Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2015.1112982

57 (2016) 20169–20176
September

Taylor & Francis
Taylor & Francis Group

Molecular dynamics simulation of seawater reverse osmosis desalination using carbon nanotube membranes

Young Mi Kim[a], Hannah Ebro[a], Joon Ha Kim[a,b,c,*]

[a]*School of Environmental Science and Engineering, Gwangju Institute of Science and Technology (GIST), Gwangju 500-712, Korea*
[b]*Center for Seawater Desalination Plant, Gwangju Institute of Science and Technology (GIST), Gwangju 500-712, Korea*
[c]*Sustainable Water Resource Technology Center, Gwangju Institute of Science and Technology (GIST), Gwangju 500-712, Korea, email: joonkim@gist.ac.kr*

Received 5 August 2015; Accepted 8 October 2015

ABSTRACT

Reverse osmosis (RO) desalination of 35,000 ppm seawater consisting of sodium and chlorine ions with water was simulated using molecular dynamics. In this study, RO simulations were performed at different pressures using carbon nanotube (CNT) membranes having varying pore diameters (8–14 Å). Results showed that a CNT membrane allowed high water fluxes because of the presence of a low energy barrier for water–carbon interactions, with continuous and ordered water chains observed inside the CNTs. The investigations into the ion rejection capability of CNT membranes revealed that (6, 6) CNTs could provide high rejection rates (>95%). The rejection of ions was mainly due to the presence of a high energy barrier caused by removing the hydrating water molecules necessary for ions to pass through the narrow CNT pore. The desalination performance of (6, 6) CNT membranes and conventional polymeric membranes was then compared. It was found that CNT membranes have a higher normalized flux and comparable ion rejection, indicating their feasibility for effective seawater desalination. Overall, this study demonstrated the usefulness of molecular dynamics in investigating membrane processes and its potential role in improving desalination performance.

Keywords: Molecular dynamics; Reverse osmosis; Desalination; Water treatment; Carbon nanotube

1. Introduction

Seawater desalination has been highly regarded as one solution to the growing problem of water stress. Among technologies now being used to purify seawater, reverse osmosis (RO) is a popular choice because of its high efficiency and lesser energy consumption and cost compared to thermal techniques [1]. However, despite continuous research and development, seawater reverse osmosis (SWRO) processes using current polyamide membranes still have limitations in terms of both water production and resistance to fouling.

Because of the increasing availability of computers having a high computational power, new types of SWRO membranes based on graphite and nanomaterials, which can improve desalination, are being studied using molecular dynamics simulations. For example, RO through boron nitride nanotubes and carbon nanotubes (CNTs) was simulated, and the performance of both nanotubes exceeded that of a polymeric

---

*Corresponding author.

membrane made of polymethyl methacrylate (PMMA) [2]. Corry [3] also investigated the transport of water and ions through CNTs and found that CNTs would be efficient for desalination. In another study, the desalination potential of carbon and silicon-carbide (SiC) nanotubes was compared using molecular dynamics [4].

To the best of the knowledge of the authors, other than Refs. [2–4], there have been few studies published to date that specifically investigate the RO of a salt solution through CNTs using molecular dynamics. In this study, molecular dynamics simulations of RO through model CNT membranes were performed in order to validate the desalination capability of CNT membranes and also to supplement existing studies. The desalination performance of CNT membranes having various diameters was simulated and compared to that of a conventional polymeric membrane used in lab- and pilot-scale experiments. Ultimately, it is hoped that this preliminary study would encourage more investigations that would lead to the prompt and actual use of CNTs as future desalination membranes.

2. Simulation details

Molecular dynamics is a step-by-step computational technique that uses the concept of Newton's second law of motion to observe the physical movement of atoms of a system and then predict properties for the system [5]. Molecular dynamics is an interdisciplinary research field that can calculate various properties by combining theories from mathematics, chemistry, physics, and computer science so as to shed light on more practical sciences, including material science, biology, environmental science, nanotechnology, and membrane science [6].

