Nanocomposite desalination membranes made of aromatic polyamide with cellulose nanofibers: synthesis, performance, and water diffusion study.

Rodolfo Cruz-Silva,[a,b] Kazuo Isu,[b] Jun Maeda,[b] Shigeru Saito,[b] Aaron Morelos-Gomez,[a,b] Celia Aguilar,[b,c] Yoshihiro Takizawa,[b,†] Ayaka Yamanaka,[d] Syogo Tejiima,[d] Kazunori Fujisawa,[a,b] Kenji Takeuchi,[a,b] Takuya Hayashi,[a,b] Toru Noguchi,[a,b] Akira Isogai,[e] and Morinobu Endo.[a,b]

[a.] Research Initiative for Supra-Materials, Faculty of Engineering, Shinshu University 4-17-1 Wakasato, Nagano-city 380-8553, Japan.

[b.] Aqua Innovation Center, Faculty of Engineering, Shinshu University 4-17-1 Wakasato, Nagano-city 380-8553, Japan.

[c.] Facultad de Ingenieria Mecánica y Electrica, FIME, Universidad Autonoma de Nuevo Leon, Ave. Pedro de Alba s/n, Ciudad Universitaria, C.P. 66455, San Nicolas de los Garza, N.L., Mexico.

[d.] Research Organization for Information Science & Technology, Sumitomo-Hamamatsucho Building, 1-18-16, Hamamatsucho, Minato-ku, Tokyo, 105-0013, Japan.

[e.] Department of Biomaterial Sciences, Graduate School of Agricultural and Life Sciences, The University of Tokyo, Bunkyo-ku, Tokyo 113-8657, Japan.

† Present Address: National Institute of Technology, Nagano College; 716 Tokuma, Nagano 381-0041, Japan.

SUPPORTING INFORMATION FILE

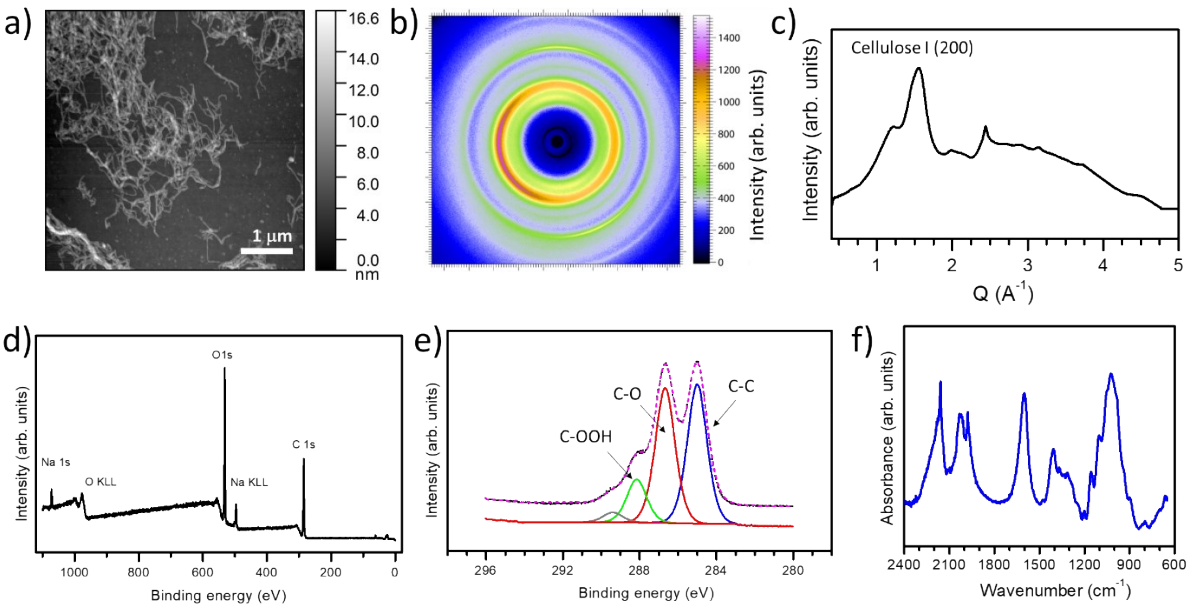

Figure S1. Characterization of Cellulose Nanofibers. a) AFM hight image (5x5 mm), b) WAXS diffraction pattern of CNF dry sample. C) shows the radial integration of the WAXS pattern. d) Wide angle XPS spectra of the dry CNF sample. e) shows the deconvoluted high-resolution C1s peak. e) FTIR spectrum of the dry CNF.

