Supporting Information

Polyelectrolyte-based Sacrificial Protective Layer for Fouling Control in RO Desalination

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Detailed materials information

A poly(diallyl-dimethylammonium chloride) (average M_w 200,000-350,000 (medium molecular weight), 20 wt. % in H_2O, CAS Number 26062-79-3), poly(sodium-4-styrenesulfonate) (average M_w ~70,000, powder, CAS Number 25704-18-1), calcium ion (Calcium chloride anhydrous, granular, <7.0 mm, >93.0%, CAS Number 10043-52-4), alginate (Alginic acid sodium salt powder, CAS Number 9005-38-3), and sodium chloride (BioReagent, suitable for cell culture, suitable for insect cell culture, suitable for plant cell culture, >99%, CAS Number 7647-14-5) were purchased from Sigma-Aldrich. Commercial reverse osmosis membrane was purchased from Dow chemical company (SW30HR). Dead-end filtration set-up was purchased from Sterlitech Corp (HP4750).

Normalized flux

Water flux was normalized by dividing by initial water flux. Thus, water flux is exactly same as initial water flux if normalized flux is one. In consecutive fouling experiments, the water flux was normalized by the initial water flux of the first cycle. The water flux was measured with a weight for one min and then used as a representative value.

Applicability of the coating under cross-flow

To confirm applicability of the coating under cross-flow, Quartz Crystal Microbalance with Dissipation monitoring measurements were performed (Q-sense E4, Biolin Scientific, Gothenburg, Sweden). The average cross-flow velocity in the E4 was $6.1-6.4 \times 10^{-4}$ m/s. The analyses were performed using a gold quartz sensor with the fundamental frequency of 5 MHz, at 22℃. Before the measurements, the sensors were cleaned with 0.01 M NaOH followed by 0.01 M HCl and rinsed with DI water. In this system, the more negative value of relative frequency, the greater the thickness of added film (zero relative frequency was the baseline, without any coating). To test the formation of the bi-layers the following steps were performed (Figure S5a):

1. DI water was passed through the systems for 30 minutes.
2. The polyelectrolyte (PDDA or PSS) was recirculated through the system until the relative frequency stabilized.
3. To remove the excess polyelectrolytes (the part which did not interact with the surface/previous polyelectrolyte layer), DI water flushed through the system until the relative frequency stabilized. The stability of each layer was tested for 30 minutes under cross-flow conditions.
4. Steps 2 and 3 were repeated ten times to form five bi-layers.

To test the stability of the coating under cross-flow conditions, DI water was continuously flushed through the systems, and the relative frequency was monitored over time. A constant relative frequency over time means that the coating is not washed out by the cross-flow (Figure S5b).

Potential stability of the coating under high shear-force

The bi-layer coating of the PDDA and PSS polyelectrolytes was applied under cross-flow (0.16 m/s) conditions representative for practice using a membrane fouling simulator (MFS, Reference: Vrouwenvelder, J.S., Hinrichs, C.W.G.J., Van der Meer, W.G.J., Van Loosdrecht, M.C.M. and Kruithof, J.C., Pressure drop increase by biofilm accumulation in spiral wound RO and NF membrane systems: role of substrate concentration, flow velocity, substrate load and

flow direction. *Biofouling*, **2009**, *25*, 543-555). The MFS contained a 20 × 4 cm reverse osmosis membrane sheet and a 34 mil (864 μm) feed channel spacer. The polyelectrolytes solution flowed through the MFS for five minutes followed by a five minutes of DI water flushing to remove the excess polyelectrolytes which did not interact with the surface/previous polyelectrolyte layer. All coating experiments were conducted under 22℃. At the end of the experiments the membranes were taken out from the flow cells, and transmission electron micrographs were acquired to check the presence of the bi-layers (Figure S6).

