

Supporting Information

for

Exploring the limitations of osmotically assisted reverse osmosis (OARO) processes: Membrane fouling and the limiting flux

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S1 AQP and BW30LE reference case simulations

Figure S1 compares the experimental and numerical water flux of the AQP and BW30LE membranes under the reference case (RC) conditions. A good correlation between the numerical and experimental results exists, indicating that the used membrane properties (A, B, and S) can be adequately used to model the OARO processes. This numerical validation forms the basis for the results presented on the foulant resistance in Figure 5.

The simulation results presented in Figure S1 verify that the RC flux reduction over the 4-hour operational period is mainly caused by the increasing transmembrane osmotic pressure difference and thus the reduced effective driving force under a constant applied hydraulic pressure. The modelled AQP feed concentration is concentrated from 0.75M to 0.82M while the draw solution is diluted from 0.75M to 0.68M. In addition, the simulation of the AQP reference case shows that the OARO sweep solution contributes towards the overall water flux. This shows that at the given feed/draw concentrations and operating fluxes, the AQP membrane is truly operated in OARO mode. On the other hand, there is no difference between the OARO and RO predicted water flux for the BW30LE membrane due to its thicker support layer and larger S value.

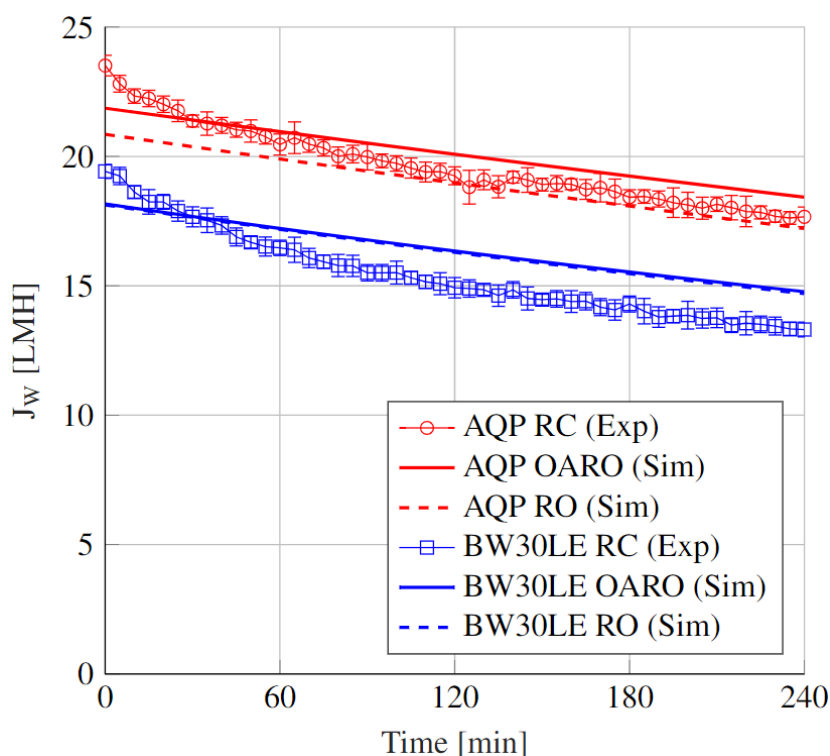


Figure S1: Comparison of the experimental and the simulated reference case results for the AQP (red) and BW30LE (blue) membranes at 50 bar and 40 bar, respectively. To show the influence of the sweep solution on the overall OARO water flux, the AQP and BW30LE membrane were also modelled in RO mode where no sweep solution is used.

S2 Plugged OARO draw spacer

As shown in Figure S2, Ca-Alg aggregates are entrapped within the 3D printed and the tricortype RO permeate carrier after the completion of the F3 fouling experiment.