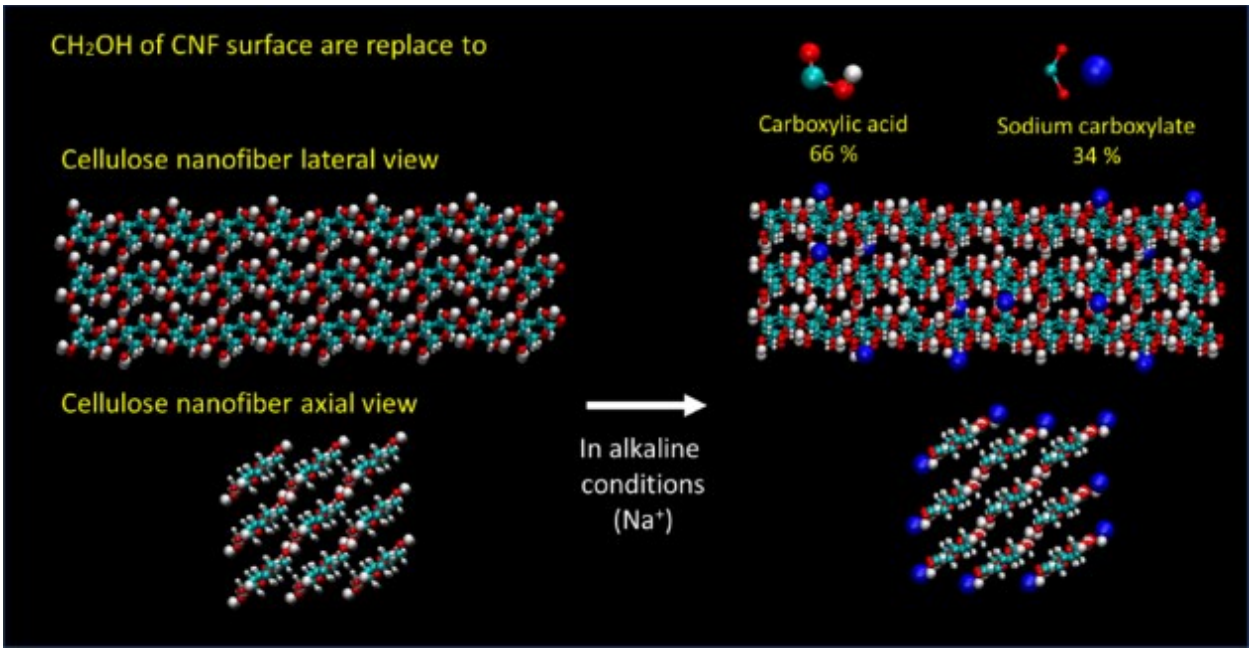

Figure S2. Modification of the cellulose crystal builder structure[47] to produce the oxidized CNF.