Figures

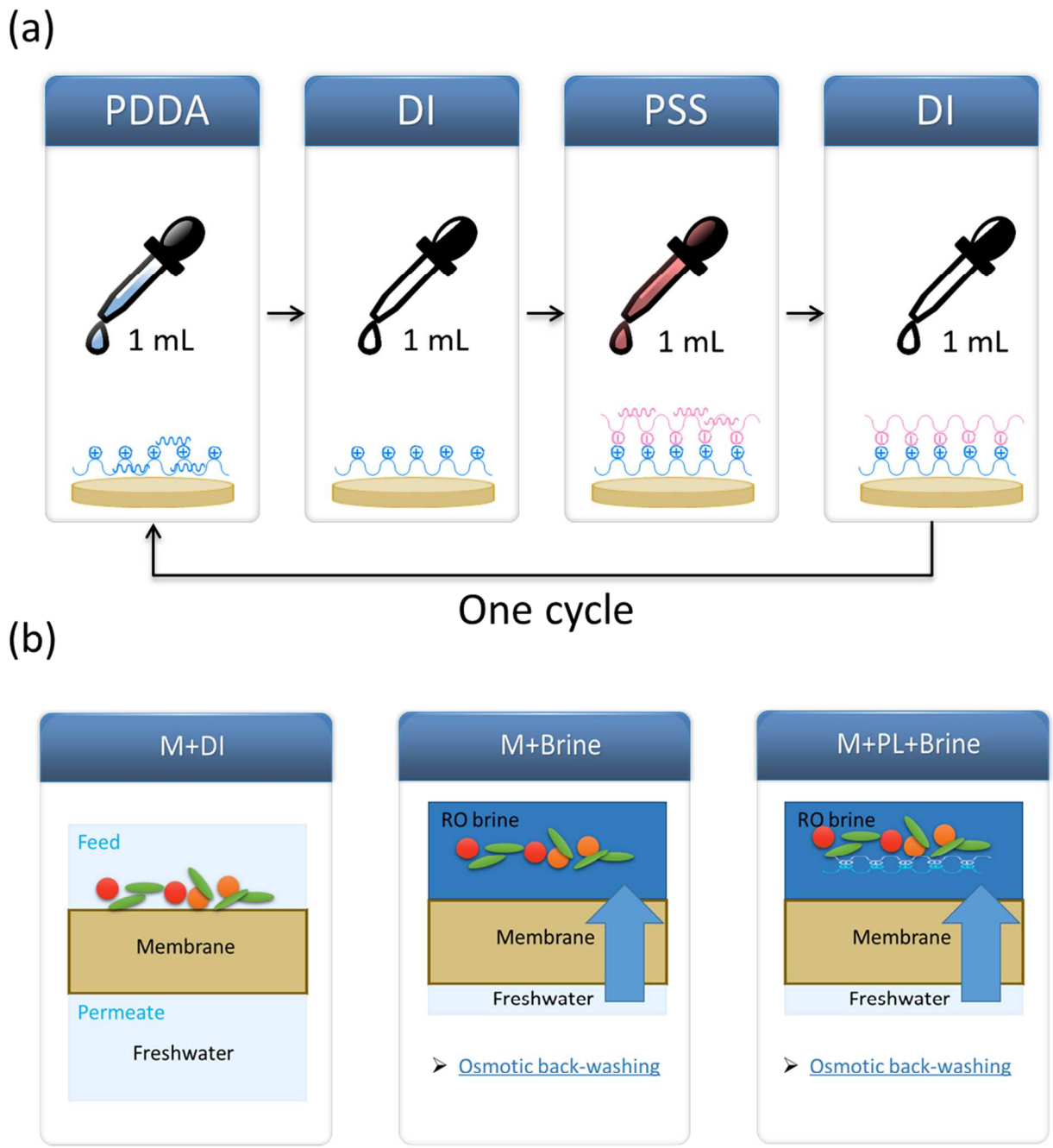

Figure S1 Schematic of (a) in-situ replenishment of a polyelectrolyte layer and (b) fouling mitigation. The fouling layer was removed only by the salt wash and not by the osmotic backwashing.

