0}} \quad (7)$$

287 where  $J_{HA0}$  corresponds to the HA permeate flux at the beginning of the filtration test.

288 The filtration performance of the membranes was evaluated considering the  
 289 performance index ( $PI$ ), which takes into account the final values of both the HA

290 permeate flux ( $J_{HAf}$ ) and the HA separation factor ( $\alpha_f$ ) obtained at the end of the HA test  
291 (after about 420 min of experiment):

$$292 \quad PI(kg/m^2h) = \frac{J_{HAf} \cdot \alpha_f}{100} \quad (8)$$

293

### 294 **3. Results and discussions**

#### 295 **3.1. Polymer solution characterization**

296 The surface tension of the PSU electrospun solution is  $35.8 \pm 1.8$  mN/m, its  
297 viscosity is  $485.3 \pm 0.8$  mPa·s and its electrical conductivity is  $9.12 \pm 0.15$   $\mu$ S/cm. Similar  
298 values for the surface tension (35.47 mN/m) and the viscosity (520 mPa·s) of the PSU  
299 dope solution (20% wt/v PSU in DMAC/acetone (9:1) mixed solvents) were reported by  
300 Yuan et al. [34] when preparing ultrafine PSU fibers by electrospinning.

#### 301 **3.2. PSU ENMs preparation and characterization**

##### 302 **3.2.1. Preliminary evaluation of PSU ENMs prepared with different HPTs and** 303 **determination of the region of interest of the HPT**

304 A preliminary HPT study (see Fig. 1) was carried out to evaluate 90 membranes  
305 treated with 30 different HPTs in terms of damage, thickness homogeneity and degree of  
306 networking (i.e. quantity of bonding points between nanofibers) after the HPT. A visual  
307 criterion was used to evaluate the damage of the membranes due to the HPT (see Fig. S1  
308 in SI), giving 0 points to membranes that were burned on most of the surface, 5 points to  
309 membranes with only few small burned spots or 10 points to membranes without any  
310 burned spot on the surface. The final thickness homogeneity of the membrane was  
311 evaluated by means of the relative error of the thickness ( $E_r = (\Delta\delta/\delta) \cdot 100$ ), giving 0,  
312 1.5, 3.5, 5, 6.5, 8.5 or 10 points to membranes with a relative error of the thickness  
313 between 40-100, 30-40, 20-30, 15-20, 10-15, 5-10 and 0-5%, respectively. Finally, SEM  
314 images of the PSU ENMs surfaces were used to evaluate the degree of networking and

315 interconnectivity of the PSU ENMs, giving 0, 2.5, 5, 7.5 or 10 points to membranes in  
316 which a percentage of nanofiber intersections bonding < 20, 20-40, 40-60, 60-80 and >  
317 80%, respectively (see Fig. S2 in SI). The individual scores from the three evaluations  
318 were averaged to obtain a normalized score from 0 to 10 for each membrane. The scores  
319 of all membranes fabricated under the same HPT condition were averaged to obtain a  
320 single score for that condition.

321 Fig. 1 shows a three-dimensional representation of the average scores of the different  
322 HPTs. A region of interest for further investigation was identified (average score > 6,  
323 orange and red colors), which corresponded to (210°C,  $t > 250$  min), (220°C,  $65 < t < 180$   
324 min) and (230°C,  $35 < t < 90$  min). Eleven different HPTs within the region of interest  
325 were used to systematically study the effects of the HPT temperature and time on the  
326 morphology and structure of the PSU ENMs as well as on their filtration performance.

327

### 328 **3.2.2. Effects of the HPT temperature and time on the morphology and structure** 329 **of PSU ENMs**

330 Table 1 summarizes the morphological characteristics of the eleven PSU ENMs  
331 treated with different HPTs. It must be pointed out that the HPTs used to treat the ENM  
332 1 (210°C/60 min), ENM 2 (210°C/90 min) and ENM 3 (220°C/60 min) were not within  
333 the region of interest, but they were useful to systematically study the effects of the  
334 changes of the HPT temperature. Figs. 2-5 show the morphological and structural  
335 properties of the PSU ENMs prepared with the different HPTs. One of the main effects  
336 of the application of the HPT was the reduction of the thickness of the ENMs, which  
337 decreased from 900 to 80-380  $\mu\text{m}$ , depending on the applied HPT.

338 The changes of the surface of the PSU ENMs when increasing the HPT temperature  
339 from 210 to 230°C can be observed in Fig. 2. For both 60 and 90 min of HPT time, an

340 increase of the mean nanofiber diameter ( $\overline{\lambda_w}$ ) (see Table 1 and Fig. 4) and nanofibers  
341 interconnectivity was observed when increasing the HPT temperature, resulting in  
342 membranes with improved integrity and a more compact structure [1, 5]. The same  
343 morphological and structural changes (i.e. increase of  $\overline{\lambda_w}$  and the number of  
344 interconnected nanofibers) were observed by Liang. et al. [25] on PVDF ENMs when  
345 increasing the applied heat treatment temperature from 150 to 160°C. The increase of  $\overline{\lambda_w}$   
346 is attributed to the shrinkage of the nanofibers at high temperatures [6, 23, 25].

347 By comparing the SEM images of 60 min of HPT time with those of 90 min (Fig. 2),  
348 it can be noticed that the effect of increasing the HPT temperature was stronger at higher  
349 HPT time. For instance, ENMs 4 and 11 resulted in larger values of  $\overline{\lambda_w}$  (i.e. thicker  
350 nanofibers, see Table 1 and Fig. 4) and higher degree of networking than that of the ENMs  
351 3 and 9, respectively. Furthermore, ENMs 4 and 11 have more and larger junctions  
352 between nanofibers compared with those of the ENMs 3 and 9.

353 As can be seen in Fig. 3, different increments of the HPT time (30 and 15 min) for  
354 the membranes treated at 220 and 230°C, respectively, were established to avoid burning  
355 the membranes, as the effects of increasing the HPT time on the structure and morphology  
356 of the membrane were notably stronger when the applied temperature was higher. In fact,  
357 the maximum applied HPT time without observing any burned spot on the membrane was  
358 180 min at 220°C, twice as long as that for the membranes treated at 230°C (90 min).

359 No connection points between nanofibers could be detected on the surface of the  
360 membranes prepared with the lowest HPT times (ENM 3, 60 min at 220°C, and ENM 8,  
361 45 min at 230°C). In these cases, the nanofibers were smaller in diameter (i.e. thinner  
362 nanofibers), cylindrical and curled. Similar nanofiber structures were also reported by  
363 Homaeigohar et al. [24] on polyethersulfone (PES) ENMs without heat-treatment.



364 When increasing the HPT time at 220 or 230°C, an enhancement of the degree of  
365 networking was observed and the nanofibers became thicker and flatter, resulting in  
366 membranes with a more compact structure. In addition, the inter-fiber spaces of the PSU  
367 ENMs, which were large and without any specific geometrical shape for low HPT times,  
368 became smaller with rounder edges when the HPT time was increased. For instance, the  
369 nanofiber network of the membrane prepared with the highest HPT time, 180 minutes at  
370 220°C (see SEM image of ENM 7 in Fig. 3), had relatively small and rounded inter-fiber  
371 spaces together with more fused nanofibers. Similar membrane morphologies were also  
372 observed in electrospun poly (lactic acid) (PLA) membranes treated for 120 min at 90°C  
373 [26].

374 Increasing the HPT temperature from 210 to 230°C led to an increase of  $\overline{\lambda_w}$  by 4.6  
375 and 18.9%, respectively, for the applied HPT times of 60 and 90 min (Fig. 4A left). It is  
376 worth noting that increasing the HPT time by only 30 min, resulted in ~4 times greater  
377 enhancement of  $\overline{\lambda_w}$  at the highest HPT temperature. A greater increase of  $\overline{\lambda_w}$  was  
378 achieved by increasing the HPT time from 60 to 180 min at 220°C and from 45 to 90 min  
379 at 230°C (22.4 and 19.7%, respectively, Fig. 4A right). Furthermore, the nanofiber  
380 diameter distribution histograms of the PSU ENMs (Fig. S3 in SI) became broader when  
381 increasing both the HPT temperature and the HPT time as claimed by Liang et al. [25].  
382 For example, the nanofiber diameter distribution of the ENM 7 treated at 220°C for 180  
383 min (0.5 to 1.6  $\mu\text{m}$ ) was wider than that of the ENM 3 treated at 220°C for 60 min (0.3 to  
384 1.2  $\mu\text{m}$ ).

385 A left shift of both the cumulative (*CFF*, Fig. 5A-B) and the differential (*DFF*, Fig.  
386 5A-B) inter-fiber space distributions along with a decrease of the mean size of the inter-  
387 fiber space ( $\overline{d_f}$ ) were observed. When the HPT temperature was increased from 210 to  
388 230°C,  $\overline{d_f}$  decreased by 15.5%, and when the HPT time was increased from 45 to 90 min,

389  $\overline{d_f}$  decreased by 18.7%. The detected reduction of  $\overline{d_f}$  was mainly caused by the increase  
390 of  $\overline{\lambda_w}$  and the degree of networking (Fig. S4 in SI). The latter effect was also reported in  
391 other previous studies [1, 26].

392 The obtained values of  $\overline{\lambda_w}$  (from  $690 \pm 30$  to  $850 \pm 40$  nm) and  $\overline{d_f}$  (from 2.6 to 3.3  
393  $\mu\text{m}$ ) for all PSU ENMs in this study (Table 1) are comparable to those reported by both  
394 Gopal et al. [3] for PSU ENMs treated at  $188^\circ\text{C}$  for 180 min ( $470 \pm 150$  nm;  $2.1 \mu\text{m}$ ) and  
395 Lui et al. [35] for PSU ENMs treated at  $190^\circ\text{C}$  for 120 min ( $663 \pm 254$  nm;  $4.5 \mu\text{m}$ ).

396 It was expected that the changes in the size of the nanofibers and the inter-fiber spaces  
397 of the PSU ENMs resulted in notable effects on the total void volume fraction and  
398 permeation properties of the membranes [36]. In fact, a gradual decrease of both the void  
399 volume fraction ( $\varepsilon$ ) and the water contact angle ( $\theta_w$ ) of the PSU ENMs was observed with  
400 the increase of the HPT temperature and time (Figs. 4B and C). The increase of the HPT  
401 temperature from  $210$  to  $230^\circ\text{C}$  caused a reduction of  $\varepsilon$  by 13.2 and 15.7% when the  
402 applied HPT time was 60 and 90 min, respectively (Fig.4B left). Meanwhile, a reduction  
403 of  $\varepsilon$  by 19.9 and 15.4% was detected when the applied HPT time was varied from 60 to  
404 180 min at  $220^\circ\text{C}$  and from 45 to 90 min at  $230^\circ\text{C}$ , respectively (Fig. 4B right). It is worth  
405 noting that although  $\varepsilon$  was reduced, it still remained sufficiently high (above 70%, see  
406 Table 1). The values of  $\varepsilon$  of the prepared PSU ENMs ranged between 72.3 (ENM 7,  
407  $220^\circ\text{C}/180$  min) to 94.2% (ENM 1,  $210^\circ\text{C}/60$  min), which is well within the range  
408 reported for non-woven PSU ultrafine fiber mats treated at  $188^\circ\text{C}$  for 360 min (80-85%)  
409 [5] and PVDF ENMs treated at  $80^\circ\text{C}$  for 30 min (85-93%) [37].

410 The reduction of  $\theta_w$  of PSU ENMs (Fig. 4C) could be due to the gradual flattening of  
411 the nanofibers when increasing the HPT temperature or time, resulting in smoother  
412 membrane surfaces [38, 39]. Increasing the HPT temperature from  $210$  to  $230^\circ\text{C}$  at a HPT

413 time of 60 min decreased the values of  $\theta_w$  from 137.4 to 125.7°; at a HPT time of 90 min  
414 it decreased the value of  $\theta_w$  from 135.9 to 115.4° (Fig. 4C left). When increasing the HPT  
415 time from 60 to 180 min at 220°C  $\theta_w$  was reduced from 135.0 to 120.4°, whereas by  
416 increasing the HPT time from 45 to 90 min at 230°C  $\theta_w$  was reduced from 135.4 to 115.4°  
417 (Fig. 4C right). During the applied HPT, the hydrophobic character of the ENMs  
418 decreased reducing the membrane water contact angles by up to 15%. However, the  
419 surfaces of all heat-treated ENMs retained their hydrophobic character with contact  
420 angles  $\theta_w > 115^\circ$  (see Table 1). Similar  $\theta_w$  values were reported for PSU ultrafine ENMs  
421 heat-treated at 188°C for 360 min ( $135 \pm 5^\circ$ ) [5]. It is to be noted that the hydrophobic  
422 character was also maintained in PVDF ENMs heat-treated at 120°C for 120 min ( $127.0$   
423  $\pm 1.1^\circ$ ) [40] and PVDF-HFP ENMs hot-pressed at 200°C for 2 s ( $125.0 \pm 2.5^\circ$ ) [21].

424 All observed trends of the morphological characteristics ( $\uparrow \overline{\lambda_w}$ ,  $\downarrow \overline{d_f}$ ,  $\downarrow \varepsilon$ ,  $\downarrow \theta_w$ ) of the  
425 PSU ENMs when increasing the HPT temperature or time, correlated well with the  
426 changes of the surface and the morphology of the PSU ENMs (higher interconnectivity  
427 and more compacted structure), which were larger for the ENMs 7 and 11.

428 The SEM images and the morphological characteristics of the membranes treated at  
429 a HPT temperature of 220°C and the membranes treated at 230°C but for half the HPT  
430 time were similar. For instance, the differences of  $\overline{\lambda_w}$ ,  $\overline{d_f}$ ,  $\varepsilon$  and  $\theta_w$  between the ENMs 5  
431 and 9 (220°C/120 min and 230°C/60 min) were smaller than 2.7% while for the ENMs 6  
432 and 10 (220°C/180 min and 230°C/90 min) the differences were smaller than 4.8%.  
433 Therefore, similar filtration properties (i.e. selectivity and permeation fluxes) of these  
434 membranes are expected.

435

### 436 3.3. MF tests

437 As mentioned above, electrospun nanofibers exhibit, due to their nanostructure, very  
438 large water contact angles compared to polymeric films made from the same material (i.e.  
439 phase inversion flat membrane prepared with the same polymer). In this study, PSU  
440 ENMs exhibited contact angles between 115-137°. However, phase-inversion PSU  
441 membranes are reported to exhibit contact angle values around 70–80° [7]. Therefore,  
442 there is an initial ‘resistance’ for water to enter a completely dry ENM. Once the ENM is  
443 wetted, the high void volume fraction of the ENM leads to relatively high flow rates.  
444 ENMs are prone to be compressed during filtration because of their high void volume  
445 fraction and their relatively poor nanofiber adhesion. Therefore, to open and wet all the  
446 inter-fiber spaces of the PSU ENMs and to ensure that the water permeate flux kept  
447 constant with filtration time at an applied pressure, a water compaction step was carried  
448 out before the MF tests. Subsequently, HA MF tests were conducted with a 15 mg/L HA  
449 solution at pH 11 for all the PSU ENMs. The filtration results of all the PSU ENMs are  
450 summarized in Table 2.