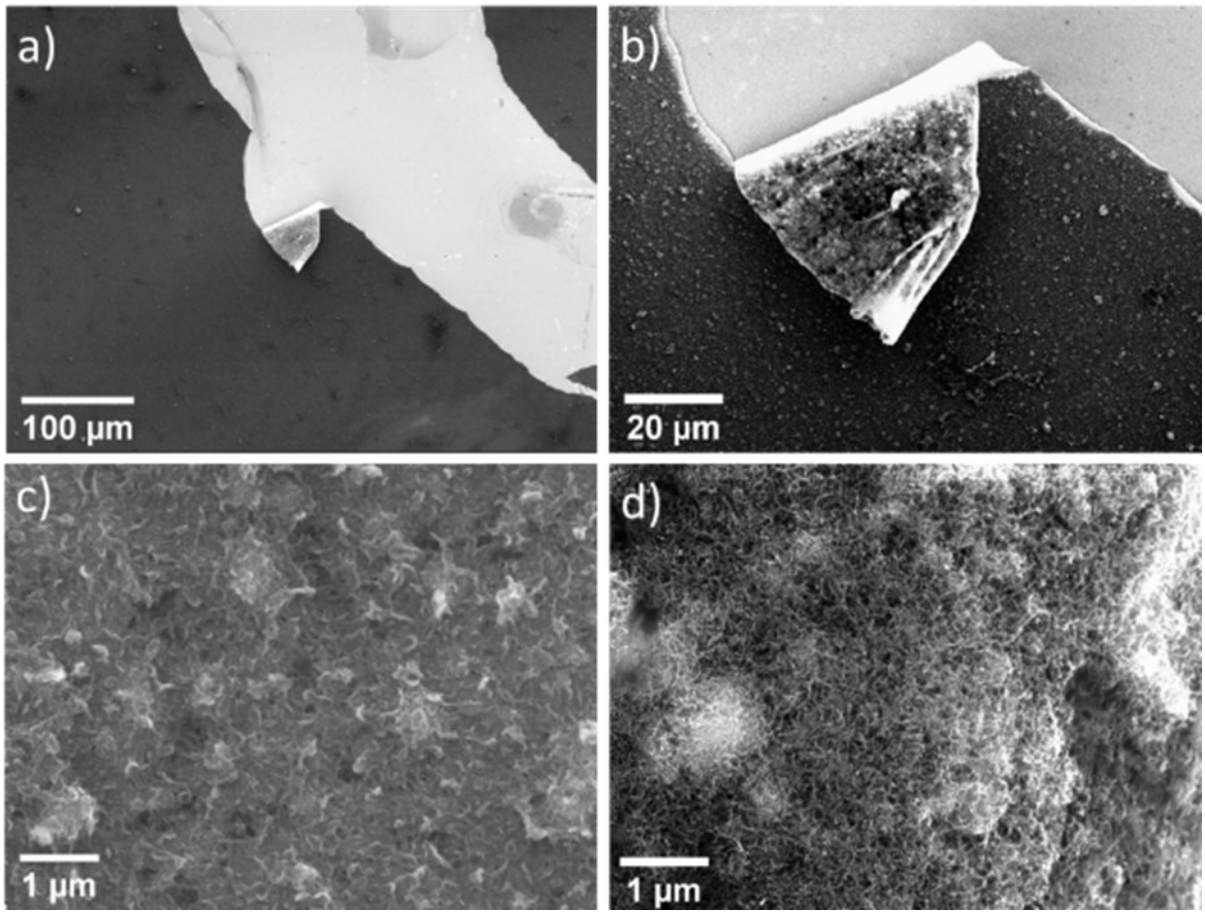

Figure S3. SEM image of the CNF-PA active layer extracted from the thin film composite membrane: a) surface and, b) Zoom showing both surface and reverse. c) detail of the surface and d) detail of the back-side of the membrane.

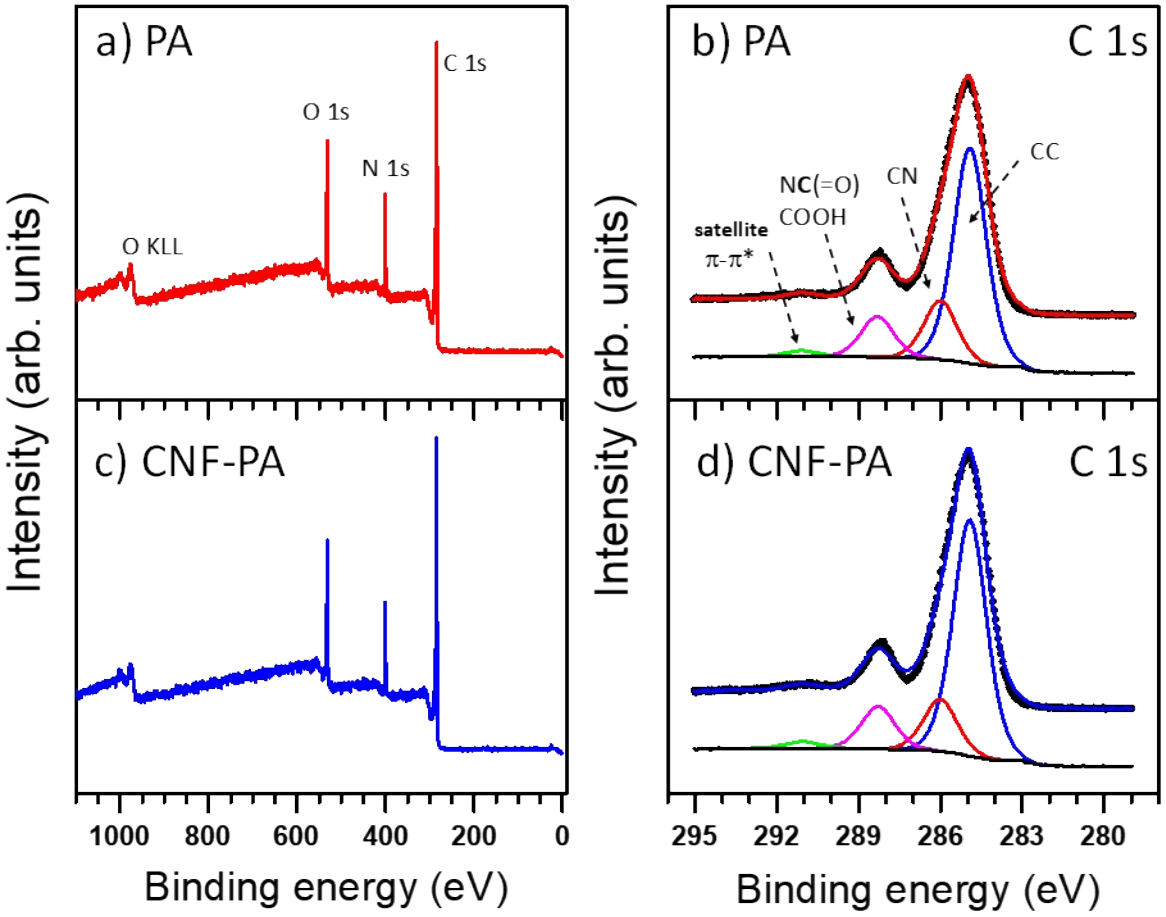

Figure S4. X-ray photoelectron spectroscopy of the as-synthesized reverse osmosis membranes. a) Wide scan of the plain PA membrane and its corresponding b) C1s core level spectrum. c) Wide scan of the CNF-PA nanocomposite membrane and its corresponding d) C 1s core level spectrum.