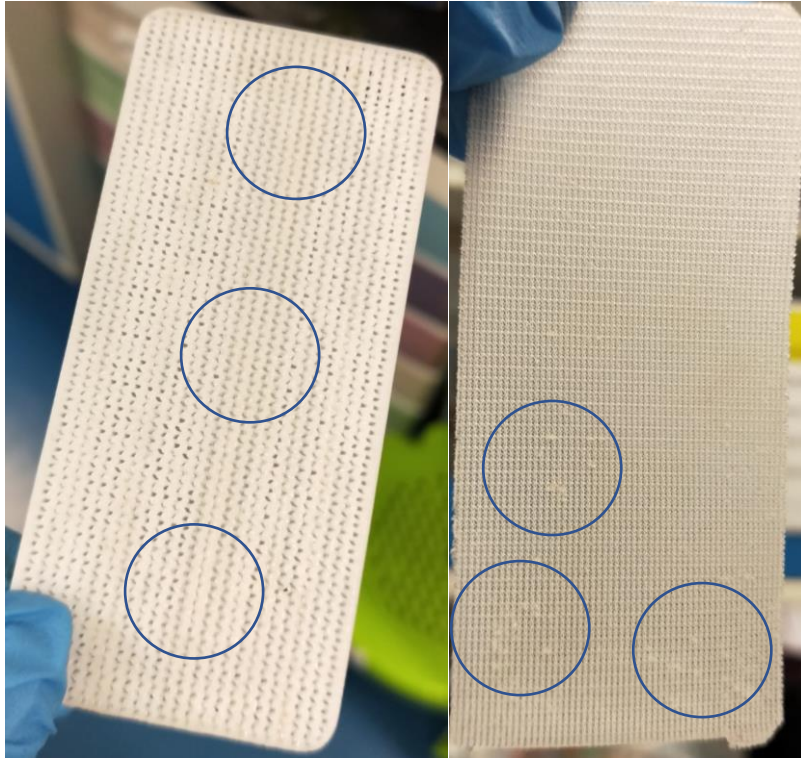


Figure S2: Plugged OARO draw spacer.

S3 The limiting flux

Operation at a higher water flux induces a greater hydrodynamic drag force F_{drag} on the foulants contained within feed towards the membrane surface; hence, foulant transportation, deposition and cake layer formation are accelerated at higher water flux J_W ^{1,2}. For small particles ($\ll 100\text{ nm}$), the lifting force and lateral migration by cross-flow can be ignored^{3,4} so that particle motion is solely described by Stokes law²:

$$F_{drag} = 6\pi\mu R_h J_W \quad (1)$$

where μ and R_h are the fluid viscosity and the characteristic hydrodynamic radius of the foulant². Foulant deposition and flux reduction continue as long as the drag force overpowers the barrier force $F_{Barrier}$, which opposes foulant deposition on the membrane surface (i.e. repulsion force between foulant and membrane ($F_{Barrier}^{f-m}$) and that between foulant and deposited foulant on the membrane ($F_{Barrier}^{f-f}$))^{4,5}. The membrane fouling rate and its reversibility greatly depend on the various foulant-membrane and foulant-foulant interactions and may include van der Waals forces, electrostatic interactions, hydration interactions and hydrogen bonds⁶. The flux stabilises once the hydrodynamic drag force reduces to levels approaching those of the barrier force²:

$$F_{Drag} = F_{Barrier} \quad (2)$$

Significant and irreversible foulant accumulation on a pristine membrane, and the associated flux reduction, are defined to occur once the water flux exceeds the so-called critical flux J_c ^{1,7,8}. In other words, the hydrodynamic drag force must exceed the barrier force offered by the membrane-foulant interactions $F_{Barrier}^{f-m}$ for fouling to occur. The critical flux is reached once:

$$F_{Drag} = F_{Barrier}^{f-m} \quad (3)$$

and is given by rearranging Equation (1) and Equation (3):

$$J_c = \frac{F_{Barrier}^{f-m}}{6\pi\mu R_h} \quad (4)$$

As stated by Tang et al.² and Bacchin⁹, pristine membranes are generally less repulsive towards foulants than their fouled counterparts, due to the stronger repulsive forces acting between the already deposited foulants and the approaching foulants:

$$F_{Barrier}^{f-m} < F_{Barrier}^{f-f} \quad (5)$$

In the case of severe membrane fouling, when the entire membrane surface is covered by a foulant cake layer, the barrier force solely depends on the interaction forces between the already deposited foulant and the approaching foulants. As defined by Tang et al. ², the so-called limiting flux is reached once:

$$F_{Drag} = F_{Barrier}^{f-f} \quad (6)$$

and is given by rearranging Equation (1) and Equation (6):

$$J_L = \frac{F_{Barrier}^{f-f}}{6\pi\mu R_h} \quad (7)$$

The electrostatic repulsion forces between the deposited foulants and the approaching foulants are strongly dependent on the feed solution chemistry (e.g. pH, ionic strength, and calcium concentration) and are at their minimum for neutral foulants ¹⁰. For example, it was observed that the $F_{Barrier}^{f-f}$ and hence the limiting flux were greatly reduced by enhanced humic acid and/or alginate fouling at lower pH operation or in the presence of higher divalent cation concentrations, due to the associated charge neutralisation of the organic foulants ^{2,11–13}. In this study the presence of high calcium ion concentrations in the feed water can explain the severe flux decline and low limiting flux that were observed in Section 3.1.

S4 The ICP self-compensation effect at different water fluxes

ICP is modelled in the osmotic resistance model using the dilutive concentration polarisation factor f_{DCP} for OARO membranes operated in AL-FS mode:

$$f_{DCP} = (1 - \exp(-J_w S/D)) \quad (8)$$

Hence, the ICP self-compensation effect is strongly dependent on the water flux J_w and the membrane's structural parameter S . Therefore, a change in f_{DCP} due to a change in J_w is given by:

$$\frac{df_{DCP}}{dJ_W} = \frac{S}{D} \exp(-J_W S/D) \quad (9)$$

A larger change in the gradient of f_{DCP} (represented by Equation (9)) represents a stronger ICP self-compensation effect, as a small change in J_W causes a larger response of the apparent driving force.

As shown in Figure S3 (a), the f_{DCP} factor rapidly approaches 1 for the BW30LE membrane due to its larger S-value. On the other hand, the increase of f_{DCP} for the AQP membrane is more gradual with J_W . The more rapid increase of f_{DCP} for the BW30LE membrane at lower operational water fluxes ($J_W \leq 4 \text{ LMH}$) means that in this range it has a stronger ICP self-compensation effect than the AQP membrane. This is verified by Figure S3 (b) where the gradient of f_{DCP} for the BW30LE membrane exceeds that of the AQP membrane. However, at higher operational water fluxes ($J_W > 4 \text{ LMH}$) the AQP membrane has a stronger ICP self-compensation effect, as the change in f_{DCP} with the water flux is greater (Figure S3 (b)).