#### 451 3.3.1. Effects of the HPT temperature and time on the filtration performance 452 of PSU ENMs

453 The effects of the HPT temperature and time on the filtration performance of the PSU  
454 ENMs were evaluated analysing the changes of the HA permeate fluxes ( $J_{HA}$ ), the HA  
455 separation factor ( $\alpha$ ) and the irreversible fouling factors ( $FR_W$ ) (Figs. 6A and B, shown  
456 as an example) with the filtration time, and by comparing their performance indexes ( $PI$ )  
457 (Fig. 8).

458 Fig. 6A shows the effects of increasing the HPT temperature (at a fixed HPT time of  
459 90 min) from 210°C to 230°C (PSU EMNs 2, 4, and 11). A considerable decrease of  $J_{HA}$   
460 along with a gradual increase of  $\alpha$  and  $FR_W$  was observed. The final HA permeate flux

461 ( $J_{HAf}$ ) of the PSU ENMs decreased by 82.2% when increasing the HPT temperature from  
462 210 to 220°C (ENM 2 to ENM 4) and by 70.6%, when increasing the HPT temperature  
463 from 220 to 230°C (ENM 4 to ENM 11). The final HA separation factor ( $\alpha_f$ ) of ENM 4  
464 (220°C) was 88.9% larger than that of ENM 2 (220°C) and that of ENM 11 (230°C) was  
465 55.9% larger than that of ENM 4. However, the respective changes of  $FR_w$  (3.6 and 2.7%)  
466 were not as noticeable as those of  $J_{HA}$  and  $\alpha$ .

467 The initial permeate flux decline ( $FD_0$ ) was 0.15, 0.19 and 0.92 for ENM 2, ENM 4 and  
468 ENM 11, respectively. This means that the permeate flux of the membrane prepared with  
469 the lowest HPT temperature (210°C, ENM 2) was reduced only by 15% during the first  
470 minutes of HA filtration whereas that of the membrane prepared with a higher HPT  
471 temperature (230°C, ENM 11) was declined by 92%.

472 These differences in the filtration performance of the membranes are mainly related to  
473 their different structural morphology. For instance, the membrane prepared with low HPT  
474 temperature (210°C, ENM 2) exhibited the largest  $\bar{d}_f$  (3.1  $\mu\text{m}$ ) and  $\varepsilon$  (92.8%) and,  
475 therefore had the highest mean HA permeate flux (i.e. average of all the HA permeate  
476 fluxes during the MF test;  $\bar{J}_{HA} = 8406 \text{ kg/m}^2\cdot\text{h}$ ) with the lowest  $\alpha_f$  value (3.7%). On the  
477 other hand, the membrane treated with the highest temperature (230°C, ENM 11) had the  
478 smallest  $\bar{d}_f$  (2.6  $\mu\text{m}$ ) and  $\varepsilon$  (78.2%) values and exhibited the lowest  $\bar{J}_{HA}$  (358  $\text{kg/m}^2\cdot\text{h}$ )  
479 with the highest  $\alpha_f$  (75%) values. It is worth nothing that although the ENM 11 had a  $\bar{J}_{HA}$   
480 value of 92.3% lower than that of ENM 2, its  $PI$  value resulted to be higher (74  $\text{kg/m}^2\cdot\text{h}$ )  
481 than that of the ENM 2 (70  $\text{kg/m}^2\cdot\text{h}$ ) because of its larger separation factor. Similar results  
482 were reported by Li et al. [26] with poly (lactic acid) (PLA) ENMs when increasing the  
483 HPT temperature from 90 to 95°C (at a fixed HPT time of 30 min). A decrease in the  
484 inter-fiber space of these membranes (from 2.3 to 2.0  $\mu\text{m}$ ) resulted in a permeate flux

485 decline (from about 26000 to 8500 L/m<sup>2</sup>h) along with an increase of the separation factor  
486 of TiO<sub>2</sub> particles (from 61 to 85%).

487 Fig. 6B shows the effects of the HPT time (at a fixed HPT temperature of 230°C) on  
488 the filtration performance of the PSU EMNs 8 (45 min), 9 (60 min), 10 (75 min) and 11  
489 (90 min). In this case, the effects on  $J_{HA}$  and  $\alpha$  when increasing the HPT time from 45 to  
490 90 min were not as noticeable as those observed when the HPT temperature was increased  
491 from 210 to 230°C. For instance, a gradual reduction of  $J_{HAf}$  (20.9, 22.3 and 47.3%) and  
492 an increase of  $\alpha_f$  (41.8, 10.3 and 5.6%) were observed when increasing the HPT time  
493 from 45 to 60, from 60 to 75 and from 75 to 90 min, respectively. The  $FR_w$  values did not  
494 follow a clear trend. The membrane with the lowest value of  $FR_w$  (95.9%) was the one  
495 treated for 60 min (ENM 6).

496 The values of  $FD_0$  for the ENMs 8, 9, 10 and 11 were 0.40, 0.55, 0.79 and 0.92,  
497 respectively, indicating that the initial permeate flux decline increased progressively  
498 when increasing the HPT time. It can also be noticed in Fig. 6B that all membranes  
499 reached a relatively constant  $J_{HA}$  value after 360 min of filtration time. As mentioned  
500 before, the changes in filtration performance of the PSU ENMs are directly related to  
501 their morphological and structural changes. The longer the HPT treatment time, the more  
502 compacted was the membrane structure and the thicker and more interconnected were  
503 their nanofibers (i.e. higher  $\bar{\lambda}_w$  and smaller  $\bar{d}_f$ ; see Table 1, Fig. 3, and Fig. 5B). These  
504 resulted in a reduction of  $\bar{J}_{HA}$  from 3481 kg/m<sup>2</sup> for ENM 8 (45 min) to 358 kg/m<sup>2</sup>.h for  
505 ENM 11 (90 min) and an enhancement of  $\alpha_f$  from 37.0 to 75.0%, respectively (see Table  
506 2). The membranes prepared with the lowest HPT time (ENM 8, 113 kg/m<sup>2</sup>.h) and the  
507 highest HPT time (ENM 11, 74 kg/m<sup>2</sup>.h) both had smaller  $PI$  values than those treated  
508 for intermediate HPT times (ENM 9, 147 kg/m<sup>2</sup>.h, and ENM 10, 133 kg/m<sup>2</sup>.h).

509 As mentioned in the introduction, fouling is a major factor limiting the application of  
510 membranes in water treatment. Thus, a characterization analysis of the organic fouling  
511 generated on the membranes after MF tests was conducted. FTIR, SEM imaging and EDS  
512 mapping were used to confirm the presence of HA across the PSU ENMs, to compare the  
513 surface morphology of the membranes before and after filtration and to measure the  
514 change of the atomic composition of the membranes due to the organic fouling (Fig. S5).

515 The  $J_{HA}$  and  $\alpha$  curves plotted in Fig. 6 can be used to study the fouling phenomenon  
516 of the PSU ENMs. HA fouling in MF membranes has two stages: i) a pore blockage that  
517 corresponds to a rapid HA permeate flux decline due to the deposition of large HA  
518 aggregates on the surface and in the pores (inter-fiber space for ENMs) of the membrane  
519 as well; ii) a cake filtration that induces a slow decrease of the HA permeate flux with  
520 filtration time until a relatively constant value of the permeate flux (known as steady-state  
521 value or asymptotic permeate flux) is reached. During this second stage a HA deposit or  
522 cake layer forms on those regions of the membrane that were covered by HA aggregates  
523 during the first stage [14, 41-44].

524 The transition between the pore blockage and the cake filtration stage is usually  
525 determined by the change of the slopes of both the permeate flux and separation factor  
526 curves with filtration time. The time ( $t_c$ ) at which this change occurs is known as the  
527 “critical point”. A smaller  $t_c$  indicates a shorter length of the initial pore blocking stage,  
528 and hence a faster fouling evolution rate. The value of  $t_c$  depends mainly on the  
529 morphological and structural characteristics of each PSU ENM (e.g. mean size of the  
530 inter-fiber space, inter-fiber space distribution, void volume fraction, mean nanofiber  
531 diameter, hydrophobicity, etc.).

532 From Fig. 6B it can be seen that the pore blockage of the PSU ENMs prepared with  
533 higher HPTs (i.e. ENMs 9, 10 and 11) occurred faster, during the first half an hour of  
534 filtration ( $t_c < 30$  min). This is attributed to their more compact structure and smaller size  
535 of the inter-fiber space, which promotes the pore blockage phenomenon [45, 46]. For  
536 these membranes, the slope of the  $\alpha$  curve was relatively small until the critical time  $t_c$   
537 (i.e. beginning of pore blockage stage) was reached. Subsequently, a considerable  
538 increase of  $\alpha$  was observed (due to the reduction of the membrane inter-fiber space during  
539 the pore blockage stage and during the formation and growth of the cake layer in the  
540 second stage), followed by a slower increase of  $\alpha$  (attributed to the reached cake layer  
541 mature stage). A relatively steady-state value of the HA separation factor ( $\alpha_f$ ) was  
542 obtained at the end of the filtration test (70.9, 75.0 and 77.6% for the ENMs 9, 10 and 11,  
543 respectively).

544 For the membranes prepared with low HPTs (i.e. ENMs 4 and 8, see Figs. 6A and B),  
545 the slope of the  $\alpha$  curve was relatively constant and close to zero during the first 125  
546 minutes of filtration (i.e. pore blockage stage with  $t_c \approx 125$  min). Then it increased  
547 considerably during the next 300 min of filtration time (i.e. cake filtration), reaching  
548 values up to 37%. The membrane prepared with the lowest HPT (i.e. ENM 2) did not  
549 retain HA, most likely due to the low quantity of bonding points between nanofibers (see  
550 SEM image in Fig 2). Unbounded nanofibers may be displaced by the hydrostatic water  
551 pressure leading to a broad inter-fiber space of the ENM and allowing HA particles to  
552 penetrate through the membrane resulting in no separation. The  $\alpha_f$  values of all the PSU  
553 ENMs ranged from 1 to 78% (see Table 2). This elucidates the clear differences of the  
554 morphological characteristics of the PSU ENMs and confirms the important influence of  
555 the HPT on the filtration performance of the membranes.



556 In the previous section it was reported that the morphological and structural  
557 characteristics of the membranes treated at a HPT temperature of 220°C during a time  $t$   
558 and those treated at 230°C during a time  $t/2$  were very similar. For this reason, a  
559 comparison of the filtration properties (i.e.  $J_{HA}$ ,  $\alpha$  and  $FR_W$ ) of the membrane pairs ENMs  
560 4-8, 5-9, 6-10 and 7-11 was performed (Fig. 7). Their  $J_{HA_f}$  values were approximately the  
561 same (see Table 2) with deviations below 10.2%. Similarly, the same tendency was  
562 observed for the curves of  $\alpha$  as a function of filtration time for each pair of membranes.  
563 In particular, the  $\alpha$  curves of the membranes prepared with lower HPTs (i.e. ENMs 4 and  
564 8) overlapped, while only small differences were detected for the pairs of membranes  
565 prepared with higher HPTs (i.e. ENMs 5-9, 6-10 and 7-11). Taking into account their  
566 mean  $\alpha$  for the entire filtration process ( $\bar{\alpha}$ ), the deviation between these values was low  
567 and ranged between 4.1 and 11.9%, the maximum deviation corresponding to the  
568 membranes prepared with the highest HPTs (i.e. ENM 7 ( $\bar{\alpha} = 39.6\%$ ) and ENM 11 ( $\bar{\alpha} =$   
569  $45.0\%$ )). It is worth noting that despite the similarities in the filtration behaviour of the  
570 pairs of membranes, higher  $\alpha_f$  values were obtained for all the membranes treated at  
571 230°C compared to those treated at 220°C for a double HPT time. By comparing the  
572 values of  $FR_W$  of the different pairs of membranes (Table 2 and Fig. 7) no clear conclusion  
573 could be drawn. The deviation of the  $FR_W$  values of the pairs of membranes prepared with  
574 higher HPTs (i.e. ENMs 6-10 and 7-11) was smaller than 0.2%, while the highest  
575 deviation (2.5%) was reached for the pair of ENMs 5-9.

576 Despite the similarities in the filtration characteristics between the pairs of membranes,  
577 PSU ENMs treated at 230°C had up to 16.4% greater  $PI$  values than PSU ENMs treated  
578 at 220°C. Therefore, it is advisable to increase the HPT temperature by 10°C and reduce  
579 the HPT time by half as it permits energy and cost savings.

### 580 3.3.2. Comparative study

581 The pure water permeability ( $PWP$ ) of all prepared PSU ENMs measured after  
582 compaction ranged from 15260 to 20563  $\text{kg/m}^2\cdot\text{h}\cdot\text{bar}$ , which is 3-fold to 100-fold higher  
583 than those achieved by highly porous lab-made PSU ENMs (1472-5648  $\text{kg/m}^2\cdot\text{h}\cdot\text{bar}$ ) [3]  
584 and PVDF ENMs (232-1984  $\text{kg/m}^2\cdot\text{h}\cdot\text{bar}$ ) [2] used for particulate removal, and similar or  
585 greater than those reported for mechanically enhanced lab-made PES ENMs (16006  
586  $\text{kg/m}^2\cdot\text{h}\cdot\text{bar}$ ) [47]. In addition, the  $PWP$  values obtained in the present study for PSU  
587 ENMs were larger than those of commercial flat sheet membranes typically used in MF  
588 processes (i.e. PVDF MF: 2436  $\text{kg/m}^2\cdot\text{h}\cdot\text{bar}$ , Model V0.2, Synder Membrane Technology  
589 [47]; PES tight MF: 327  $\text{kg/m}^2\cdot\text{h}\cdot\text{bar}$ , Model LX, Synder Membrane Technology [47];  
590 GVHP MF: 8875  $\text{kg/m}^2\cdot\text{h}\cdot\text{bar}$ , Millipore [43]; PES OMEGA MF: 6783  $\text{kg/m}^2\cdot\text{h}\cdot\text{bar}$ ,  
591 Filtron Technology [12]; PVDF DURAPORE MF: 5217  $\text{kg/m}^2\cdot\text{h}\cdot\text{bar}$ , Millipore [12]; PES  
592 HPWP MF: 14761  $\text{kg/m}^2\cdot\text{h}\cdot\text{bar}$ , Millipore; see Table 3). These values confirm the  
593 structural advantages of the ENMs over traditional water filtration membranes, such as  
594 their three-dimensional-inter-pore connectivity and high void volume fractions (i.e.  
595 higher porosity leads to more channels for water flow) [46, 48]. In addition, the treated  
596 PSU ENMs had a small water entry pressure (below 1 bar), which is convenient for low-  
597 pressure water purification and therefore for MF applications.