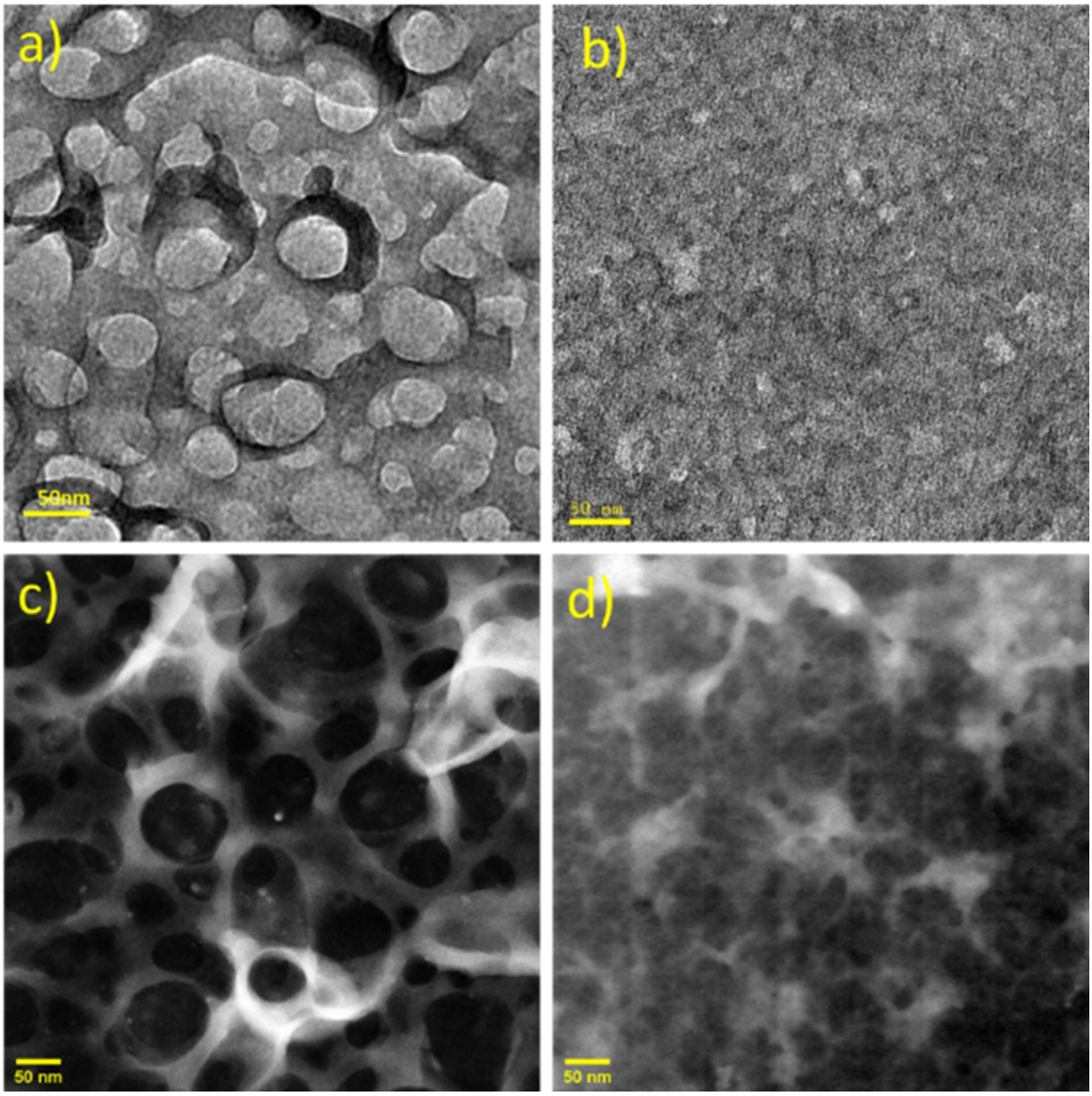

Figure S5. TEM images of the a) PA and b) CNF-PA membranes. The corresponding STEM images are shown in c) PA and d) CNF-PA.