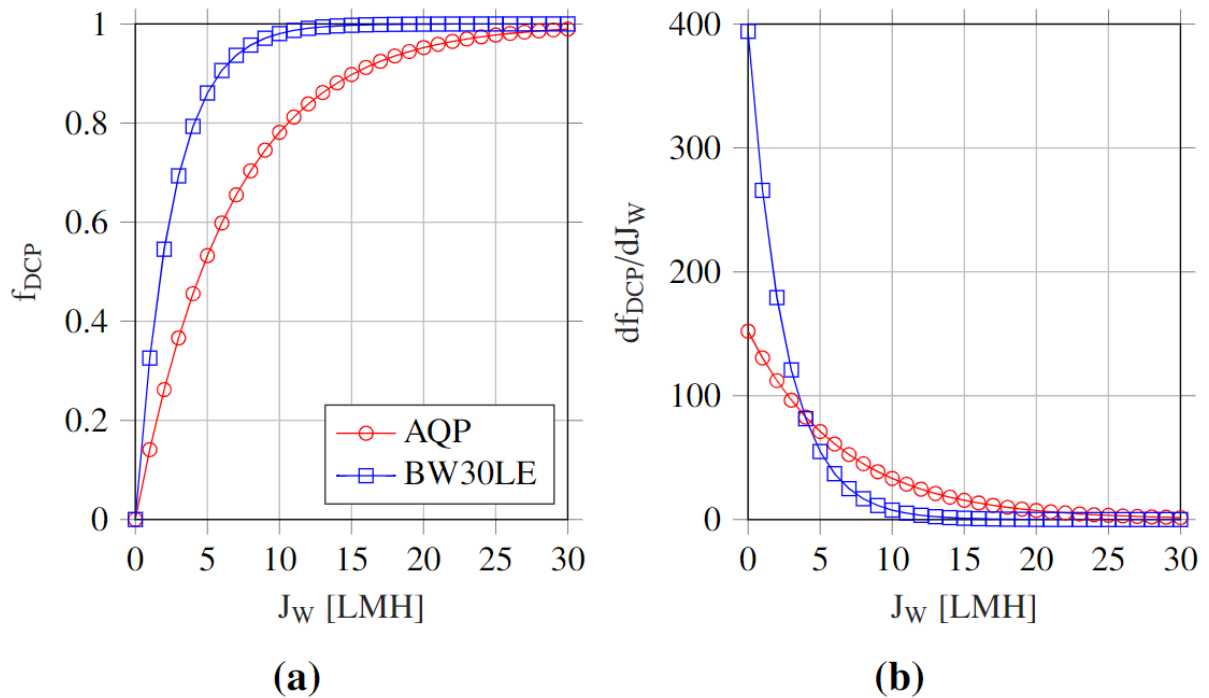


Figure S3: (a) The dilutive concentration polarisation factor f_{DCP} and (b) its derivative with respect to the water flux. The S-value of the AQP and BW30LE membrane are $810 \mu\text{m}$ and $2100 \mu\text{m}$, respectively.

S5 Foulant resistance at different operating pressures

Figure S4 visualises the dilutive concentration polarization factor, the effective driving force and the foulant resistance calculated using the experimental data presented in Section 3.2. and using the equations presented in Section 2.5. As the membrane properties slightly alter depending on the operational pressure¹⁴, different in A, B and S have been use in obtaining these results. The used A, B and S values of the AQP membrane are given in Table S1.

Table S1: A, B and S values of the AQP membrane at different operating pressures¹⁴

Operating Pressure	A [LMH/bar]	B [LMH]	S [μm]
30 bar	2.25	2.05	700
40 bar	2.20	1.75	800
50 bar	2.15	1.55	750
60 bar	2.10	1.35	650