In this study, all molecular dynamics simulations were performed using LAMMPS [7]. The initial arrangement of the simulated system is shown in Fig. 1. The system consisted of a CNT membrane (graphene sheets and CNT), two water chambers (pure water (PW) and seawater (SW) chambers), and two graphene sheets that were used to control the hydrostatic pressure. Five armchair-type CNTs of different diameters (8–14 Å) were used: (6, 6), (7, 7), (8, 8), (9, 9), and (10, 10). Parameters used for the uncharged sp^2-hybridized carbon atoms, which were used to build the CNT and graphene sheets, were obtained from those employed in a previous study [8]. Water was modeled using the TIP3P model [9], while parameters for sodium and chloride ions were obtained from Joung and Cheatham [10]. The NaCl concentration of the SW chamber was approximately 35,000 ppm, similar to the concentration of typical seawater. Pairwise interactions were then calculated based on the standard 12/6 Lennard-Jones potential with an additional Coulombic term. Lorentz-Berthelot mixing rules [11,12] were used to calculate the interactions of non-identical atom pairs; calculations were performed using the standard velocity-Verlet integrator.

For all simulations, a 2 fs time step was used and the temperature was maintained at 298.15 K. During the 600 ps equilibration, the SW and PW chambers were separately equilibrated and not allowed to mix, i.e. plugs were present to block the openings of the CNT pores. During the production runs, the membrane plugs were removed and pressure was applied to the particles of the SW chamber to push them against the CNT membrane. The effect of pressure was investigated using six different values for RO pressure: 5,000, 7,500, 10,000, 12,500, 25,000, and 37,500 bar. Ultra-high pressures (i.e. very high compared to normal RO pressures) were used in this study in order to more easily observe the permeation events, given the limited time scale of the molecular dynamics simulations.

3. Results and discussion

3.1. Water transport in CNT membrane

Water flow profiles were obtained from the molecular dynamics simulations. In Fig. 2(a), as the CNT diameter was increased, the total water that permeated the CNT membrane also increased as more "water chains" were accommodated by larger pores (Fig. 2(c)). This increase was attributed to the lower energy barrier to water flow for bigger CNTs, as observed during RO simulations through (5, 5) to (8, 8) CNTs [3]. The effect of pressure on water flow through (6, 6) CNTs was also investigated; Fig. 2(b) shows that a higher pressure resulted in the transfer of more water molecules to the PW chamber within a shorter time.

From the slope of the water profiles, the water flux was obtained and plotted against the pressure and pore radius. In Fig. 3(a), it can be seen that the simulated water flux varied linearly with pressure, similar to the results of previous studies [2,3,13,14], and as predicted from the Hagen–Poiseuille (HP) equation (Eq. (1)). However, the molecular dynamics fluxes were exceptionally high compared to those predicted by the HP equation, which is rooted in the concept of classical fluid mechanics.