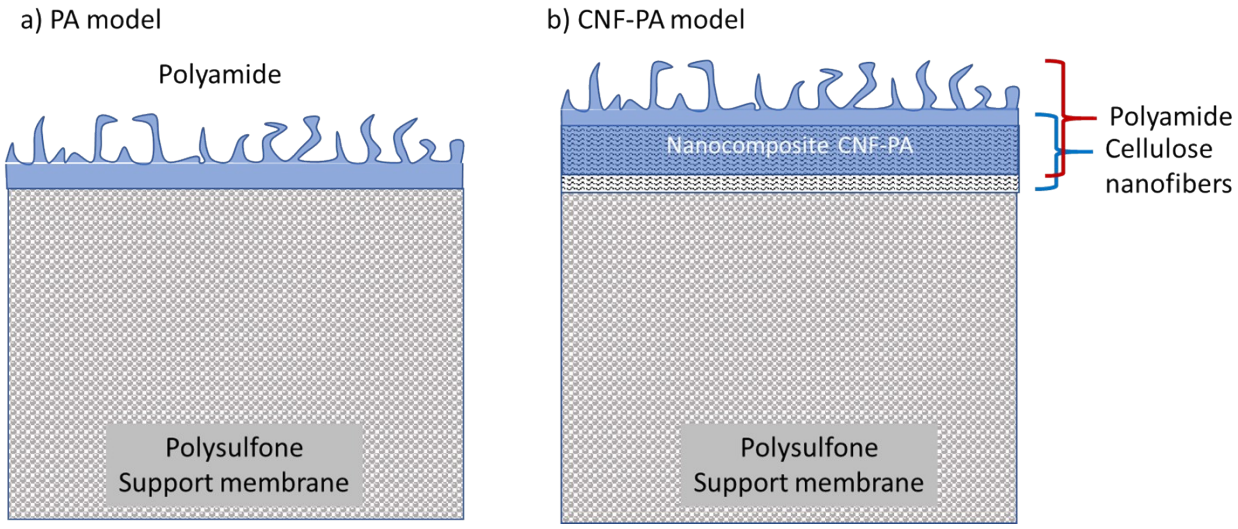

Figure S6. Proposed morphological models for the membranes prepared in this study. a) Typical PA membrane and b) CNF-PA composite membrane with a gradient composition.

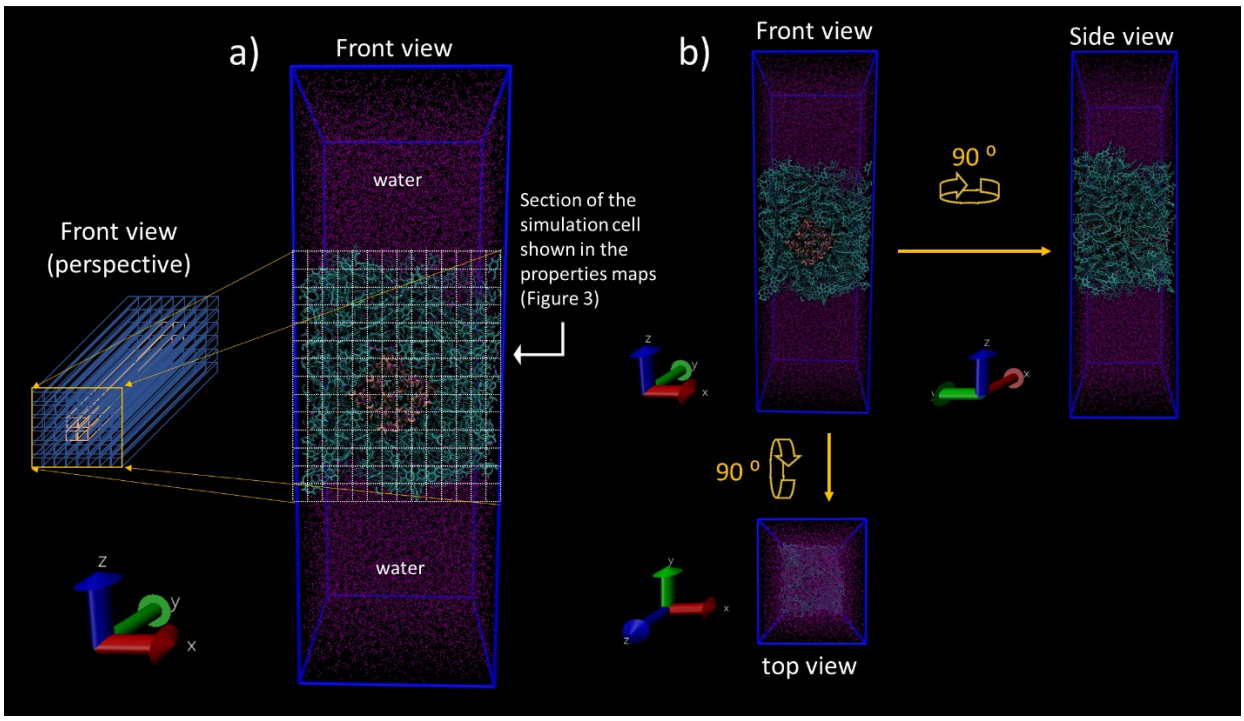

Figure S7. Computation of the membrane properties using the grid average method. a) The cell was divided in columns parallel to the Y axis. The atoms in the column have the same distance to the CNF and to the top and bottom of the membrane, while the column has a homogeneous composition. Because the properties analyzed are a function of the distance to the CNF and the top and bottom of the membranes, they can be averaged. b) shows different angles of the simulated cell

