**Supporting information** 

# Multiple approaches to the buildup of asymmetric polyelectrolyte multilayer membranes for efficient water purification

Esra te Brinke, Iske Achterhuis, Dennis M. Reurink, Joris de Grooth and Wiebe M. de Vos\*

Membrane Science and Technology

University of Twente

MESA+ Institute for Nanotechnology

P.O. Box 217, 7500 AE Enschede, The Netherlands

\* E-mail: w.m.devos@utwente.nl

# Micropollutants

Micropollutant	Chemical structure	Mw (Da)	pK <sub>a,acidic</sub> <sup>(a)</sup>	pK <sub>a,basic</sub> <sup>(a)</sup>
atenolol		267.34	14.1	9.67
atrazine		215.69	14.5	4.2
bezafibrate		360.81	3.84	-
bisphenol A	но он	228.29	9.78	-
bromothymol blue	Br HO HO ONIS Br HO OH	624.38	8.41	-
naproxen		229.25	4.19	-
phenolphthalein	но	318.32	9.16	-
sulfamethoxazole	$H_2N$	253.28	6.16	1.97

## Table S1. Structure, molecular weight and pKa values of the micropollutants used in this study

<sup>(a)</sup> pK<sub>a</sub> values obtained from ChemAxon

### **Module fabrication**

Single hollow fiber membranes were potted in 22 cm long polyethylene tubing (inner diameter 4 mm, outer diameter 6 mm) to make them fit with Festo connections. Before potting, a small hole was cut in the middle of the tubing to allow capture of the permeate. After inserting the membrane, 3-4 cm of the tubing was filled with a polyurethane 2 component glue (1:7 hardener:resin ratio) at both sides, while ensuring that the membrane is completely surrounded by glue. After overnight hardening of the glue (room temperature), a few millimeters were cut from each end of the modules to create smooth membrane in- and outlets.



Figure S1. Single membrane modules for membrane analysis in a crossflow setup.

#### **Asymmetric PSS/PAH layers**



Figure S2. Growth and properties of asymmetric PSS/PAH layers. a: Reflectometry of asymmetric PSS/PAH buildup, with a bottom layer coated at 500 mM NaCl and top layers coated at different ionic strengths. Compared with the PDADMAC/PSS bottom layers, the growth of the bottom layer is now linear and slower because of the lack of interpenetration. Error bars: standard error, n=3. b: Permeability, salt retention and micropollutant retention of symmetric and asymmetric PSS/PAH membranes. The asymmetric membranes do have a better permeability, but micropollutant retention is not improved. Error bars: standard error, n=4.

#### Scanning electron microscopy



Figure S3. Cross-section scanning electron microscopy images of the inner surface of the uncoated support membrane (top), PSS/PDADMAC + PSS/PAH 13+8 layers coated at 500 mM NaCl (center) and PSS/PAH 21 layers coated at 500 mM NaCl (bottom). The polyelectrolyte multilayers on top of the support membrane are clearly visible. As expected, the asymmetric layer with a PSS/PDADMAC bottom layer (~100 nm) is thicker than the PSS/PAH layer (~50 nm).



#### Glutaraldehyde-crosslinked PSS/PAH permeability

Figure S4. Change in permeability of a 21 layer PSS/PAH membrane (500 mM NaCl) upon 5 hours of glutaraldehyde crosslinking. We measure a 43% drop in permeability, which is more than the 30% drop observed after 5 hours crosslinking of an asymmetric layer (PSS/PDADMAC + PSS/PAH, 13+8 layers, 500 mM NaCl). In unpublished work we observed that the relative drop in permeability is depending on total layer thickness, probably because glutaraldehyde is not able to completely penetrate the layer, especially when the surface densifies as a result of the crosslinking reaction. Therefore we expect that by optimizing layer thickness, the permeability of the asymmetric membrane can be significantly improved by reducing both PSS/PDADMAC and PSS/PAH layer thickness, while the permeability of a full PSS/PAH layer can only be marginally improved because the thickness of the crosslinked layer is rather invariable.





Figure S5. Changes in PSS/PDADMAC + PSS/PAH (13+8 layers, coated at 500 mM NaCl) salt retentions after crosslinking with 7.5 mM glutaraldehyde. While magnesium retentions decrease slightly, probably because of a small decrease in positive charge density after crosslinking part of the primary amines of PAH, sodium retentions increase significantly. This can be explained by a higher density of the PEM layer after crosslinking, such that salts of a monovalent cation that were not well retained before crosslinking, will be retained better. The relatively high increase in retention of the bulky sodium sulphate fits well with this explanation.