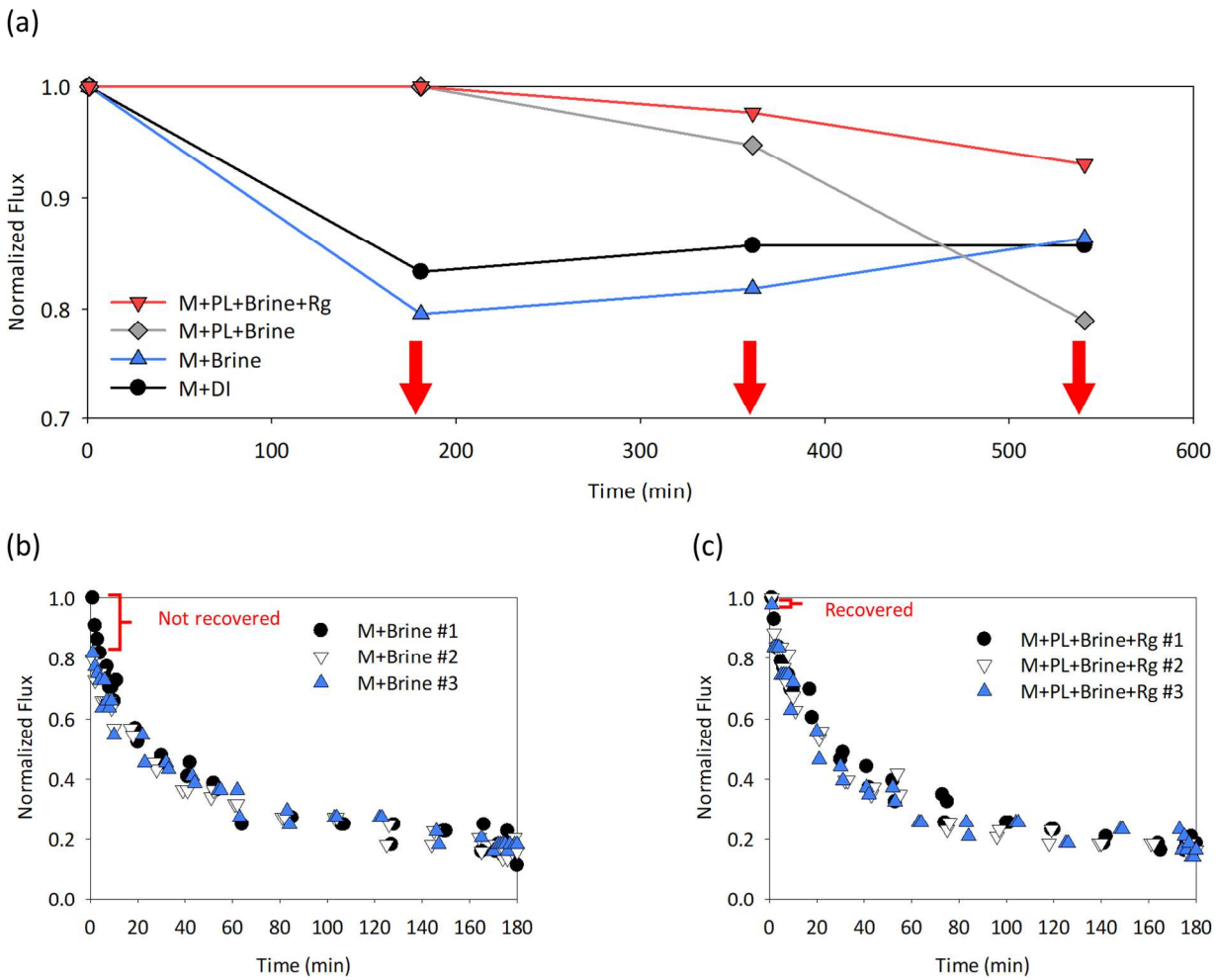

Figure S2 (a) Normalized initial water flux tendency for four consecutive fouling test. Cleaning was done after each three hours of fouling (red arrows). Each data point after cleaning indicates the first normalized flux after each cleaning step. Overlaid fouling and water flux tendency for (b) pristine membrane and (c) developed membrane over three cycles.