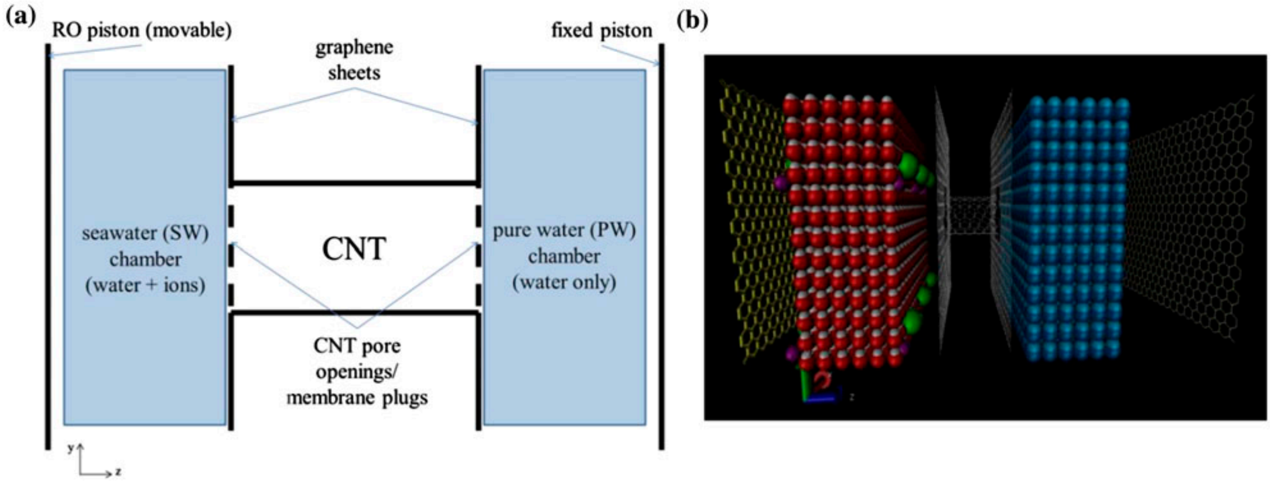

Fig. 1. Components of the system used in this study, shown as (a) a schematic diagram and (b) a snapshot of the system at t = 0 ps (rendered using visual molecular dynamics (VMD) software).

