Reverse osmosis at the nanoscale: investigating desalination membranes using classical molecular dynamics

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Desalination and molecular dynamics

- Scarcity of drinking water is a significant issue in Canada and abroad- and reverse osmosis technology has played a significant role in combating it.

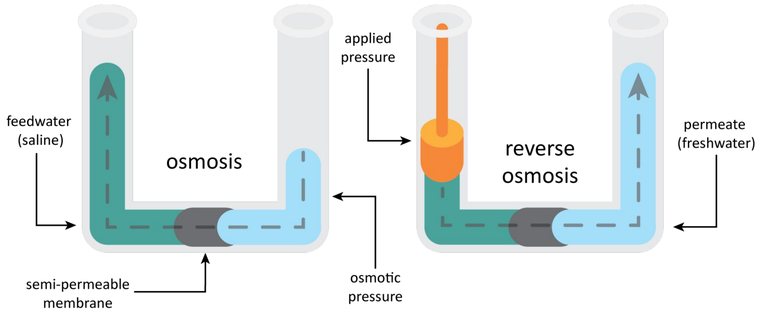
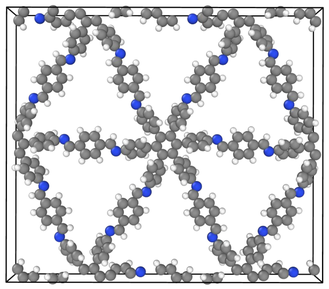


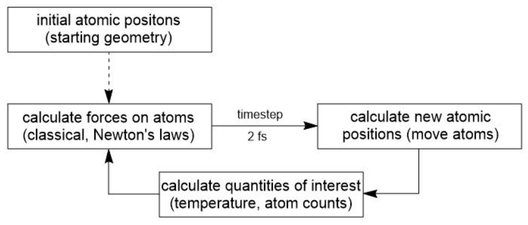
Fig. 1. Contrasting osmosis and reverse osmosis.



- Covalent organic frameworks are of interest as materials for desalination because of their high stability, crystallinity, and controllable porosity.

Fig. 2. A monolayer membrane of the COF investigated in this work, HPB-COF.

- Molecular dynamics (quantum and classical) is a useful method for investigating the time-evolution of a chemical system; here it is applied to investigate water desalination using COF based membranes.



Goals

- Build a classical molecular dynamics model to simulate reverse osmosis desalination
- Evaluate stability of simulation, and predict quantities of importance in desalination, such as salt rejection or water flux
- Use the simulations results to identify potential improvements to the model

Software used

- Classical molecular dynamics calculations were performed using LAMMPS.
- Periodic density functional theory calculations (geometry/cell optimization, valence density) were performed in CP2K with the PBE0 hybrid functional and TZVP-MOLOPT basis sets.
- Partial charges were assigned to membrane atoms using the density-derived electrostatic and chemical method with Chargemol.

Building the simulation

- The simulation box (4.2 x 3.7 x 30 nm) comprises a COF membrane, saline and freshwater regions on opposite sides of the membrane, and two graphene pistons at the system's edge. Different reverse-osmotic pressure gradients will be applied using the graphene pistons.

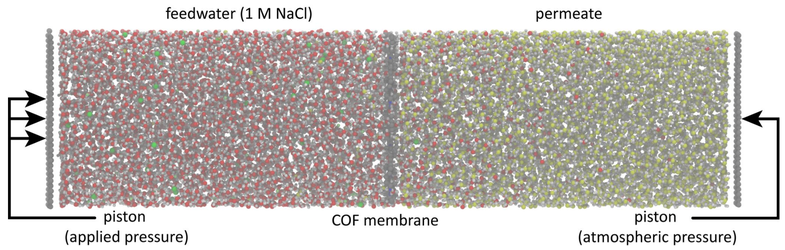
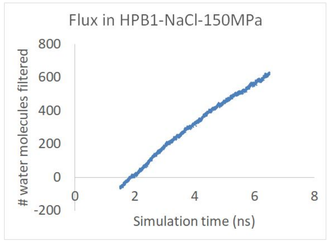


Fig. 3. A typical simulation architecture used in this work. The oxygen atoms of feedwater are red, and the oxygen atoms of initial freshwater are yellow.