598 (**Table 3:** Ref. [2, 3, 7, 12, 26, 43, 47, 49])

599 In this study, the final permeate fluxes ( $J_f$ ) measured after 7 hours of filtration for the  
600 PSU ENMs with the highest  $PI$  values (i.e. ENMs 9 and 10) are 188 and 232  $\text{kg/m}^2\cdot\text{h}$   
601 (Table 3). These values are 3.7 to 4.5 times greater than the obtained one in our previous  
602 study (51.3  $\text{kg/m}^2\cdot\text{h}$ ) [7]. In addition, the values of  $\alpha_f$  of ENMs 9 and 10 are 6.5 and 18.2%

603 greater than the highest value obtained in our former work (60%) [7]. Thus, the optimized  
604 HPT improved the filtration performance index ( $PI$ ) of the membranes up to 5-fold [7].

605 The final normalized permeate fluxes ( $J_f$ ) by the applied pressure ( $\Delta P$ ) of the ENMs 9  
606 and 10 (232 and 188 kg/m<sup>2</sup>.h.bar) are 63 and 32% greater than that of the eco-efficient,  
607 micro-porous, lab-made PLA ENM 1 (143 kg/m<sup>2</sup>.h.bar) [26]. The values of  $\alpha_f$  measured  
608 for ENMs 9 and 10 are also 5 and 16% higher than that of the PLA ENM 1. The values  
609 of  $PI$  of ENMs 9 and 10 are therefore 53 and 69% greater than that of PLA ENM 1, which  
610 confirms the high filtration performance of the heat-treated optimized ENMs.

611 The commercial MF membranes (PES MF, PVDF MF and PCTE MF) used by Yuan  
612 and Zydney [12] for the treatment of 2 mg/L HA solutions had up to 33% smaller  $J_f$   
613 values than those of the PSU ENMs 9 and 10, which were used to treat higher  
614 concentrated HA solutions (15 mg/L). This is probably due to their lower porosity and  
615 smaller mean pore size. However, the commercial MF membranes exhibited higher  $\alpha_f$   
616 values (up to 49%) when compared with the PSU ENMs 9 and 10, mainly caused by their  
617 smaller mean pore size. Considering that the average size of HA particles in a basic  
618 environment ranges from 0.3 to 4 nm [7] and the mean size of the inter-fiber space of the  
619 PSU ENMs ranges from 2 to 4  $\mu$ m, the values of  $\alpha_f$  obtained for the ENMs 9 and 10 (63.9  
620 and 70.9%, respectively) can be considered reasonably good. The measured values of  $\alpha_f$   
621 are probably affected by both the high tortuosity of the ENMs (i.e. HA molecules are  
622 expected to be more prone to mechanical entrapment in the thread-like network of an  
623 ENM [46]) and the rejection mechanism in a fibrous structured membrane, which  
624 includes sieving, electrostatic attraction, diffusion and inertia [47].

625 For sake of comparison, a commercial PES MF membrane (HPWP, hydrophilic,  
626 Millipore) was tested in this study following exactly the same filtration procedure than

627 that of the PSU ENMs. The results are also summarized in Table 3. The PES MF  
628 commercial membrane has lower  $J_f$  value (up to 55%) but a higher  $\alpha_f$  (up to 18%) than  
629 the ENMs 9 and 10. However, its  $PI$  value ( $82 \text{ kg/m}^2\cdot\text{h}$ ) is 44 and 38% lower than that of  
630 the ENMs 9 and 10 (i.e. 147 and  $133 \text{ kg/m}^2\cdot\text{h}$ , respectively) (Fig. S6 in SI). This result  
631 elucidates the good performance of the treated-optimized PSU ENMs for MF  
632 applications.

633 The values of  $FR_w$  obtained for all PSU ENMs ranged from 81.9 to 99%, and are higher  
634 than those reported by Schäfer et al. [43] during MF of 20 mg/L HA solution at pH 8  
635 (81%) and 5 mg/L HA solution at pH 10 (73%) with a MF commercial hydrophilic  
636 membrane (GVWP,  $0.22 \mu\text{m}$  pore size; Millipore). The reduction of the irreversible  
637 fouling factor of PSU ENMs is important to extend the membrane lifetime for filtration  
638 application. Different ways have been adopted to improve the  $FR_w$  including surface  
639 modification of ENMs by interfacial polymerization (IP) technique [33, 50].

640 Compared to other ENMs with HPT used for filtration [2, 5, 7, 24, 26, 37, 51, 52], the  
641 total manufacturing time of PSU ENMs of the present study was shorter. For other  
642 reported membranes the electrospinning process took between 1 and 8 hours, up to 10  
643 times longer than the electrospinning fabrication time ( $t_e$ ) used in this study (45 min). In  
644 addition, the HPT times used for the treated-optimized PSU ENMs of the present study  
645 were 60-75 min, up to 18-fold shorter than the time (120-1080 min) reported for other  
646 membranes.

647

#### 648 **4. Conclusions**

649 Different HPTs were investigated to improve the filtration performance of PSU  
650 ENMs. The effects of the HPT temperature (i.e. 210, 220,  $230^\circ\text{C}$ ) and time (i.e. 45, 60,

651 75, 90, 120, 150, 180 min) on their morphology and structure were studied systematically.  
652 It was observed that increasing either the HPT temperature or time resulted in a reduction  
653 of  $\bar{d}_f$  along with an increase of both  $\bar{\lambda}_w$  and the number of connections between  
654 nanofibers, which led to an improvement of the structural integrity of the membranes. A  
655 gradual decrease of the  $\varepsilon$  and  $\theta_w$  values of the PSU ENMs was obtained when the HPT  
656 temperature or the HPT time was increased, which resulted in membranes with smoother  
657 surfaces. No connection points between nanofibers could be detected when the  
658 membranes were prepared at a low HPT temperature (ENMs 1-2 (210°C)) or for a short  
659 HPT time (ENMs 3 (60 min) and 8 (45 min)).

660 The main effects of increasing either the HPT temperature or the HPT time on the  
661 filtration properties of the membranes were a reduction of the HA permeate flux and an  
662 improvement of the HA separation factor.

663 It was observed that the fouling evolution rate of the PSU ENMs prepared with higher  
664 HPTs (i.e. ENMs 10 and 11) was faster. Pore blockage occurred earlier ( $t_c < 30$  min) in  
665 these membranes compared to those prepared with lower HPTs (i.e. ENMs 4 and 8), in  
666 which pore blockage took place during the first 125 minutes of the filtration process.

667 Similar morphological characteristics as well as filtration performance were  
668 observed for the membranes treated at 220°C and those treated at 230°C for half the  
669 heating time. Despite these similarities, the values of  $\alpha_f$  of the membranes treated at  
670 230°C were up to 14.6% higher than those of the membranes treated at 220°C, resulting  
671 in up to 16.4% better performance indexes. From these results it can be concluded that it  
672 is better to perform HPT at a higher temperature, because the reduction in HPT time  
673 permits energy and cost savings.

674 Compared to the best PSU ENMs (i.e. ENMs 9 and 10), lower *PI* value was obtained  
675 for the commercial PES MF membrane (HPWP, Millipore) tested under the same

676 filtration procedure to that followed for the PSU ENMs. This confirms the good  
677 performance of the prepared PSU ENMs for MF applications.

678 The significantly higher *PWP* of PSU ENMs compared to commercial flat sheet  
679 filtration membranes allows the use of lower pressures and thus reduces energy  
680 consumption during filtration. Together with their short manufacturing time, this property  
681 makes PSU ENMs fabricated with the optimized HPT conditions very promising  
682 candidates to reduce the overall costs and energy consumption of MF applications.

683

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#### 689 **References**

- 690 [1] Y. Huang, Q.L. Huang, H. Liu, C.X. Zhang, Y.W. You, N.N. Li, C.F. Xiao, Preparation,  
691 characterization, and applications of electrospun ultrafine fibrous PTFE porous membranes, *J.*  
692 *Membr. Sci.*, 523 (2017) 317-326.
- 693 [2] R. Gopal, S. Kaur, Z. Ma, C. Chan, S. Ramakrishna, T. Matsuura, Electrospun nanofibrous  
694 filtration membrane, *J. Membr. Sci.*, 281 (2006) 581-586.
- 695 [3] R. Gopal, S. Kaur, C.Y. Feng, C. Chan, S. Ramakrishna, S. Tabe, T. Matsuura, Electrospun  
696 nanofibrous polysulfone membranes as pre-filters: Particulate removal, *J. Membr. Sci.*, 289  
697 (2007) 210-219.
- 698 [4] J. Doshi, D.H. Reneker, Electrospinning process and applications of electrospun fibers, *J.*  
699 *Electrostat.*, 35 (1995) 151-160.
- 700 [5] Z. Ma, M. Kotaki, S. Ramakrishna, Surface modified nonwoven polysulphone (PSU) fiber mesh  
701 by electrospinning: A novel affinity membrane, *J. Membr. Sci.*, 272 (2006) 179-187.
- 702 [6] S.-S. Choi, Y.S. Lee, C.W. Joo, S.G. Lee, J.K. Park, K.-S. Han, Electrospun PVDF nanofiber web  
703 as polymer electrolyte or separator, *Electrochim. Acta*, 50 (2004) 339-343.
- 704 [7] P. Arribas, M. Khayet, M.C. García-Payo, L. Gil, Self-sustained electro-spun polysulfone nano-  
705 fibrous membranes and their surface modification by interfacial polymerization for micro- and  
706 ultra-filtration, *Sep. Purif. Technol.*, 138 (2014) 118-129.
- 707 [8] Y. Liu, R. Wang, H. Ma, B.S. Hsiao, B. Chu, High-flux microfiltration filters based on  
708 electrospun polyvinylalcohol nanofibrous membranes, *Polymer*, 54 (2013) 548-556.

709 [9] S. Homaeigohar, J. Koll, E.T. Lilleodden, M. Elbahri, The solvent induced interfiber adhesion  
710 and its influence on the mechanical and filtration properties of polyethersulfone electrospun  
711 nanofibrous microfiltration membranes, *Sep. Purif. Technol.*, 98 (2012) 456-463.

712 [10] H.-C. Kim, B.G. Choi, J. Noh, K.G. Song, S.-h. Lee, S.K. Maeng, Electrospun nanofibrous PVDF–  
713 PMMA MF membrane in laboratory and pilot-scale study treating wastewater from Seoul Zoo,  
714 *Desalination*, 346 (2014) 107-114.

715 [11] A. Baji, Y.-W. Mai, S.-C. Wong, M. Abtahi, P. Chen, Electrospinning of polymer nanofibers:  
716 Effects on oriented morphology, structures and tensile properties, *Compos. Sci. Technol.*, 70  
717 (2010) 703-718.

718 [12] W. Yuan, A.L. Zydney, Humic acid fouling during microfiltration, *J. Membr. Sci.*, 157 (1999)  
719 1-12.

720 [13] N. Yang, X. Wen, T.D. Waite, X. Wang, X. Huang, Natural organic matter fouling of  
721 microfiltration membranes: Prediction of constant flux behavior from constant pressure  
722 materials properties determination, *J. Membr. Sci.*, 366 (2011) 192-202.

723 [14] R. Seifollahy Astaraee, T. Mohammadi, N. Kasiri, Analysis of BSA, dextran and humic acid  
724 fouling during microfiltration, experimental and modeling, *Food Bioprod. Process.*, 94 (2015)  
725 331-341.

726 [15] Y. Su, C. Li, W. Zhao, Q. Shi, H. Wang, Z. Jiang, S. Zhu, Modification of polyethersulfone  
727 ultrafiltration membranes with phosphorylcholine copolymer can remarkably improve the  
728 antifouling and permeation properties, *J. Membr. Sci.*, 322 (2008) 171-177.

729 [16] A.-R. Cho, D.M. Shin, H.W. Jung, J.C. Hyun, J.S. Lee, D. Cho, Y.L. Joo, Effect of annealing on  
730 the crystallization and properties of electrospun polylactic acid and nylon 6 fibers, *J. Appl. Polym.*  
731 *Sci.*, 120 (2011) 752-758.

732 [17] L. Huang, S.S. Manickam, J.R. McCutcheon, Increasing strength of electrospun nanofiber  
733 membranes for water filtration using solvent vapor, *J. Membr. Sci.*, 436 (2013) 213-220.

734 [18] X. Ran, Z. Jia, C. Han, Y. Yang, L. Dong, Thermal and mechanical properties of blends of  
735 polylactide and poly(ethylene glycol-co-propylene glycol): Influence of annealing, *J. Appl. Polym.*  
736 *Sci.*, 116 (2010) 2050-2057.

737 [19] H.-C. Chen, C.-H. Tsai, M.-C. Yang, Mechanical properties and biocompatibility of  
738 electrospun polylactide/poly(vinylidene fluoride) mats, *J. Polym. Res.*, 18 (2011) 319-327.

739 [20] S. Kaur, R. Barhate, S. Sundarrajan, T. Matsuura, S. Ramakrishna, Hot pressing of electrospun  
740 membrane composite and its influence on separation performance on thin film composite  
741 nanofiltration membrane, *Desalination*, 279 (2011) 201-209.

742 [21] B.S. Lalia, E. Guillen-Burrieza, H.A. Arafat, R. Hashaikeh, Fabrication and characterization of  
743 polyvinylidene fluoride-co-hexafluoropropylene (PVDF-HFP) electrospun membranes for direct  
744 contact membrane distillation, *J. Membr. Sci.*, 428 (2013) 104-115.

745 [22] Y. Liao, R. Wang, M. Tian, C. Qiu, A.G. Fane, Fabrication of polyvinylidene fluoride (PVDF)  
746 nanofiber membranes by electro-spinning for direct contact membrane distillation, *J. Membr.*  
747 *Sci.*, 425-426 (2013) 30-39.

748 [23] Y. You, S. Won Lee, S. Jin Lee, W.H. Park, Thermal interfiber bonding of electrospun poly(l-  
749 lactic acid) nanofibers, *Mater. Lett.*, 60 (2006) 1331-1333.

750 [24] S.S. Homaeigohar, K. Buhr, K. Ebert, Polyethersulfone electrospun nanofibrous composite  
751 membrane for liquid filtration, *J. Membr. Sci.*, 365 (2010) 68-77.

752 [25] Y. Liang, S. Cheng, J. Zhao, C. Zhang, S. Sun, N. Zhou, Y. Qiu, X. Zhang, Heat treatment of  
753 electrospun Polyvinylidene fluoride fibrous membrane separators for rechargeable lithium-ion  
754 batteries, *J. Power Sources*, 240 (2013) 204-211.

755 [26] L. Li, R. Hashaikeh, H.A. Arafat, Development of eco-efficient micro-porous membranes via  
756 electrospinning and annealing of poly (lactic acid), *J. Membr. Sci.*, 436 (2013) 57-67.

757 [27] S.S. Homaeigohar, H. Mahdavi, M. Elbahri, Extraordinarily water permeable sol–gel formed  
758 nanocomposite nanofibrous membranes, *J. Colloid Interface Sci.*, 366 (2012) 51-56.

759 [28] S.S. Homaeigohar, M. Elbahri, Novel compaction resistant and ductile nanocomposite  
760 nanofibrous microfiltration membranes, *J. Colloid Interface Sci.*, 372 (2012) 6-15.