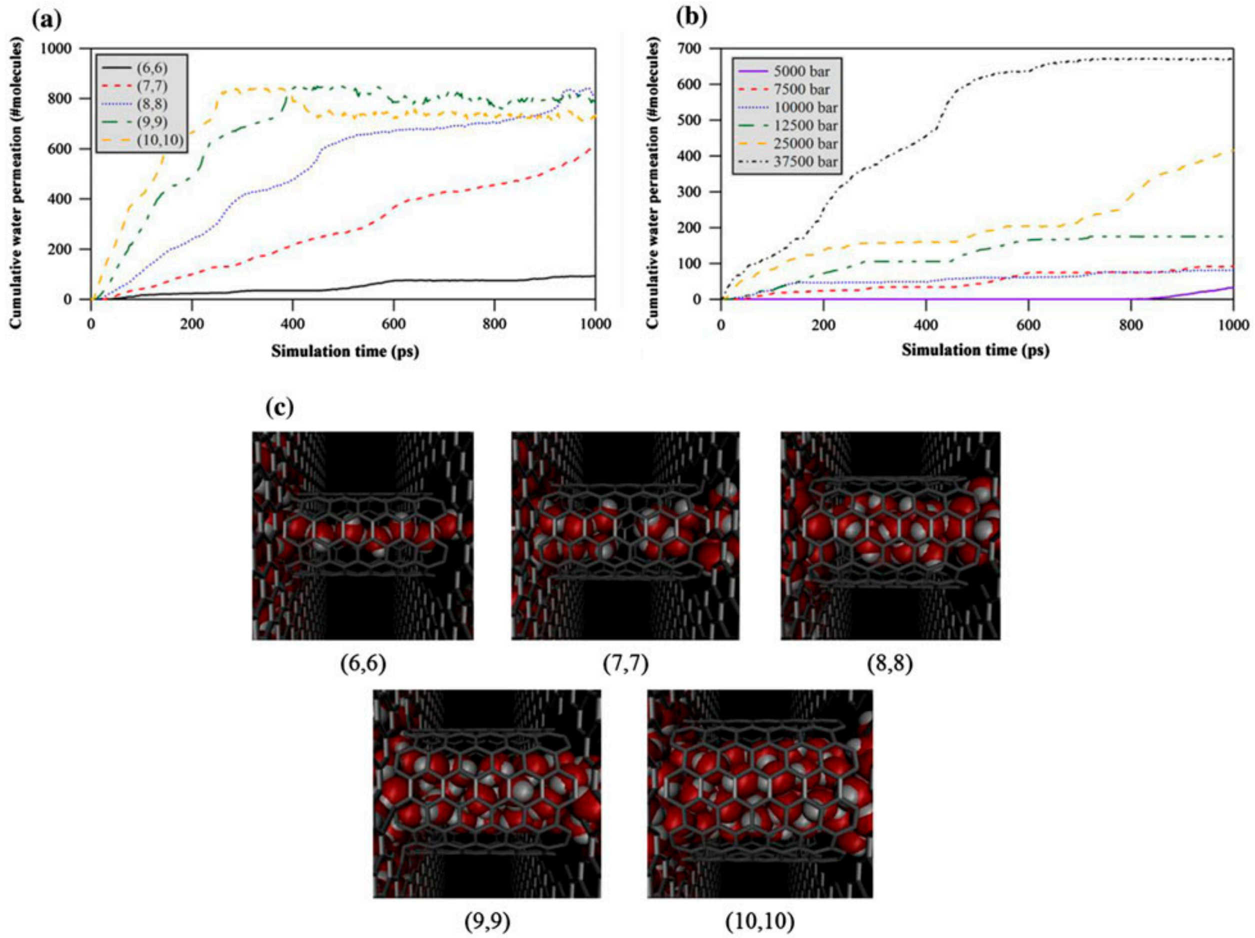

Fig. 2. Water flow profiles through (a) CNT membranes of varying diameters (pressure: 7,500 bar), (b) through a (6, 6) CNT membrane at varying operating pressures, and (c) simulation snapshot of water permeating the CNT pore (rendered using VMD software).

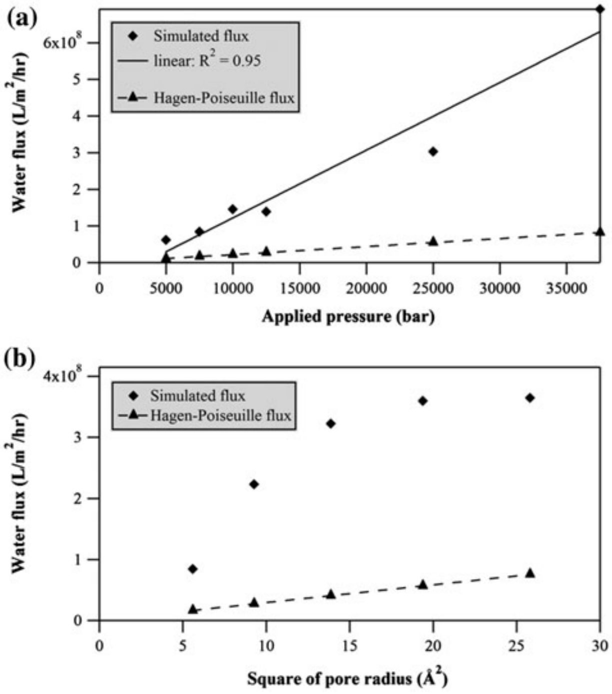

Fig. 3. Theoretical and simulated water flux as a function of (a) pressure and (b) CNT pore size.

$$J_w = L_p\Delta P = \frac{r_p^2}{8\eta\left(\frac{L_z}{A_k}\right)}\Delta P \tag{1}$$

In this study, the simulated membrane consisted of a single straight pore represented by the carbon nanotube, which has a defined effective radius r_p and length L_z. In Eq. (1), J_w is the water flux, L_p is the water permeability coefficient, ΔP is the hydrostatic pressure difference, η is the viscosity of water, and A_k is the membrane porosity. One of the assumptions of the HP equation is that there is a no-slip condition at the walls of a straight cylindrical tube when a real fluid flows through it [15]. However, it was found that the velocity inside the wall of the CNT pore was not zero because of the presence of weak interactions between carbon and water [14]; thus, this no-slip condition does not hold in the case of water flowing through a narrow CNT membrane. Moreover, high water flux through CNT could also be explained by the smoothness (almost frictionless) of the CNT interior surface and by the narrowness of the pore diameter [13,14,16]. These observations indicate that water flow through CNT is not governed by classical laws of fluid mechanics, but a separate area known as “nanofluidics” [17]. This is also supported by the non-linear relation observed between the flux and the square of the pore radius (Fig. 3(b)), which is similar to a previous study [18] and which contradicts the prediction of Eq. (1).

Through molecular dynamics simulations, it was shown that CNTs have the potential to be used as desalination membranes because they allow a high water flux even though CNTs are hydrophobic in nature. In fact, this hydrophobicity even contributes to the high speed of water transport through CNTs [13,17]. In a previous study, the potential of the mean force (PMF) profile along the water passage showed that the energy barrier at the pore entrance was $5.273\,k_BT$, whereas inside the CNT it was $0.47\,k_BT$ [2]. This indicates that as long as the water molecules can overcome the barrier at the entrance, they will have no problem passing through the CNT pore. The fast transport of water through CNTs can be attributed to several factors (e.g. presence of low energy barrier, smoothness of CNT walls, etc.), and to the fact that the CNT membrane system is a nanofluidic system that is not governed by laws of fluid mechanics, particularly by the Hagen–Poiseuille relation.