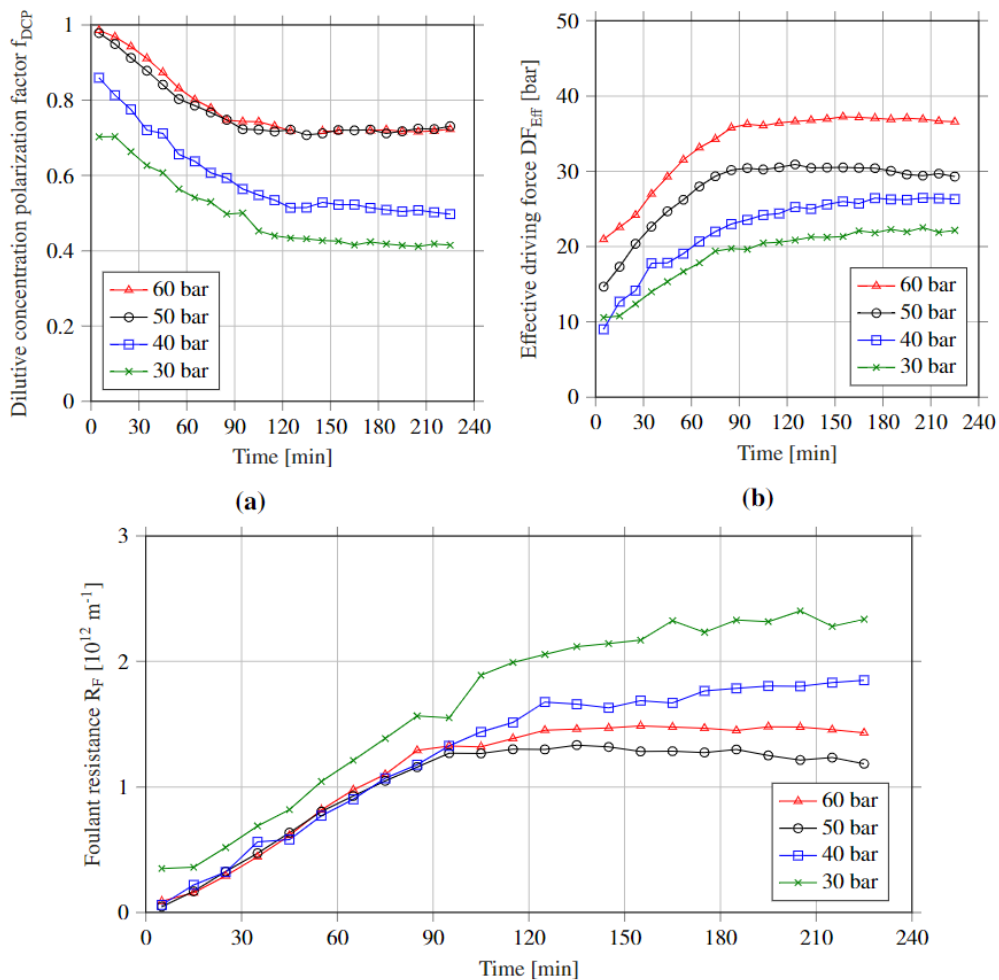


Figure S4: (a) Visualisation of the ICP self-compensation effect for the AQP membrane at different operating pressures using the change of f_{DCP} as indicator, (b) the change of the effective driving force with fouling progression, and (c) the calculated foulant resistance of the AQP membrane at different operating pressures during the F5 fouling scenario.

The presented findings show that f_{DCP} reduces significantly for the 40 bar and 30 bar cases while the same f_{DCP} value is reached for 50 bar and 60 bar cases. This reduction in f_{DCP} leads to a significant increase in the effective driving force due to lower ICP. Hence, the effective driving force of the 30 bar case increases by approximately 120% over the operational period whereas that of the 60 bar case increases only by 90% due to the ICP self-compensation effect. The greater increase in DF_{Eff} results in a higher foulant resistance when the operating pressure is lower due to the increased ICP self-compensation effect. This is an interesting finding and will be more systematically investigated in subsequent studies on OARO.

S6 Ideal OB of the AQP and BW30LE membrane

Figure S5 compares the efficacy of the ideal OB strategy for both the AQP and BW30LE membrane. As shown in the figure, the magnitude of the backwash water flux is significantly lower for the BW30LE membrane than for the AQP membrane, due to the larger S value (and thus more severe ICP) of the BW30LE membrane. Farooque et al.¹⁵ and Blandin et al.¹⁶ state that the feed solutes diffuse into the membrane's substrate during osmotic backwashing and hence, concentrative ICP in the membrane's thick substrate causes a severe flux decline during backwashing. This explains why the BW30LE membrane with the thicker substrate has the lower backwash flux. However, as shown in the figure, the initial water flux is fully recovered after each cleaning cycle for both membranes. While the water flux can be fully recovered for the alginate fouled BW30LE membrane, the flux recovery is uncertain for other organic foulants that may be present in other OARO feed solutions. During the fouling experiments, the BW30LE and AQP membrane do not reach the same final water flux after each fouling cycle. Therefore, it can be assumed that the fouling duration is not sufficiently long for both membranes to reach the limiting flux of approximately 9 LMH.