761 [29] Y. Liao, C.H. Loh, M. Tian, R. Wang, A.G. Fane, Progress in electrospun polymeric nanofibrous  
762 membranes for water treatment: Fabrication, modification and applications, *Prog. Polym. Sci.*,  
763 77 (2018) 69-94.

764 [30] C. Migliaresi, D. Cohn, A. De Lollis, L. Fambri, Dynamic mechanical and calorimetric analysis  
765 of compression-molded PLLA of different molecular weights: Effect of thermal treatments, *J.*  
766 *Appl. Polym. Sci.*, 43 (1991) 83-95.

767 [31] D. Aussawasathien, C. Teerawattananon, A. Vongachariya, Separation of micron to sub-  
768 micron particles from water: Electrospun nylon-6 nanofibrous membranes as pre-filters, *J.*  
769 *Membr. Sci.*, 315 (2008) 11-19.

770 [32] K. Smolders, A.C.M. Franken, Terminology for Membrane Distillation, *Desalination*, 72  
771 (1989) 249-262.

772 [33] M.N.A. Seman, M. Khayet, N. Hilal, Nanofiltration thin-film composite polyester  
773 polyethersulfone-based membranes prepared by interfacial polymerization, *J. Membr. Sci.*, 348  
774 (2010) 109-116.

775 [34] X. Yuan, Y. Zhang, C. Dong, J. Sheng, Morphology of ultrafine polysulfone fibers prepared by  
776 electrospinning, *Polym. Int.*, 53 (2004) 1704-1710.

777 [35] L. Liu, Z. Pan, Properties of hydrophilic chitosan/polysulfone nanofibrous filtration  
778 membrane, *J. Eng. Fiber. Fabr.*, 9 (2014) 76-86.

779 [36] D. Hussain, F. Loyal, A. Greiner, J.H. Wendorff, Structure property correlations for  
780 electrospun nanofiber nonwovens, *Polymer*, 51 (2010) 3989-3997.

781 [37] M. Essalhi, M. Khayet, Self-sustained webs of polyvinylidene fluoride electrospun  
782 nanofibers at different electrospinning times: 1. Desalination by direct contact membrane  
783 distillation, *J. Membr. Sci.*, 433 (2013) 167-179.

784 [38] A. Marmur, Wetting on hydrophobic rough surfaces: to be heterogeneous or not to be?,  
785 *Langmuir*, 19 (2003) 8343-8348.

786 [39] B. Bhushan, Y. Chae Jung, Wetting study of patterned surfaces for superhydrophobicity,  
787 *Ultramicroscopy*, 107 (2007) 1033-1041.

788 [40] H. Savoji, D. Rana, T. Matsuura, S. Tabe, C. Feng, Development of plasma and/or chemically  
789 induced graft co-polymerized electrospun poly(vinylidene fluoride) membranes for solute  
790 separation, *Sep. Purif. Technol.*, 108 (2013) 196-204.

791 [41] S. Hong, M. Elimelech, Chemical and physical aspects of natural organic matter (NOM)  
792 fouling of nanofiltration membranes, *J. Membr. Sci.*, 132 (1997) 159-181.

793 [42] C.-C. Ho, A.L. Zydney, A Combined Pore Blockage and Cake Filtration Model for Protein  
794 Fouling during Microfiltration, *J. Colloid Interface Sci.*, 232 (2000) 389-399.

795 [43] A.I. Schäfer, U. Schwicker, M.M. Fischer, A.G. Fane, T.D. Waite, Microfiltration of colloids  
796 and natural organic matter, *J. Membr. Sci.*, 171 (2000) 151-172.

797 [44] W. Yuan, A. Kocic, A.L. Zydney, Analysis of humic acid fouling during microfiltration using a  
798 pore blockage–cake filtration model, *J. Membr. Sci.*, 198 (2002) 51-62.

799 [45] K. Xiao, Y. Shen, X. Huang, An analytical model for membrane fouling evolution associated  
800 with gel layer growth during constant pressure stirred dead-end filtration, *J. Membr. Sci.*, 427  
801 (2013) 139-149.

802 [46] K. Xiao, J. Sun, Y. Mo, Z. Fang, P. Liang, X. Huang, J. Ma, B. Ma, Effect of membrane pore  
803 morphology on microfiltration organic fouling: PTFE/PVDF blend membranes compared with  
804 PVDF membranes, *Desalination*, 343 (2014) 217-225.

805 [47] J. Bae, I. Baek, H. Choi, Mechanically enhanced PES electrospun nanofiber membranes  
806 (ENMs) for microfiltration: The effects of ENM properties on membrane performance, *Water*  
807 *Res.*, 105 (2016) 406-412.

808 [48] L. Marbelia, M. Mulier, D. Vandamme, K. Muylaert, A. Szymczyk, I.F.J. Vankelecom,  
809 Polyacrylonitrile membranes for microalgae filtration: Influence of porosity, surface charge and  
810 microalgae species on membrane fouling, *Algal Res.*, 19 (2016) 128-137.

811 [49] X. Zhuang, L. Shi, K. Jia, B. Cheng, W. Kang, Solution blown nanofibrous membrane for  
812 microfiltration, *J. Membr. Sci.*, 429 (2013) 66-70.



- 813 [50] M.N. Abu Seman, M. Khayet, N. Hilal, Development of antifouling properties and  
814 performance of nanofiltration membranes modified by interfacial polymerisation, *Desalination*,  
815 273 (2011) 36-47.
- 816 [51] A.M. Bazargan, M. Keyanpour-rad, F.A. Hesari, M.E. Ganji, A study on the microfiltration  
817 behavior of self-supporting electrospun nanofibrous membrane in water using an optical  
818 particle counter, *Desalination*, 265 (2011) 148-152.
- 819 [52] S. Kaur, Z. Ma, R. Gopal, G. Singh, S. Ramakrishna, T. Matsuura, Plasma-Induced Graft  
820 Copolymerization of Poly(methacrylic acid) on Electrospun Poly(vinylidene fluoride) Nanofiber  
821 Membrane, *Langmuir*, 23 (2007) 13085-13092.

822

**Table 1:** Prepared PSU ENMs with different heat post-treatments and their corresponding morphological characteristics: thickness ( $\delta$ ), weighted arithmetic mean of the nanofiber diameters ( $\overline{\lambda_w}$ ) with its corresponding weighted standard deviation ( $\overline{s_w}$ ), water contact angle ( $\theta_w$ ), void volume fraction ( $\varepsilon$ ) and mean size of the inter-fiber space ( $\overline{d_f}$ ).

Membrane	Heat treatment		Morphological characteristics				
	$T$ (°C)	$t$ (min)	$\delta$ ( $\mu\text{m}$ )	$\overline{\lambda_w} \pm \overline{s_w}$ ( $\mu\text{m}$ )	$\theta_w$ (°)	$\varepsilon$ (%)	$\overline{d_f}$ ( $\mu\text{m}$ )
ENM 1	210	60	$338 \pm 15$	$0.69 \pm 0.03$	$137.4 \pm 1.7$	$94.1 \pm 0.2$	$3.35 \pm 0.03$
ENM 2	210	90	$373 \pm 24$	$0.70 \pm 0.06$	$135.9 \pm 2.1$	$92.8 \pm 0.4$	$3.12 \pm 0.02$
ENM 3	220	60	$380 \pm 69$	$0.70 \pm 0.03$	$135.0 \pm 3.2$	$90.2 \pm 1.1$	$2.98 \pm 0.03$
ENM 4	220	90	$251 \pm 47$	$0.73 \pm 0.02$	$128.1 \pm 3.3$	$83.6 \pm 1.7$	$2.89 \pm 0.05$
ENM 5	220	120	$116 \pm 33$	$0.74 \pm 0.07$	$125.2 \pm 2.8$	$79.5 \pm 2.5$	$2.80 \pm 0.05$
ENM 6	220	150	$106 \pm 18$	$0.77 \pm 0.04$	$121.0 \pm 2.8$	$77.1 \pm 2.2$	$2.72 \pm 0.05$
ENM 7	220	180	$92 \pm 18$	$0.85 \pm 0.04$	$120.4 \pm 2.6$	$72.3 \pm 1.5$	$2.65 \pm 0.05$
ENM 8	230	45	$257 \pm 17$	$0.69 \pm 0.06$	$135.4 \pm 3.3$	$92.3 \pm 1.2$	$3.20 \pm 0.04$
ENM 9	230	60	$213 \pm 65$	$0.72 \pm 0.02$	$125.7 \pm 3.1$	$81.7 \pm 2.1$	$3.04 \pm 0.05$
ENM 10	230	75	$82 \pm 29$	$0.76 \pm 0.03$	$119.3 \pm 1.7$	$80.8 \pm 1.7$	$2.85 \pm 0.03$
ENM 11	230	90	$147 \pm 17$	$0.83 \pm 0.04$	$115.4 \pm 3.6$	$78.2 \pm 2.6$	$2.67 \pm 0.03$

**Table 2:** Filtration performance of PSU ENMs prepared with different heat post-treatments: initial water permeate flux ( $J_{w_0}$ ), mean humic acid (HA) permeate flux ( $\overline{J_{HA}}$ ), final HA permeate flux ( $J_{HAf}$ ), final HA separation factor ( $\alpha_f$ ), irreversible fouling factor ( $FR_w$ ) and performance index ( $PI$ ).

Membrane	Heat treatment		Filtration characteristics					
	$T$ (°C)	$t$ (min)	$J_{w_0}$ ( $10^2 \frac{\text{kg}}{\text{m}^2\text{h}}$ )	$\overline{J_{HA}}$ ( $10^2 \frac{\text{kg}}{\text{m}^2\text{h}}$ )	$J_{HAf}$ ( $\frac{\text{kg}}{\text{m}^2\text{h}}$ )	$\alpha_f$ (%)	$FR_w$ (%)	$PI$ ( $\frac{\text{kg}}{\text{m}^2\text{h}}$ )
ENM 1	210	60	196 ± 21	116 ± 12	8590 ± 919	0.8 ± 1.0	81.9 ± 2.8	65 ± 22
ENM 2	210	90	199 ± 22	84.1 ± 9.0	1899 ± 203	3.7 ± 1.2	93.1 ± 1.1	70 ± 14
ENM 3	220	60	205 ± 22	66.6 ± 7.1	1923 ± 206	0.8 ± 1.1	91.7 ± 1.3	16 ± 10
ENM 4	220	90	204 ± 22	27.7 ± 3.0	337 ± 36	33.1 ± 2.0	96.4 ± 0.5	111 ± 14
ENM 5	220	120	194 ± 19	10.0 ± 0.7	222 ± 18	57.2 ± 0.6	98.3 ± 0.3	127 ± 10
ENM 6	220	150	182 ± 19	4.5 ± 0.5	170 ± 18	65.3 ± 0.5	96.8 ± 0.5	111 ± 12
ENM 7	220	180	153 ± 17	3.2 ± 0.3	104 ± 11	65.5 ± 0.4	98.9 ± 0.2	68 ± 7
ENM 8	230	45	184 ± 20	34.8 ± 3.7	306 ± 33	37.0 ± 0.6	97.7 ± 0.4	113 ± 12
ENM 9	230	60	206 ± 22	20.0 ± 2.1	232 ± 26	63.6 ± 0.7	95.9 ± 0.6	147 ± 17
ENM 10	230	75	203 ± 22	9.9 ± 1.1	188 ± 20	70.9 ± 0.4	96.8 ± 0.5	133 ± 14
ENM 11	230	90	156 ± 17	3.6 ± 0.4	99 ± 11	75.0 ± 0.3	99.0 ± 0.1	74 ± 8

**Table 3:** Morphological characteristics and filtration performance of lab-made ENMs and commercial MF membranes: thickness ( $\delta$ ), void volume fraction ( $\varepsilon$ ), mean pore size (MPS), mean nanofiber diameter ( $\bar{\lambda}_f$ ), transmembrane pressure ( $\Delta P$ ), pure water permeability ( $PWP$ ), initial water permeate flux ( $J_{w0}$ ), initial permeate flux ( $J_i$ ), final permeate flux ( $J_f$ ), final water flux ( $J_{wf}$ ), final separation factor ( $\alpha_f$ ) and irreversible fouling factor ( $FR_w$ ).

Membrane <sup>1</sup>	Morphological characteristics				Filtration performance											Ref
	$\delta$ ( $\mu\text{m}$ )	$\varepsilon$ (%)	MPS ( $\mu\text{m}$ )	$\bar{\lambda}_f$ (nm)	Filtration mode	$\Delta P$ (bar)	$PWP^2$ (LMH /bar)	Solution <sup>3</sup>	Particle size ( $\mu\text{m}$ )	$J_{w0}$ (LMH)	$J_i^4$ (LMH)	$J_f$ (LMH)	$J_{wf}$ (LMH)	$\alpha_f$ (%)	$FR_w$ (%)	
PSU ENM <sup>L</sup>	135	-	2.1	470	Dead-end	0.5	4568	10 ppm PS Ms	1	2284	1000	538	675	92	70	[3]
							4924		0.5	2462	1867	1433	1120	47	55	
							5544		0.1	2772	2667	2438	2684	14	3	
PVDF ENM <sup>L</sup>	300	-	4-10.6	360	Dead-end	0.57	351	500 ppm PS Ms	5	200	200	133	200	91	0	[2]
						0.66	1970	100 ppm PS Ms	1	1300	1066	530	530	98	59	
PES ENM <sup>L</sup>	200	76.5	0.42	600	Dead-end	1	16006	Kaolin Ms	1.6	16006	15990	3143	11844	100	26	[47]
PES tight MF <sup>C</sup>	220	-	0.1	-	Dead-end	1	2436	Kaolin Ms	1.6	2436	2421	1000	-	99.4	-	
PVDF MF <sup>C</sup>	205	-	0.2	-	Dead-end	1	327	Kaolin Ms	1.6	327	312	143	-	98.8	-	
GVWP MF <sup>C</sup>	125	70	0.22	-	Dead-end	1	6378	5 mg/L HA (pH 10)	-	6378	-	-	1722	29	73	[43]
							7874	20 mg/L HA (pH 8)	-	7874	-	-	1496	6	81	
GVHP MF <sup>C</sup>	125	75	0.22	-	Dead-end	1	7924	5 mg/L HA (pH 8)	-	7924	-	-	1981	16	75	
PSU ENM <sup>L</sup>	178	-	-	1110	Cross-flow	1	16513	15 mg/L HA (pH 11)	~0.004	16513	-	51	69	60	99	[7]
PVDF ENM 1 <sup>L</sup>	86	87.2	4.78	163	Dead-end	1	23880*	100 ppm PS Ms	1	23880*	-	-	-	87	-	[49]
PVDF ENM 2 <sup>L</sup>	78	85.7	3.30	163	Dead-end	1	15590*	100 ppm PS Ms	1	15590*	-	-	-	91	-	
PLA ENM 1 <sup>L</sup>	180	31.4	2.3	$\geq 900$	Dead-end	0.75	78000	0.12 wt% TiO <sub>2</sub>	0.01-0.5	58500**	25947*	107*	-	61.0*	-	[26]
PLA ENM 2 <sup>L</sup>	130	27.6	1.4	$\geq 900$	Dead-end	0.75	78000	0.12 wt% TiO <sub>2</sub>	0.01-0.5	58500**	8463*	52*	-	84.3*	-	
PLA ENM 3 <sup>L</sup>	120	18.0	2.0	$\geq 900$	Dead-end	0.75	78000	0.12 wt% TiO <sub>2</sub>	0.01-0.5	58500**	1002*	27*	-	85.6*	-	
PES MF <sup>C</sup>	-	$\approx 70$	0.16	-	Dead-end	0.69	6783	2 mg/L HA	-	4680	3865	202	-	95	-	[12]
PVDF MF <sup>C</sup>	125	$\approx 70$	0.22	-	Dead-end	0.69	5217	2 mg/L HA	-	3600	3600	159*	-	93*	-	
PCTE MF <sup>C</sup>	25	13.8	0.22	-	Dead-end	0.69	4957	2 mg/L HA	-	3420	1565	155	-	87	-	
PSU ENM 9 <sup>L</sup>	213	81.7	3.06	720	Cross-flow	1	20563	15 mg/L HA (pH 11)	~0.004	20563	17540	232	834	63.9	95.9	This study
PSU ENM 10 <sup>L</sup>	89	80.8	2.82	760	Cross-flow	1	20269	15 mg/L HA (pH 11)	~0.004	20269	8036	188	643	70.9	96.8	
PES HPWP MF <sup>C</sup>	137	70-84	0.45	-	Cross-flow	1	14761	15 mg/L HA (pH 11)	~0.004	14761	1120	106	216	77.6	98.5	