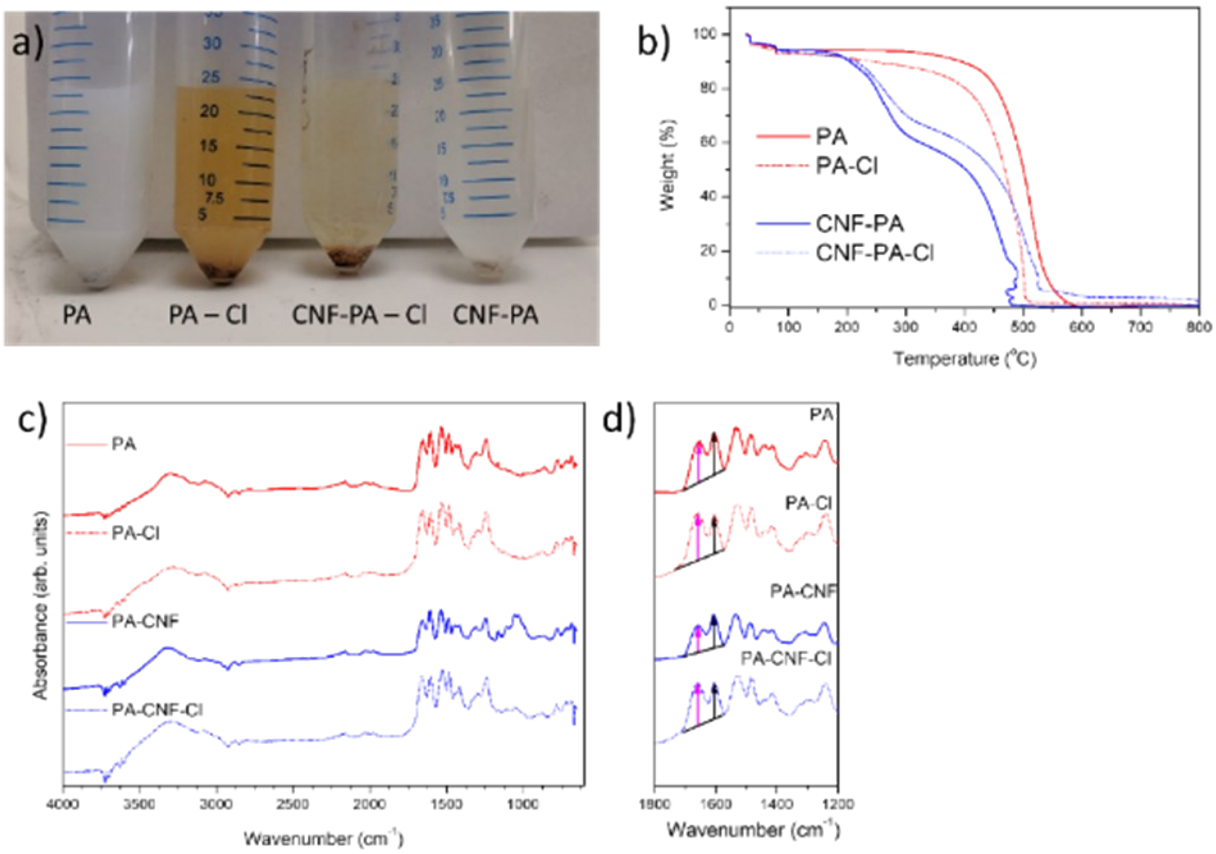

Figure S8. Chemical analysis of the PA and PA-CNF powder samples before and after chlorination at 4800 ppm-h. a) Photographic images of the water suspensions., b) thermogravimetric analysis, c) FTIR spectra, d) degree of chlorination by the COOH/CONH ratio, e) Raman spectra.