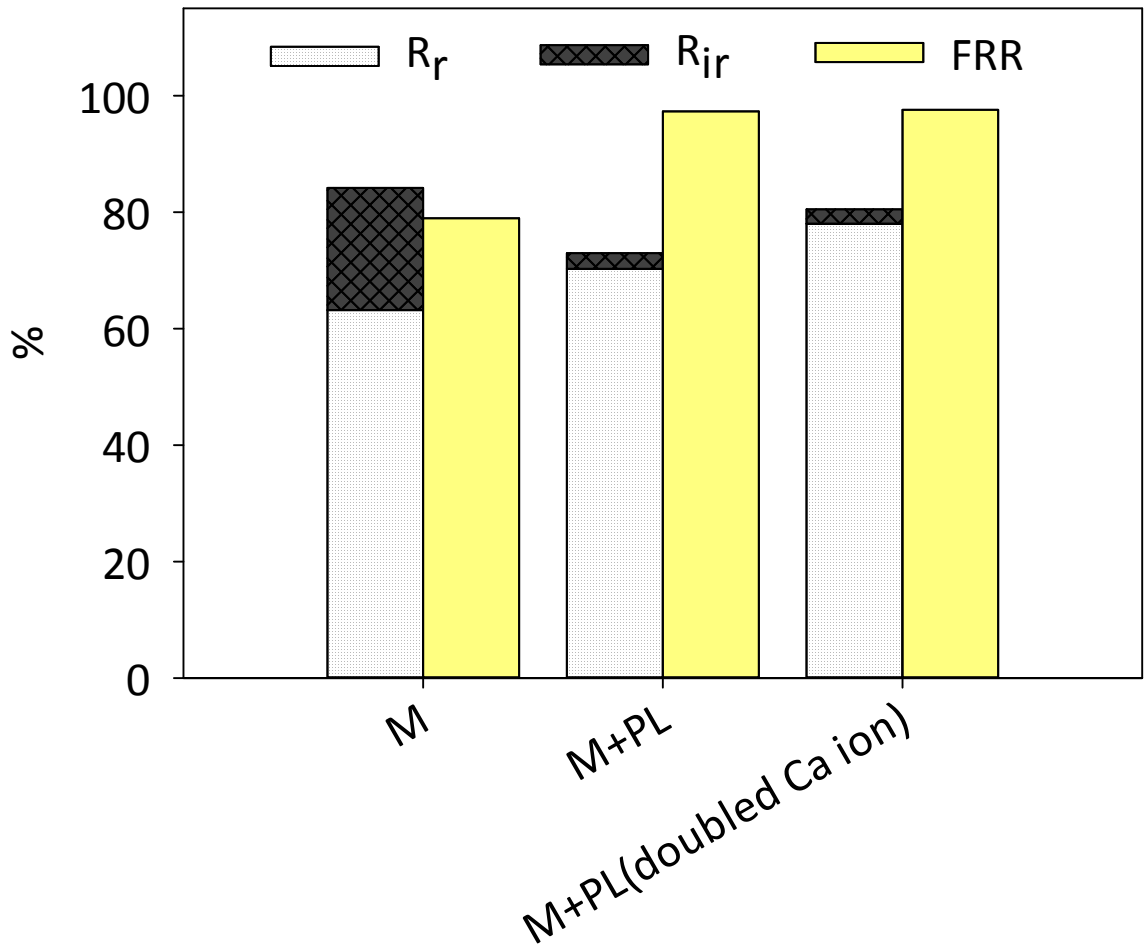

Figure S3 Effect of calcium ion in feed water on cleaning efficiency via bridge-effect. R_r: reversible fouling ratio, R_{ir}: irreversible fouling ratio, FRR: flux recovery ratio.