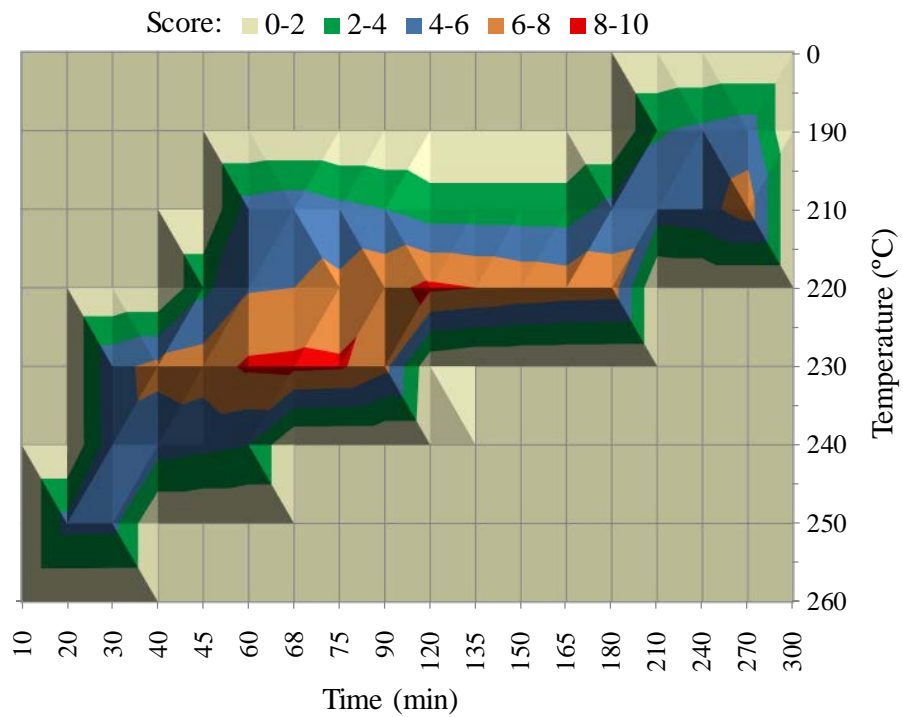
<sup>1</sup>L = lab-made membrane; C = commercial membrane; ENM = electrospun nanofiber membrane; PSU = polysulfone; PVDF = polyvinylidene fluoride; PES = polyethersulfone; UF = ultrafiltration; MF = microfiltration; PLA = poly (lactic acid).

<sup>2</sup>LMH = L/m<sup>2</sup>.h

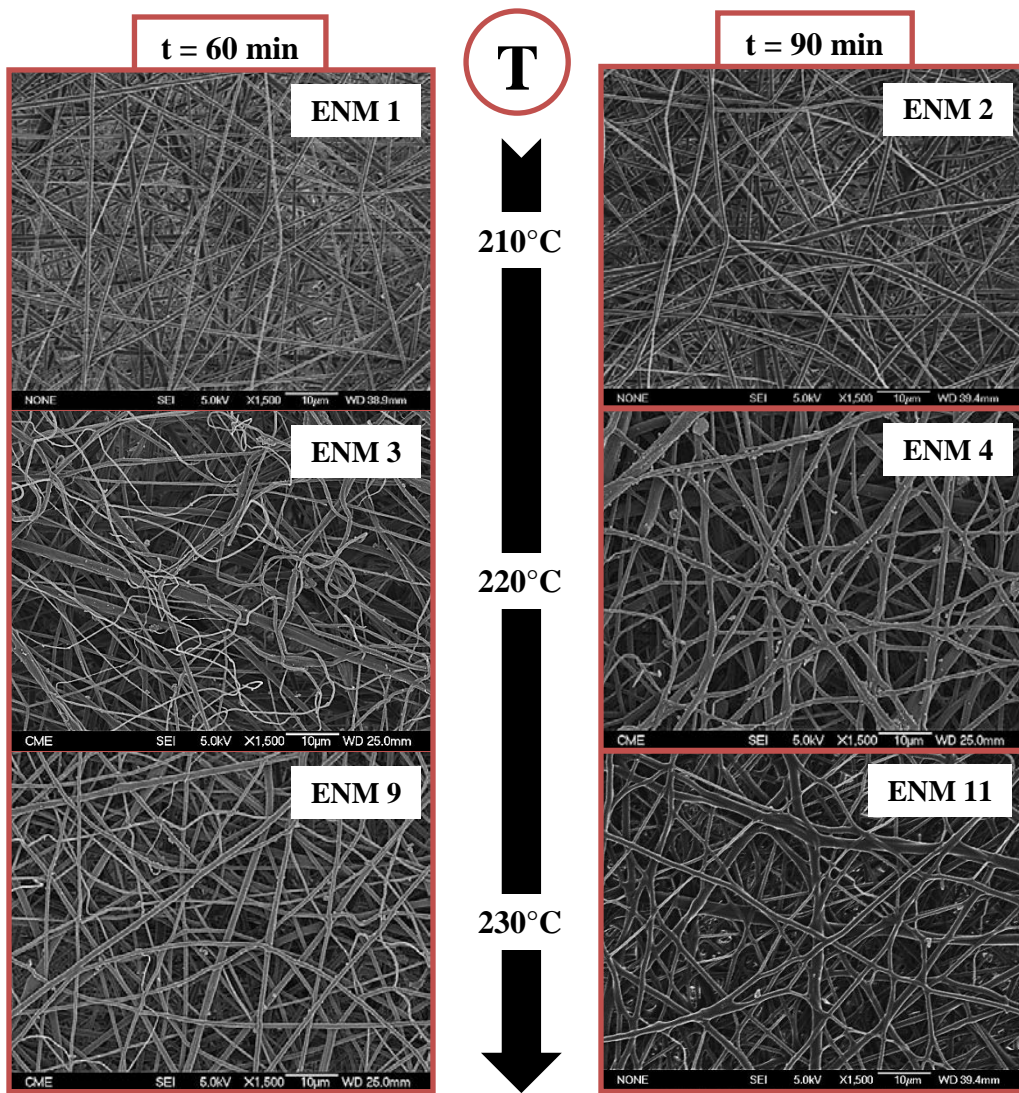
<sup>3</sup>PS = polystyrene; Ms = microparticles; HA = humic acid.

<sup>4</sup>The initial permeate flux for the membranes of this study corresponds to the HA permeate flux after 2.5 min of the filtration test.

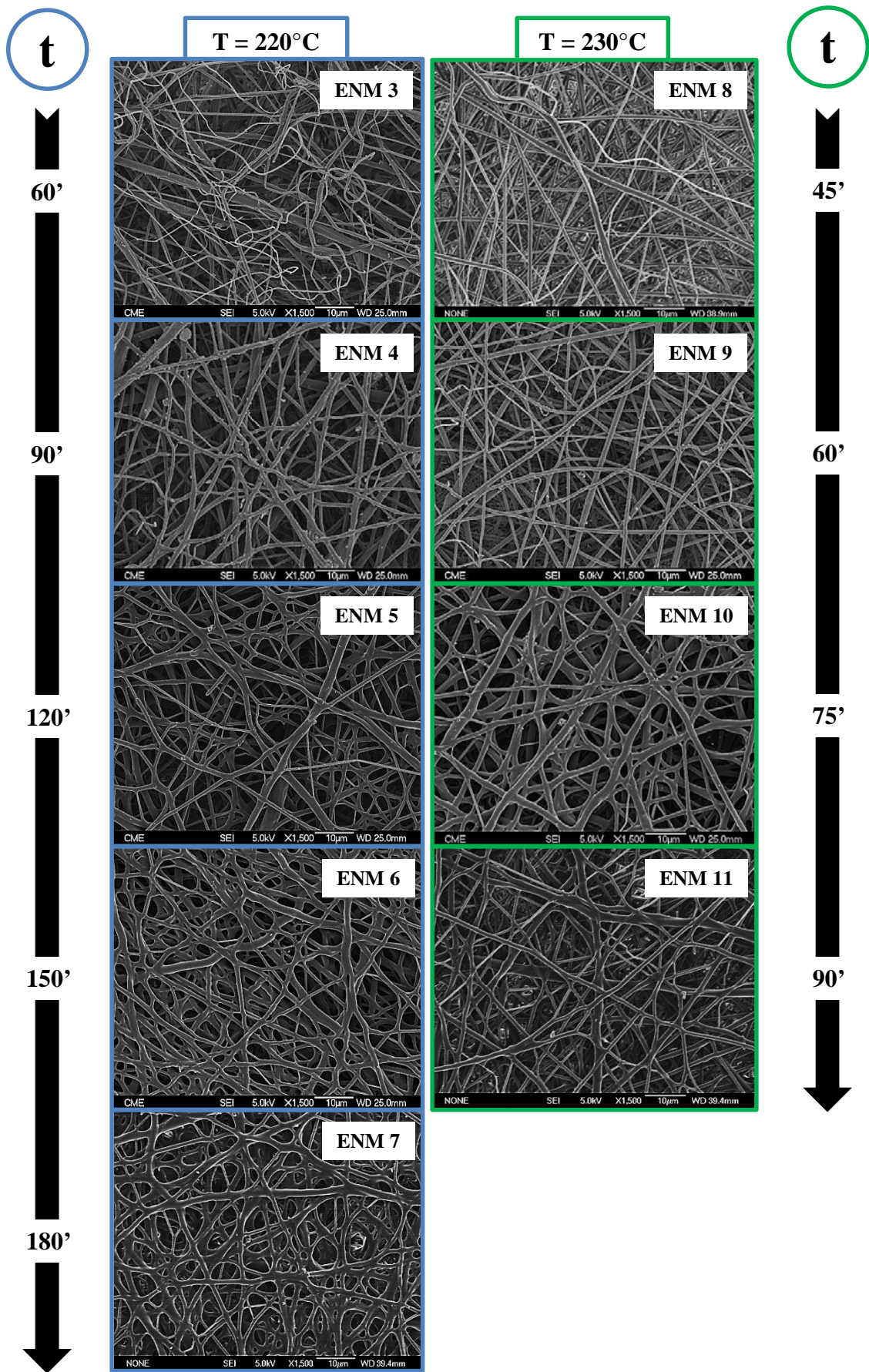
\*Estimated values taken from figures plotted in the corresponding reference; \*\* Average value.



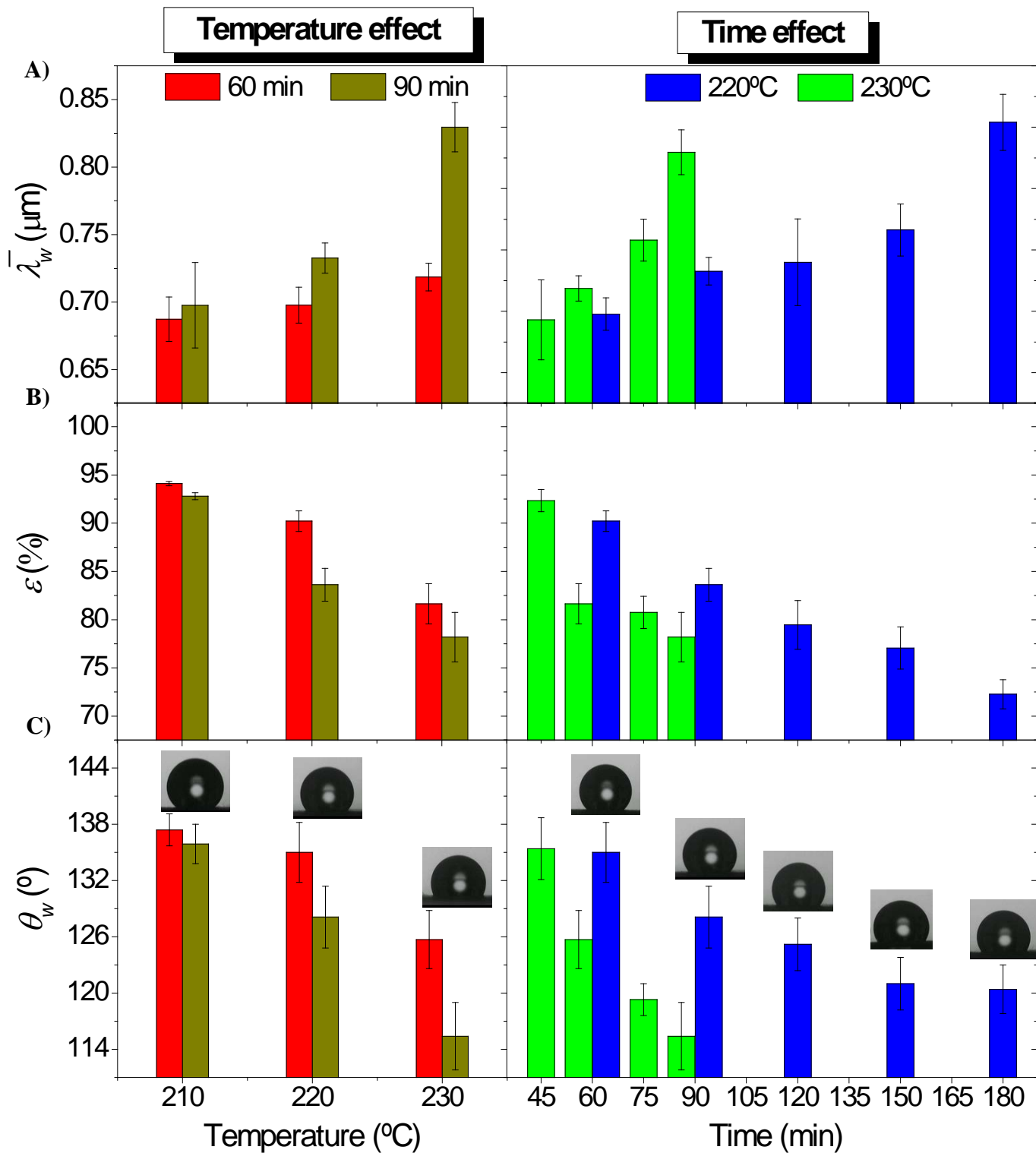
**Fig. 1.** 3D surface graph showing the result of the preliminary evaluation of the PSU ENMs treated with different heat post-treatments (HPTs).