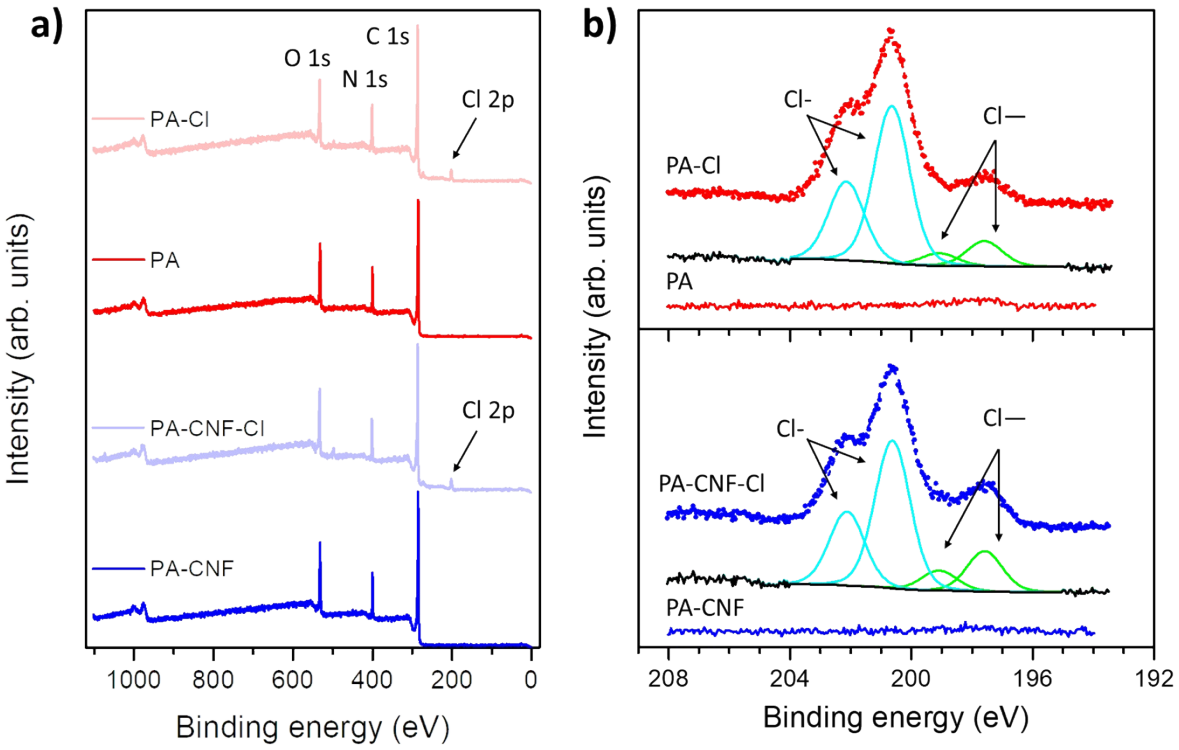

Figure S9. XPS study of the PA and the CNF-PA membranes before and after chlorination. a) wide scan, b) Cl 2p core-level spectra.

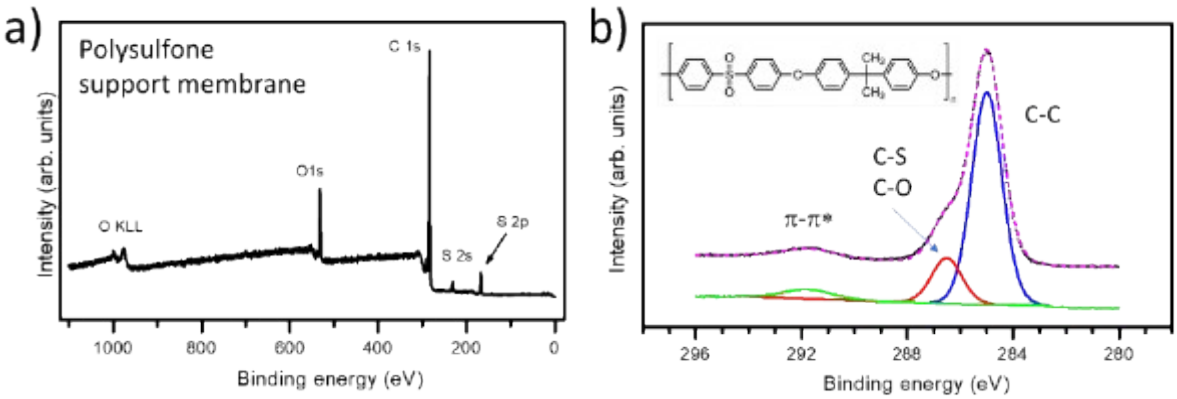

Figure S10. X-ray photoelectron spectroscopy of the polysulfone support membrane. a) wide scan and b) C 1s core-level peak.

Table S1. Surface atomic elemental composition and C 1s components deconvolution quantification of the as obtained membranes.

Surface elemental analysis					
Sample	**Peak**	**Position**	**FWHM**	**Raw Area**	**%At Conc**
PA	C 1s	285.0	1.8	21595	76.8
	O 1s	531.5	1.7	9912	12.0
	N 1s	400.2	1.5	5600	11.1
	Cl 2p	197.8	0.5	57	0.1
CNF-PA	C 1s	285.0	1.8	22994	77.0
	O 1s	531.5	1.7	10571	12.1
	N 1s	400.3	1.5	5842	10.9
	Cl 2p	198.2	0.1	44	0.1
C 1s components deconvolution					
Name	**Position**	**FWHM**	**Raw Area**	**Area (RSF*T*MFP)**	**%At Conc**
PA	284.9	1.4	14639	14639	67.0
	286.0	1.4	4003	4003	18.3
	288.3	1.4	2778	2778	12.7
	291.1	1.4	425	425	2.0
PA-CNF	284.9	1.4	16375	16375	70.1
	286.0	1.4	3592	3592	15.4
	288.3	1.4	2950	2950	12.6
	291.0	1.4	455	455	2.0

CALCULATION OF SALT REJECTION AND PERMEATE FLUX

After conditioning and compaction the PA and PA-CNF Samples were evaluated using a cross-flow system working at 5.5 MPa and a NaCl concentration of 3.2 wt% as shown in **Figure S11**. A stainless steel cell was used to keep the membrane under pressure. Circular samples of 2.5 cm in diameter were tested. Flow was kept at approximately 500 mL/min within the stainless-steel cell. The permeate flux was calculated using a balance with continuous datalogging (EW-1500i) and an online conductivity-meter (Horiba-LAQUA ES-71) with suitable conducting electrodes (9382-10D and 3574-10C, Horiba).