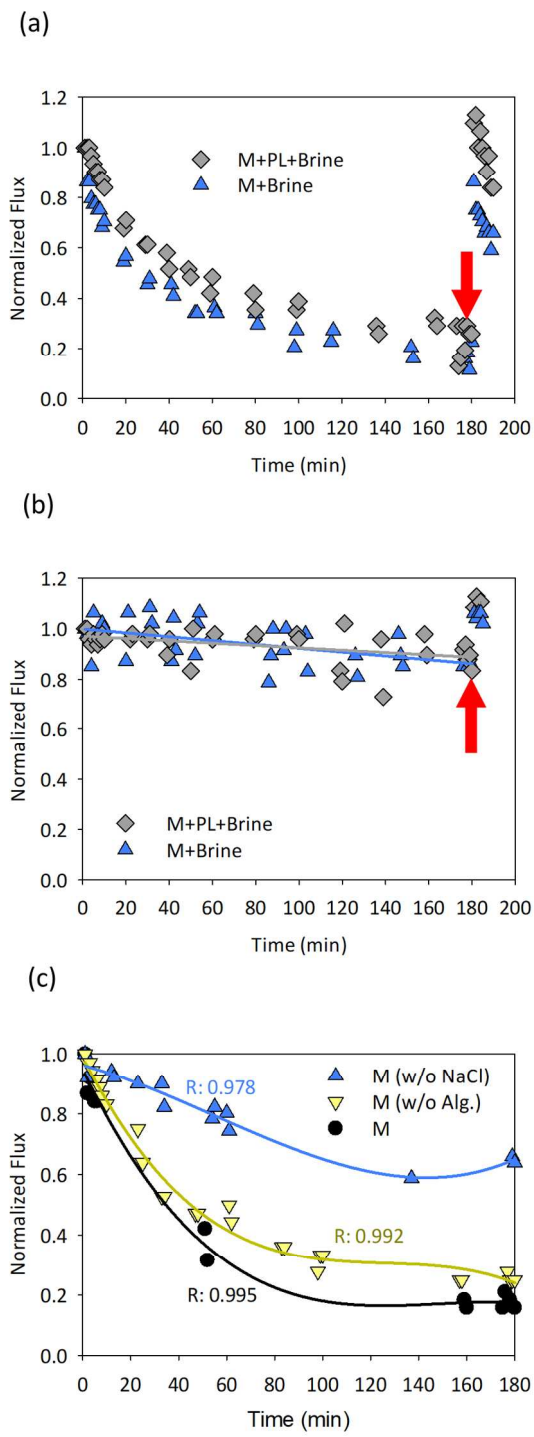

Figure S4 Effect of loosely bound fouling on water flux. Cleaning was done after each three hours of fouling (red arrows). (a) 20 ppm alginate was used instead of 200 ppm and (b) 60 rpm stirring was applied during fouling (other fouling conditions are same as (a)). (c) role of alginate and sodium chloride on flux decline over time (100 ppm Ca^{2+} ion was added for all cases).