**Fig. 2.** SEM images of the surface of PSU ENMs prepared with a HPT time of 60 and 90 min at a HPT temperature of 210, 220 and 230°C. All images were taken at X1500 magnification.

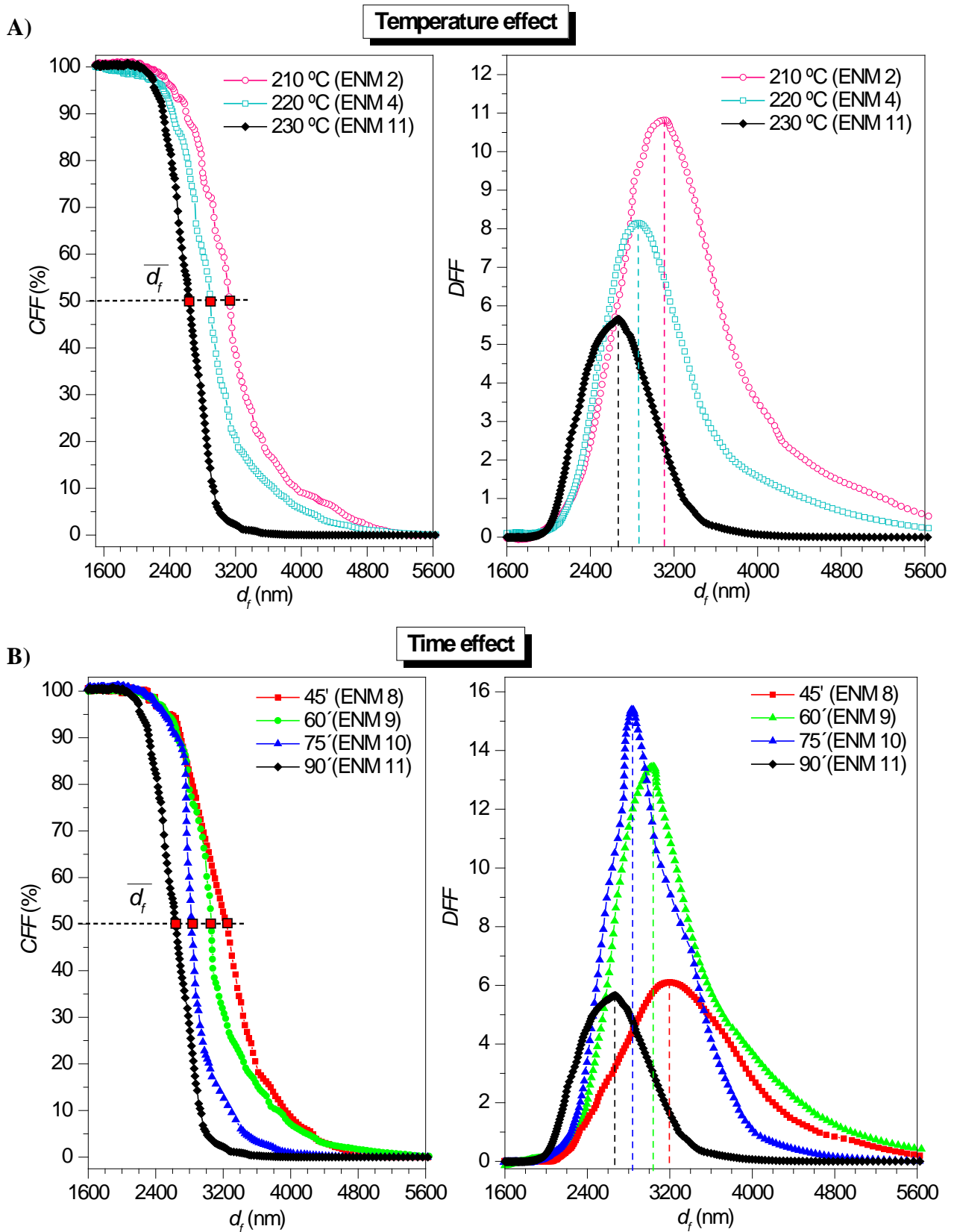


**Fig. 3.** SEM images of the surface of PSU ENMs prepared with a HPT temperature of 220 and 230°C at different HPT times (from 45 to 180 min). All SEM images were taken at X1500 magnification.

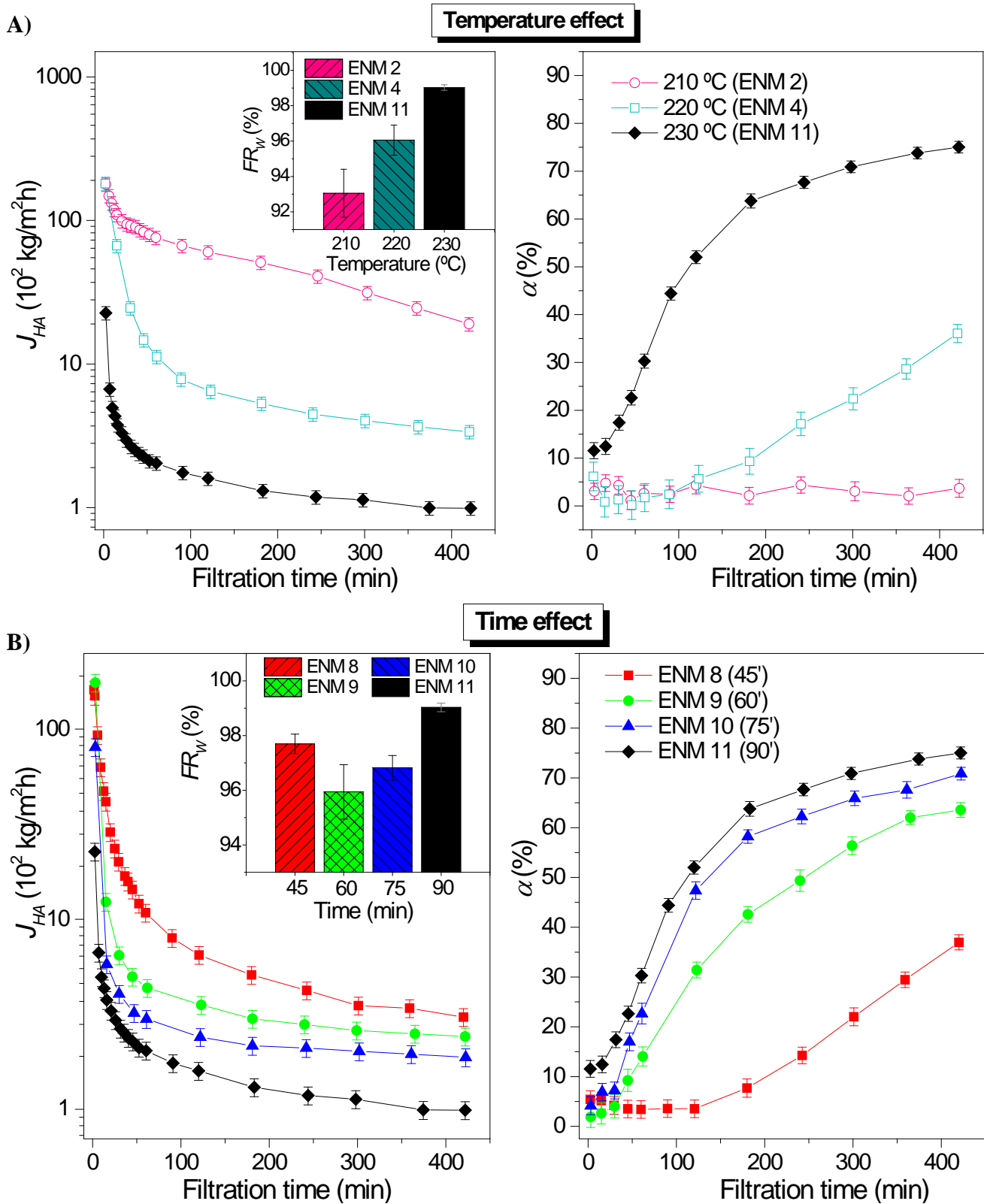


**Fig. 4.** Effects of HPT temperature and time on the morphological characteristics of PSU ENMs: A) weighted arithmetic mean of the fiber diameters ( $\bar{\lambda}_w$ ), B) void volume fraction ( $\varepsilon$ ) and C) water contact angle ( $\theta_w$ ). Contact angles micrographs in C) are added as supporting information of the graphics.

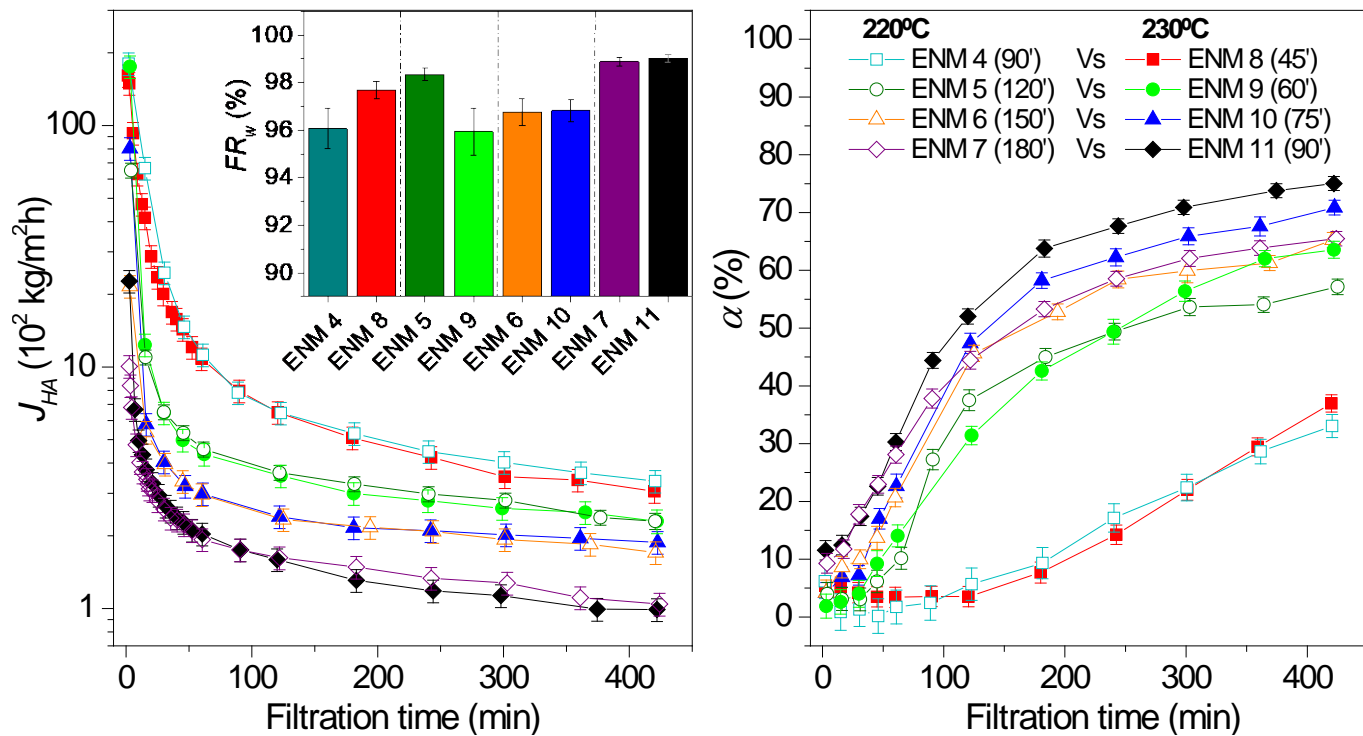




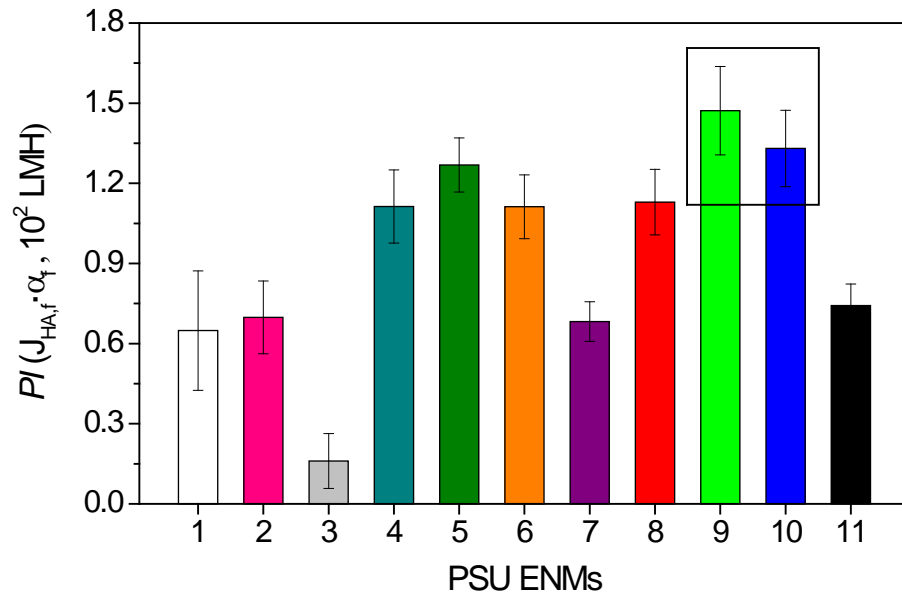
**Fig. 5.** Effects of HPT temperature (A) and time (B) on the mean size of the inter-fiber space ( $\bar{d}_f$ ), the inter-fiber space distribution or differential filter flow (*DFF*) and the cumulative filter flow distribution (*CFF*) of the PSU ENMs.



**Fig. 6.** Humic acid permeate flux ( $J_{HA}$ ), separation factor ( $\alpha$ ) and irreversible fouling factor ( $FR_w$ ) of the PSU ENMs prepared with a HPT temperature of 210, 220 and 230°C for 90 min HPT time (A), and with 230°C HPT temperature for 45, 60, 75 and 90 min HPT time (B). The filtration tests were conducted with 15 mg/L HA feed aqueous solution at pH 11 and  $10^5$  Pa transmembrane pressure ( $\Delta P$ ).



**Fig. 7.** Humic acid permeate flux ( $J_{HA}$ ), selectivity ( $\alpha$ ) and irreversible fouling factor ( $FR_w$ ) of the PSU ENMs prepared at different HPT conditions. The filtration tests were conducted with 15 mg/L HA feed aqueous solution at pH 11 and  $10^5$  Pa transmembrane pressure ( $\Delta P$ ).