The NaCl rejection, R (%), was calculated using the following Equation (1)

$$R = \frac{C_f - C_p}{C_f} \times 100\ (\%) \qquad (1)$$

where C_f and C_p are the feed and the permeate concentrations of the solution, respectively. The permeation flux J ($Lm^{-2}h^{-1}$) was calculated using Equation (2)

$$J = \frac{\Delta V}{A\Delta t}(Lm^{-2}h^{-1}) \qquad (2)$$

where ΔV (L) is the volume of permeated water collected during the permeation time Δt (h) and A (m^2) is the effective surface area of the membrane samples.

For the fouling experiments the normalized permeate flux $J_r(t)$ was calculated using Equation (3):

$$J_r(t) = J(t)/J_0 \qquad (3)$$

where $J(t)$ ($m^3\ m^{-2}\ d^{-1}$) is the flux after the addition of BSA the foulants and J_o is the flux after the compaction of the membrane.

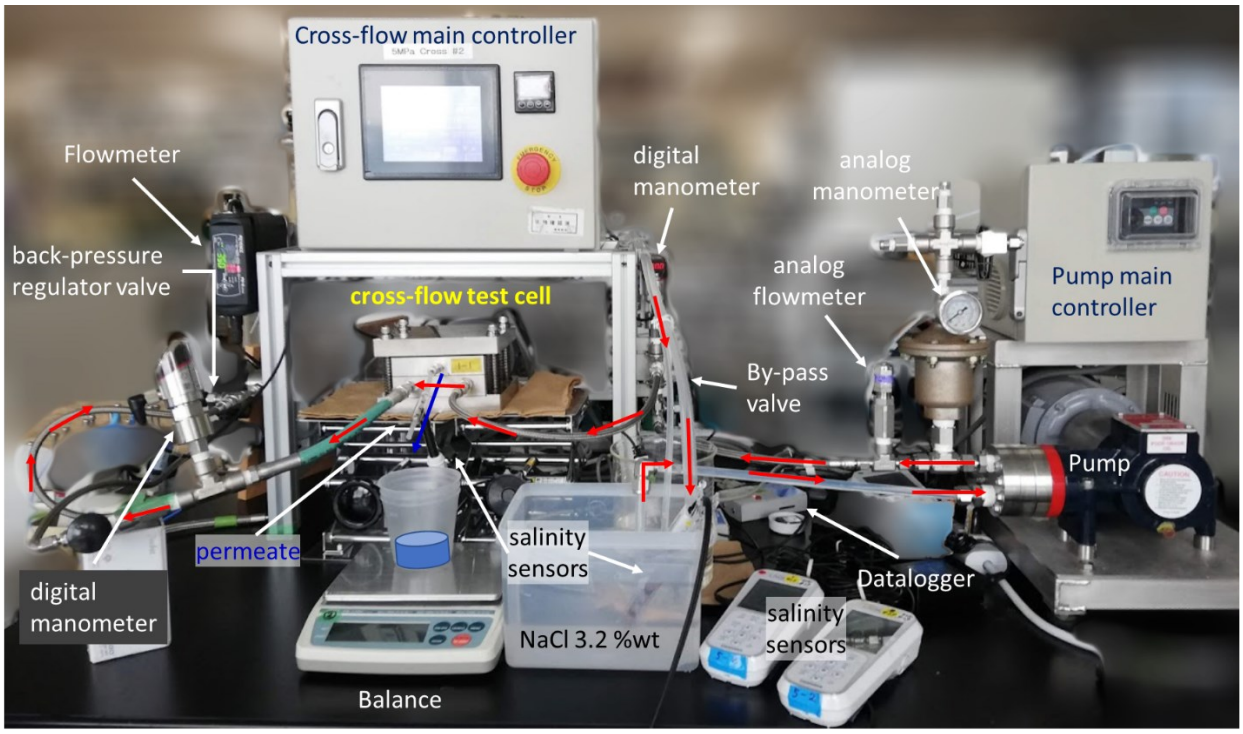

Figure S11. Experimental set-up using during the cross-flow desalination tests. Datalogging of the salinity of the feed and permeate, permeate mass flow rate, and transmembrane pressure was carried out. The red arrows indicate the flow of the feed, while the blue arrow shows the permeate flow that fells in a container that is continually weighted. During long operation manual adjustment of the feed reservoir salinity is necessary and is carried out without interruption of the operation.