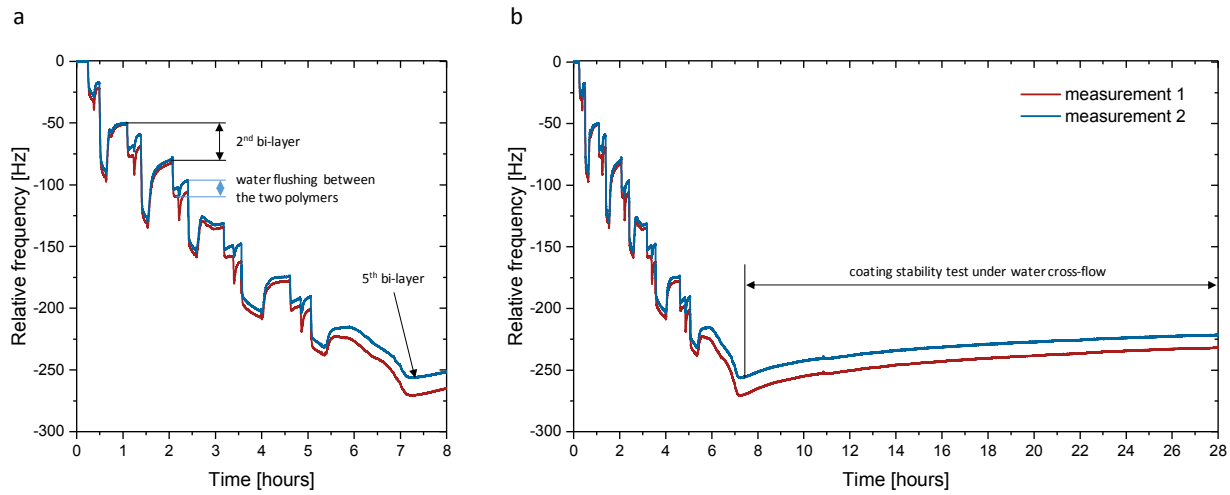

Figure S5 QCM-D measurements under cross-flow conditions ($6.1-6.4 \times 10^{-4}$ m/s) for (a) an RO membrane of with five bi-layers and (b) the coating stability over time. Each relative frequency decrease corresponds to deposition of the coating polyelectrolytes (PDDA, PSSA respectively) followed by a relative frequency increase indicating water flushing. Stable relative frequency shows that there is no attachment or detachment from the coated surface over time under cross-flow condition with DI water.

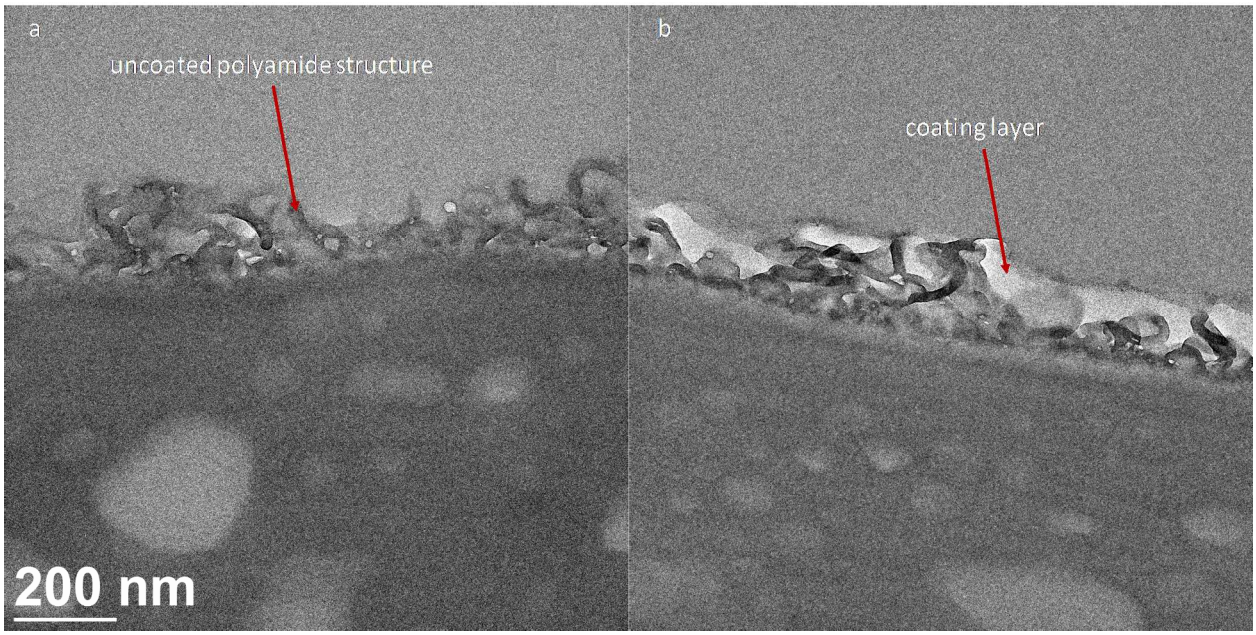

Figure S6 Transmission electron microscopy (TEM) images of the (a) pristine and (b) coated membranes. The coating was applied under 0.16 m/s cross-flow velocity in a membrane fouling simulator (MFS) with 34 mil (864 µm) feed spacer.