**Figure 8:** Performance index (*PI*) of the PSU ENMs prepared with different HPT conditions.

## Supporting Information

### Heat-treated optimized polysulfone electrospun nanofibrous membranes for high performance wastewater microfiltration

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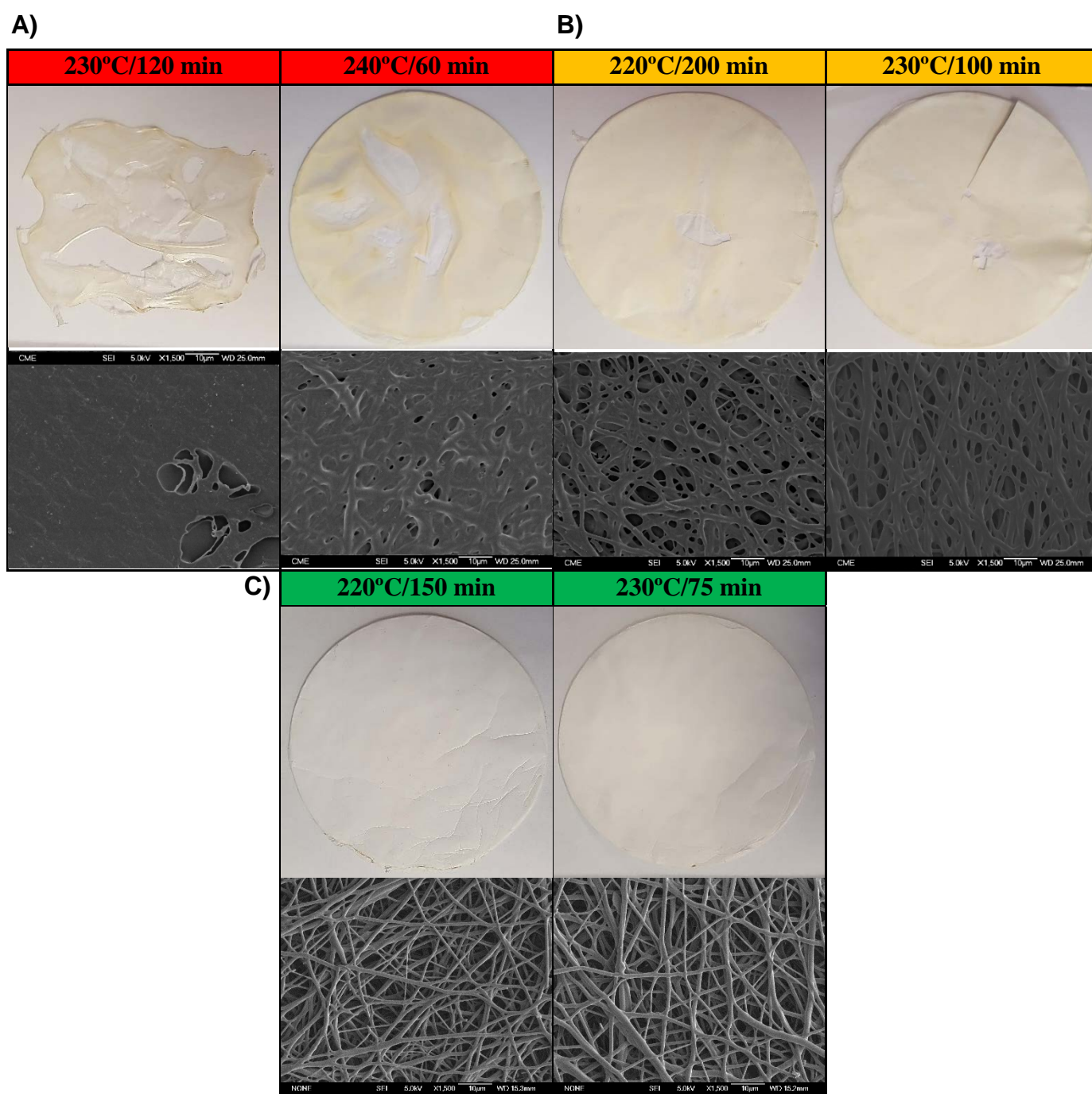
<sup>4</sup>Genetics and Eco-Physiology Research Group, School of Forest Engineering, University Polytechnic of Madrid, Avda. Complutense s/n, 28040, Madrid (Spain).

\* Corresponding authors: khayetm@fis.ucm.es; paulaarribas@ucm.es

Tel. +34-91-3944448; +34-91-3945185

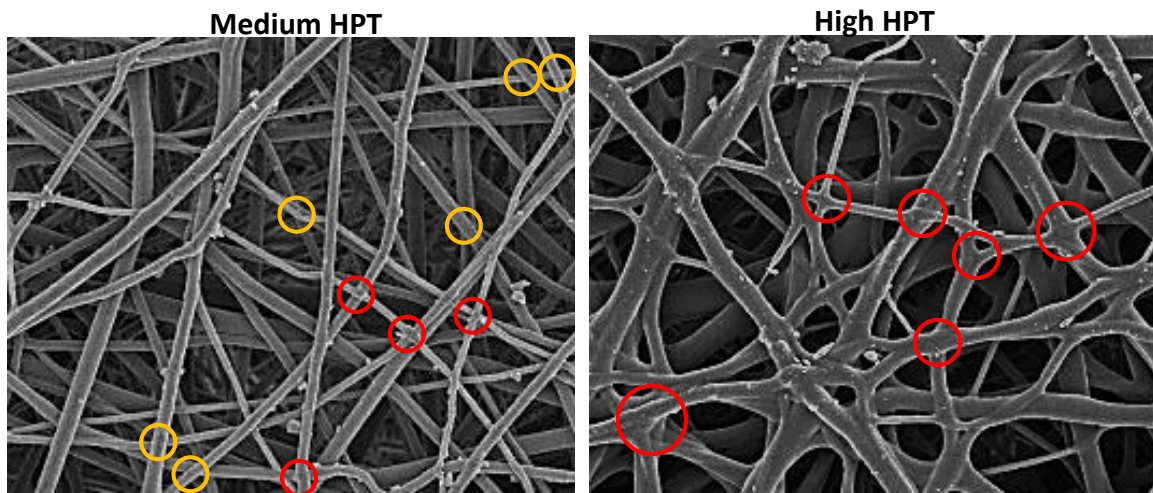
Fax. +34-91-3945191

Figure S1 shows examples to understand the way to evaluate the damage of the membranes due to the heat post-treatment (HPT). As it can be observed in Fig. S1, almost the entire surface of some of the membranes after the HPT step was burned (Fig. S1-A, red color). These membranes could not be used in filtration. Other membranes had only few burned spots on the surface, making their surface heterogeneous and not desirable for filtration tests (Fig. S1-B, yellow color). Finally, some membranes did not show visual damage and were therefore good candidates to be used for water treatment (Fig. S1-C, green color).



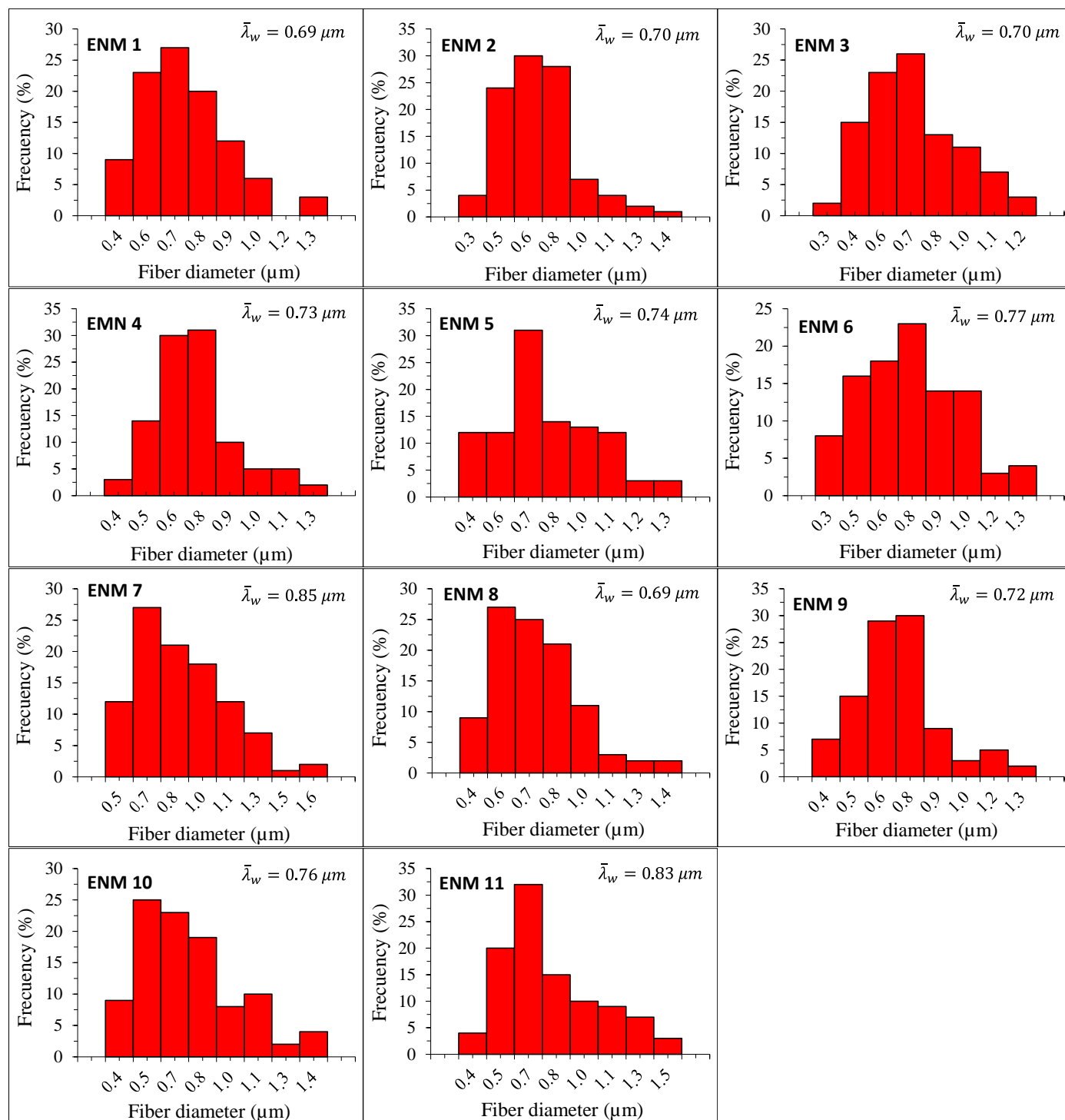
**Fig. S1.** Visual criterion to evaluate the damage of the membranes due to the HPT. Pictures of the PSU ENMs after the HPT (top) with their corresponding SEM image of the surface (bottom). A) Membranes graded with 0 points, B) 5 points and C) 10 points.

Figure S2 shows, as an example, how to evaluate the degree of networking and interconnectivity of the PSU ENMs after the application of the HPT. Firstly, the total number of the nanofibers intersections were quantified using their corresponding SEM surface images. Subsequently, the intersections in which the nanofibers are clearly fused together were identified. In this way, the degree of networking ( $DN$ ) of each PSU ENM is given by the percentage ratio between these two values (i.e.  $DN = \text{bonding points between nanofibers} / \text{total nanofibers intersections}$ ). Images of Fig. S2 show two examples of the nanofibers structure on the surface of PSU ENMs treated with a medium (230°C/60 min) and a high (230°C/75 min) HPT. The yellow circles represent some normal intersections between nanofibers while the red circles represent points with fused nanofibers, i.e. bonding points between nanofibers.



**Fig. S2.** Evaluation of the degree of networking and interconnectivity of the PSU ENMs after the application of the heat post-treatment (HPT). SEM images of the nanofibers structure on the surface of PSU ENMs treated with a medium (230°C/60 min) and a high (230°C/75 min) HPT. The yellow circles represent some normal intersections between nanofibers while the red circles represent points with fused nanofibers.

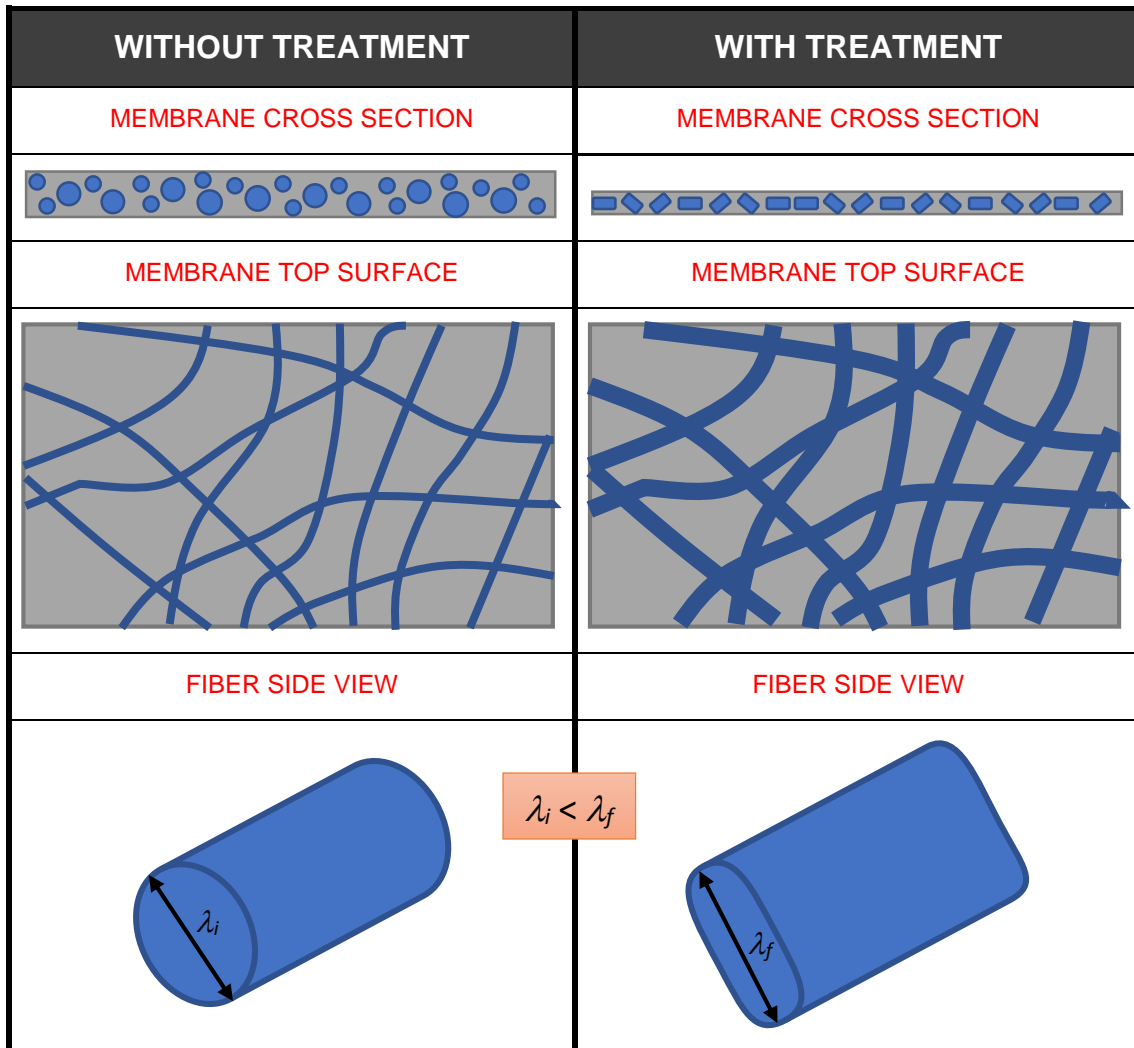
Figure S3 summarizes the nanofiber diameter distribution (i.e. nanofiber diameter histogram) of the treated PSU ENMs, obtained by statistical analysis applied on the nanofiber diameter measurements evaluated by UTHSCSA Image Tool 3.0 software.