- The simulation box (4.2 x 3.7 x 30 nm) comprises a COF membrane, saline and freshwater regions on opposite sides of the membrane, and two graphene pistons at the system's edge. Different reverse-osmotic pressure gradients will be applied using the graphene pistons.
- Simulations are heated (NVT ensemble) at 350 K for 1 ns, equilibrated (NVT) for 2 ns, and subject to a pressure gradient (100-200 MPa) for 10 ns.
- Different salts (NaCl) and number of membrane layers (HPB1, HPB2, HPB3) are used.

Running the simulation



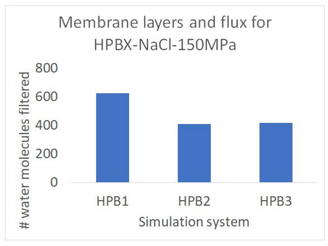
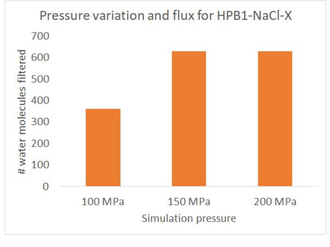


Fig. 4. Investigation of flux in multi-layered membranes: HPB1, HPB2 and HPB3. Linear flux is observed.

- Flux with respect to time is linear, which is what the system should produce.
- Interestingly, HPB2 and HPB3 have identical fluxes- suggesting that there may effectively only one energetic barrier to overcome.



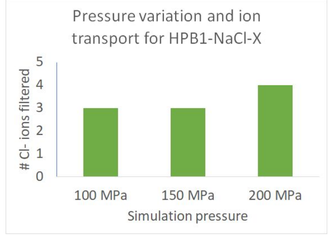
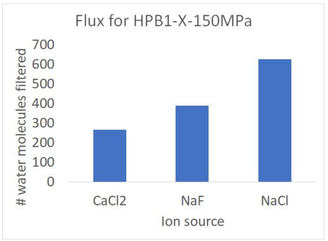


Fig. 5. Flux and salt rejection with varying pressure. Complete rejection of sodium. Out of 95 chloride ions in solution, only a maximum of four are transported through the membrane.

- The HPB1 system appears to reach a maximum flux somewhere between 150 and 200 MPa. The system appears to have effective salt rejection, but more sampling is required.



- Different ion sources appear to affect the water flux considerably.
- For both $CaCl_2$ (0.5 M) and NaF (1 M), complete salt rejection is observed.

Fig. 6. Calculated water flux comparison for different salt solutions.

Conclusions

- We have successfully designed and analyzed a classical molecular dynamics model of reverse osmosis desalination.
- The model successfully predicts flux quantities, allowing for the investigation of systems containing different ions, and having different membrane thicknesses.
- The model predicts similar flux values for two-layer and three-layer membranes, suggesting the primary energetic hurdle is crossing the second membrane.
- Ion transport (salt rejection) quantities are predicted by the model, but a more concentrated solution may increase the number of ion-pore interactions and better sample ion transport.

Future work

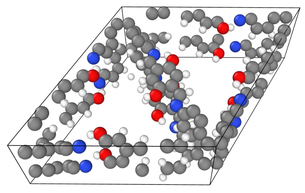


Fig. 7. Optimized unit cell of HPB-OH, Functionalized with hydroxyl groups.

- Additional membrane layer calculations are being performed to better understand the transition from membrane monolayers to bulk membrane.
- Functional modifications will be made to the HPB membrane to study the effect of hydrophilic/hydrophobic groups on reverse osmosis desalination.

References and acknowledgments

This research was supported by the Jamie Cassels Undergraduate Research Awards, University of Victoria; Supervised by Dr. Heather Buckley (Civil Engineering). Poster produced Mar 10, 2024.

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