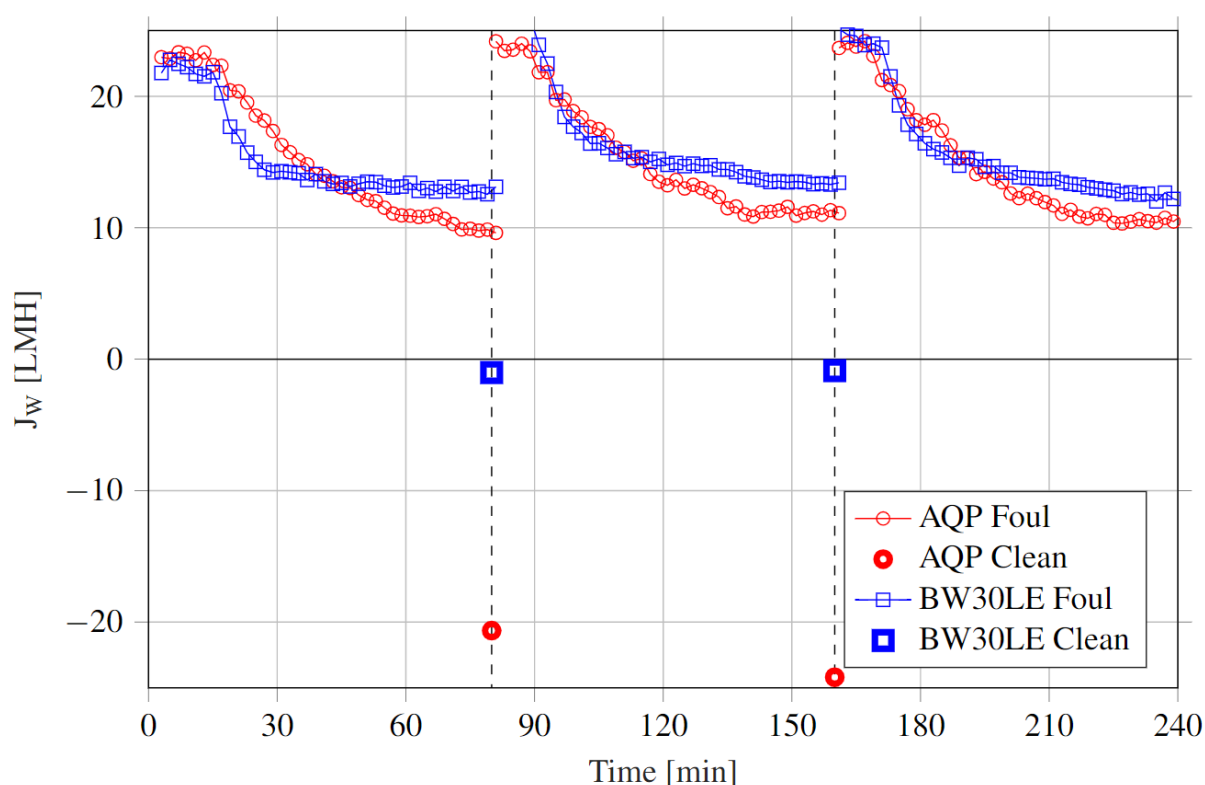


Figure S5: Comparing the effectiveness of the ideal OB cleaning strategy on the AQP and BW30LE membrane. The AQP membrane and BW30LE membrane are operated at 50 bar and 40 bar with a CFV of 10 cm/s during the fouling cycles. Each of the three fouling cycles lasted 80 min, to give a total fouling duration of 4 hours whereas each cleaning cycle lasted 10 minutes.

References

- (1) Bacchin, P.; Aimar, P.; Field, R. W. Critical and Sustainable Fluxes: Theory, Experiments and Applications. *J. Memb. Sci.* **2006**, 281 (1), 42–69. <https://doi.org/https://doi.org/10.1016/j.memsci.2006.04.014>.
- (2) Tang, C. Y.; Leckie, J. O. Membrane Independent Limiting Flux for RO and NF Membranes Fouled by Humic Acid. *Environ. Sci. Technol.* **2007**, 41 (13), 4767–4773. <https://doi.org/10.1021/es063105w>.
- (3) Zhu, X.; Elimelech, M. Colloidal Fouling of Reverse Osmosis Membranes: Measurements and Fouling Mechanisms. *Environ. Sci. Technol.* **1997**, 31 (12), 3654–3662. <https://doi.org/10.1021/es970400v>.
- (4) Song, L.; Elimelech, M. Particle Deposition onto a Permeable Surface in Laminar Flow. *J. Colloid Interface Sci.* **1995**, 173 (1), 165–180. <https://doi.org/10.1006/jcis.1995.1310>.
- (5) Belfort, G.; Davis, R. H.; Zydney, A. L. The Behavior of Suspensions and Macromolecular Solutions in Crossflow Microfiltration. *Journal of Membrane Science*. Elsevier November 28, 1994, pp 1–58. [https://doi.org/10.1016/0376-7388\(94\)00119-7](https://doi.org/10.1016/0376-7388(94)00119-7).
- (6) Lee, S.; Kim, S.; Cho, J.; Hoek, E. M. V. Natural Organic Matter Fouling Due to Foulant-Membrane Physicochemical Interactions. *Desalination* **2007**, 202 (1–3), 377–384. <https://doi.org/10.1016/j.desal.2005.12.077>.