**Fig. S3.** Nanofibers diameter histograms of the treated PSU ENMs.



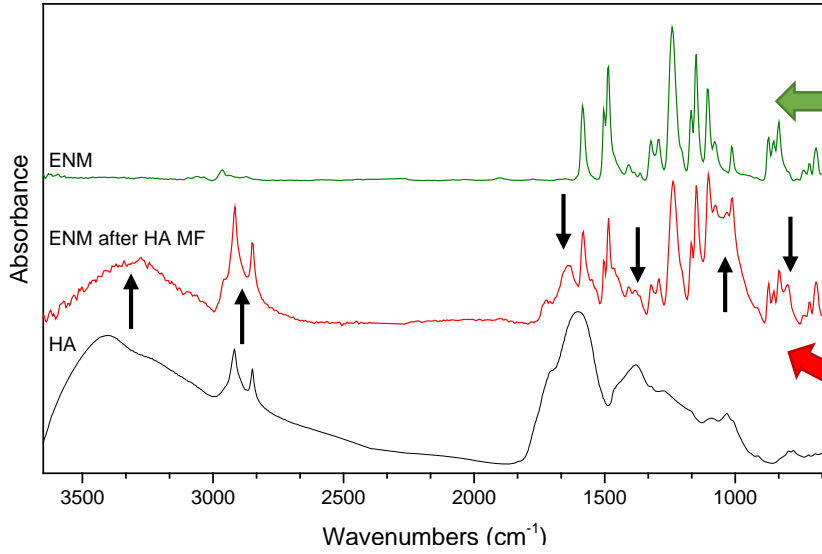
Figure S4 is a sketch showing the effects of the heat post-treatment (HPT) on the nanofiber diameters and the size of the inter-fiber space of the ENMs. ENMs after fabrication via electrospinning had a thickness of about  $900 \pm 50 \mu\text{m}$ . To carry out the HPT, the ENMs are attached to a copper support and introduced in a ceramic oven. After the HPT is completed, the thickness of the ENMs was reduced and varied in the range of 80-380  $\mu\text{m}$ . One of the main effects observed with the increase of the HPT temperature or time was the increase of the nanofiber diameters ( $\overline{\lambda_w}$ ) of the membranes along with a decrease of the mean size of the inter-fiber space ( $\overline{d_f}$ ), i.e., nanofibers became flatter and thicker along the membrane, resulting in a decrease in the mean size of the inter-fiber space.



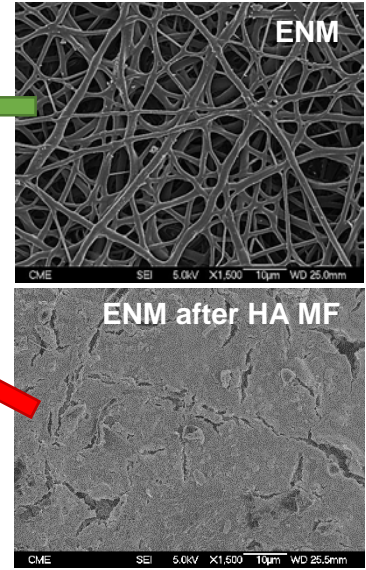
**Fig. S4.** Sketch of the effects of the heat post-treatment (HPT) on the nanofiber diameters and the size of the inter-fiber space of the ENMs. The parameters  $\lambda_i$  and  $\lambda_f$  represent the initial and final diameter of the nanofibers, respectively.

Figure S5 shows as an example some of the techniques used for the analysis of the fouling of the PSU ENMs. From the FTIR analysis (see Fig. S5-A) it can be observed the appearance of characteristic peaks of the humic acid (HA) on the spectra of the ENM after HA microfiltration (MF) (indicated with black arrows over the graph), what confirms the presence of HA in the membranes after filtration. The surface and the cross-section of the self-sustained PSU ENMs were examined by a field emission scanning electron microscope (FESEM, JEOL Model JSM-6330F) equipped with an energy-dispersive spectrometer (EDS, Oxford Instruments X-Max). The accumulation of HA on the surface of the ENMs can be observed from the SEM bottom image of Fig. S5-B. EDS in mapping mode together with the software INCA (Oxford Instruments) were used to determine the elemental composition of the ENMs before and after HA MF along the cross-section of the membrane samples. This elemental analysis was performed in three differentiate areas: the bottom side (i.e. facing the permeate), the center side and the top side (i.e. facing the feed). The cross section SEM images of Fig. S5-C correspond to the PSU ENM after HA MF. The elemental analysis areas are highlighted with a pink square over the cross section SEM images. The graph under these images summarizes the relative percentage (i.e. Element/C) of the atomic composition of the ENM before and after HA MF in the three areas of interest. Before HA filtration, the relative percentage concentration of sulfur (S/C) and oxygen (O/C) detected in the membrane was practically the same in the three areas of interest, i.e. there was a homogeneous distribution of these elements across the membrane. In addition, the concentration ratio of O/C across the membrane was higher than that of S/C, which is in concordance with the chemical formula of the PSU (i.e.  $C_{27}H_{46}O_4S_1$ ). After HA filtration, a 13 to 25% decrease of the S/C ratio and a 7 to 22% increase of the O/C ratio across the membrane were observed as well as the emergence of new elements such as aluminum (Al), silicon (Si) and iron (Fe) coming from the HA. It is worth noting that the O/C ratio was higher in the top side (0.27) than that of the bottom and center sides (0.21 and 0.20, respectively), probably due to the higher accumulation of HA in the top side of the membrane. In the same way, the concentration ratio of the new elements (i.e. Al/C, Si/C, Fe/C) was not homogeneous across the membrane. Although the analysis shows that fouling occurs along the whole cross-section of the membrane, the accumulation of these elements increase in the order: bottom side < center side < top side, being the Al/C, Si/C and Fe/C concentration ratios 79, 84 and 100 % higher, respectively, in the top side than in the bottom side.

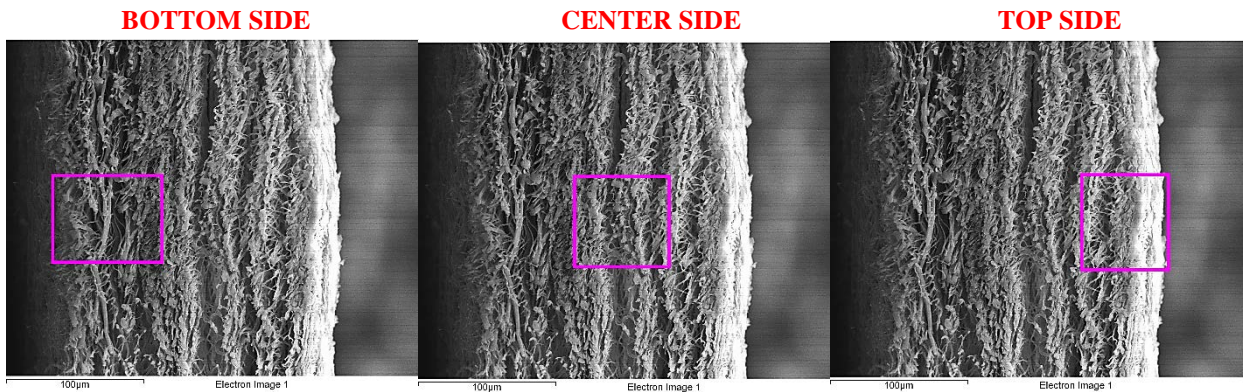
**A) FTIR**



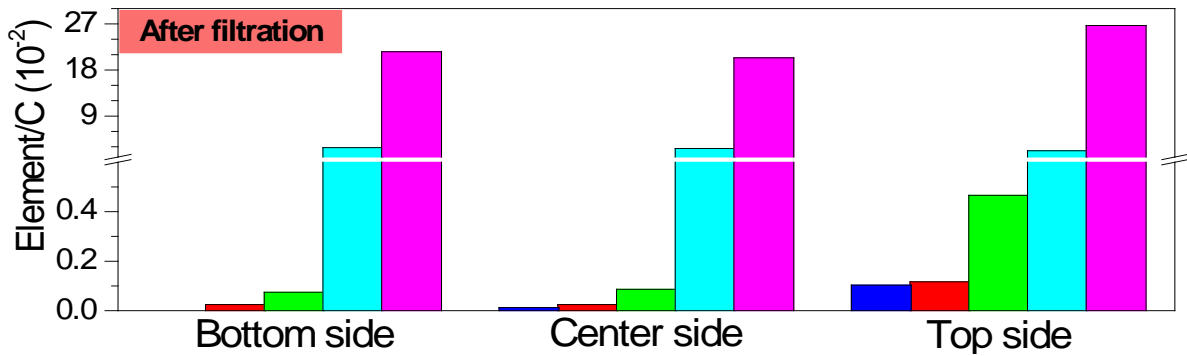
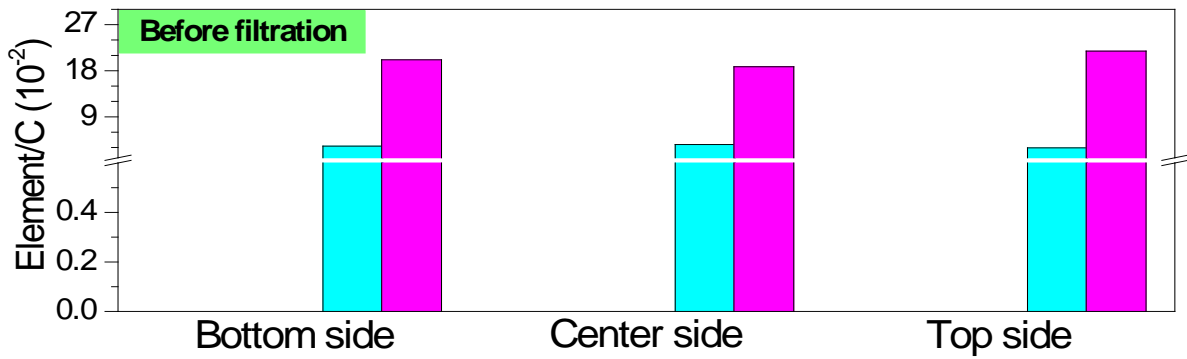
**B) SEM**



**C) EDS-MAPPING**

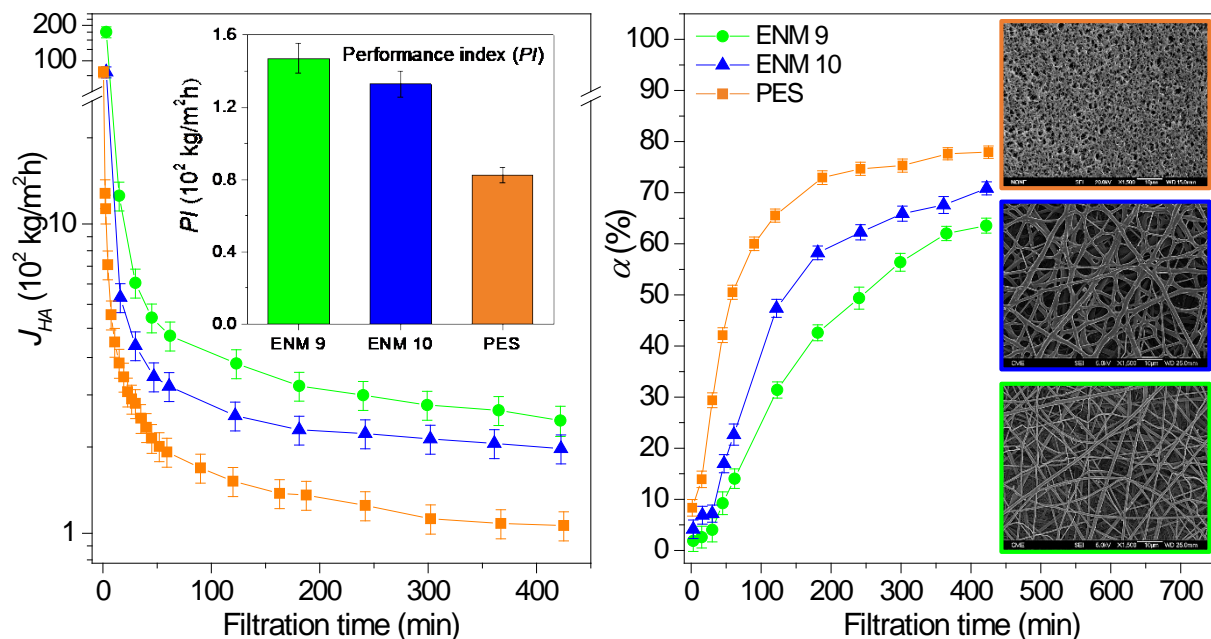


Al/C Si/C Fe/C S/C O/C



**Fig. S5.** Example of the characterization analysis of the organic fouling of the PSU ENMs. A) FTIR spectra of the HA and the ENM before and after filtration. B) SEM surface images of the ENM before and after filtration (X1500). C) SEM cross section images of the ENM after filtration taken during the EDS mapping analysis in the bottom, centre and top sides of the membrane. The graph under the images summarizes the relative percentage (i.e. Element/C) of the atomic composition of the ENM before and after HA MF in the bottom, center and top sides.

Figure S6 shows the main results of the filtration parameters analyzed during the HA MF tests conducted with the treated-optimized PSU ENMs 9 and 10 (i.e. HPT of 230°C/60 min and 230°C/75 min, respectively) and the PES MF commercial membrane. SEM surface images of the membranes before HA MF test are included to realize the initial differences in the morphological structure of the membranes.



**Fig. S6.** Humic acid permeate flux ( $J_{HA}$ ), separation factor ( $\alpha$ ) and performance index ( $PI$ ) of the PSU ENMs 9 and 10 prepared with a HPT of 230°C/60 min and 230°C/75 min, respectively, and PES MF commercial membrane. The filtration tests were conducted with 15 mg/L HA feed aqueous solution at pH 11 and  $10^5$  Pa transmembrane pressure ( $\Delta P$ ). The inset pictures are SEM surface images of the membranes before HA MF test.