- (7) *Osmotically Driven Membrane Processes*; Du, H., Thompson, A., Wang, X., Eds.; IntechOpen, 2018. <https://doi.org/10.5772/intechopen.68607>.
- (8) Nguyen, T.-T.; Kook, S.; Lee, C.; Field, R. W.; Kim, I. S. Critical Flux-Based Membrane Fouling Control of Forward Osmosis: Behavior, Sustainability, and Reversibility. *J. Memb. Sci.* **2019**, 570–571, 380–393. <https://doi.org/https://doi.org/10.1016/j.memsci.2018.10.062>.
- (9) Bacchin, P. A Possible Link between Critical and Limiting Flux for Colloidal Systems: Consideration of Critical Deposit Formation along a Membrane. In *Journal of Membrane Science*; Elsevier, 2004; Vol. 228, pp 237–241. <https://doi.org/10.1016/j.memsci.2003.10.012>.
- (10) Tang, C. Y.; Kwon, Y. N.; Leckie, J. O. Effect of Membrane Chemistry and Coating Layer on Physiochemical Properties of Thin Film Composite Polyamide RO and NF Membranes. II. Membrane Physiochemical Properties and Their Dependence on Polyamide and Coating Layers. *Desalination* **2009**, 242 (1–3), 168–182. <https://doi.org/10.1016/j.desal.2008.04.004>.
- (11) She, Q.; Wong, Y. K. W.; Zhao, S.; Tang, C. Y. Organic Fouling in Pressure Retarded Osmosis: Experiments, Mechanisms and Implications. *J. Memb. Sci.* **2013**, 428, 181–189. <https://doi.org/10.1016/j.memsci.2012.10.045>.
- (12) Hong, S.; Elimelech, M. Chemical and Physical Aspects of Natural Organic Matter (NOM) Fouling of Nanofiltration Membranes. *J. Memb. Sci.* **1997**, 132 (2), 159–181. [https://doi.org/10.1016/S0376-7388\(97\)00060-4](https://doi.org/10.1016/S0376-7388(97)00060-4).
- (13) Tang, C. Y.; Kwon, Y. N.; Leckie, J. O. Fouling of Reverse Osmosis and Nanofiltration Membranes by Humic Acid-Effects of Solution Composition and Hydrodynamic Conditions. *J. Memb. Sci.* **2007**, 290 (1–2), 86–94. <https://doi.org/10.1016/j.memsci.2006.12.017>.
- (14) Peters, C. D.; Ng, D. Y. F.; Hankins, N. P.; She, Q. A Novel Method for the Accurate Characterization of Transport and Structural Parameters of Deformable Membranes Utilized in Pressure- and Osmotically Driven Membrane Processes. *J. Memb. Sci.* **2021**, 638, 119720. <https://doi.org/10.1016/J.MEMSCI.2021.119720>.
- (15) Farooque, A. M.; Al-Jeshi, S.; Saeed, M. O.; Alreweli, A. Inefficacy of Osmotic Backwash Induced by Sodium Chloride Salt Solution in Controlling SWRO Membrane Fouling. *Appl. Water Sci.* **2014**, 4 (4), 407–424. <https://doi.org/10.1007/s13201-014-0158-x>.
- (16) Blandin, G.; Verliefde, A. R. D.; Le-Clech, P. Pressure Enhanced Fouling and Adapted Anti-Fouling Strategy in Pressure Assisted Osmosis (PAO). *J. Memb. Sci.* **2015**, 493, 557–567. <https://doi.org/10.1016/j.memsci.2015.07.014>.