3.2. *Ion transport in CNT membrane*

The salt rejection capability of a CNT membrane was investigated by counting the number of ions that passed through the CNT pore during the simulation. Fig. 4 shows the effect of CNT size and applied pressure on ion rejection; rejection decreases when either the diameter of the CNT pore or the hydrostatic pressure is increased. The effective radii of all model CNTs were bigger than the VdW radii of sodium ions (1.02 Å) and chloride ions (1.81 Å) [19], indicating that rejection by the CNT membrane was not directly related to size exclusion. Salt ions were rejected because of the steric hindrance and a large energy barrier at the entrance of the CNT pore [2]. In other words, there will be an energy cost when they are brought close to each other because of the overlapping of electron clouds in the confined space. Hence, in the case of water flowing inside narrow CNT pores, these steric effects are important. However, steric effects, in this case, are not as important as the effect of energy barriers, as explained below.

As the pore radius was increased, the water structure inside the nanotube began to influence ion rejection. As seen in Fig. 2(c), in a (6, 6) CNT, water molecules traverse inside the nanotubes in single file, whereas for bigger armchair nanotubes water molecules are arranged in two or more water chains. This fact affects ion rejection because of the way the ions are hydrated inside the CNTs. When salt dissociates

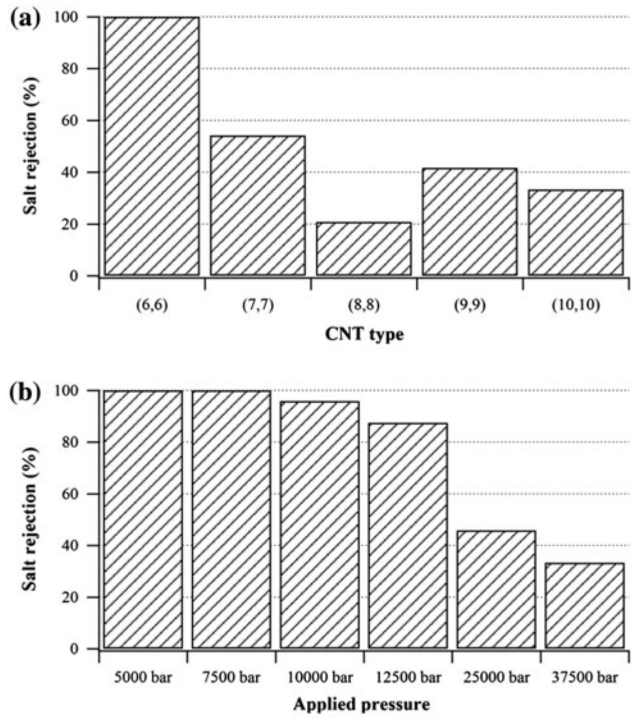

Fig. 4. Ion rejection as a consequence of (a) CNT diameter and (b) applied pressure.

in water, the ions become hydrated and water molecules surround them and become "attached" to them. However, because the CNT pores were narrow, ions passing through the channel were forced to separate from the water molecules that hydrate them. This separation requires a large amount of energy in order to be accomplished; this is also known as the cost of dehydration [20]. Hence, it was observed that RO performed at higher pressures reduced the ion rejection rate because there was a larger force applied on the ions to overcome the energy barrier due to dehydration. Moreover, in the case of comparing the rejection of different CNT sizes, it was seen that larger CNTs have lower rejection capabilities because they can allow ions to pass through with many of the hydrating water molecules still attached to them, resulting in a lower energy barrier. For sodium ions, the typical hydration number was found to be 3–4 [21], while it was around 6 for chloride ions [22]. Fig. 5 shows that a sodium and chloride ion entering a (6, 6) CNT was hydrated by only two or three water molecules, whereas inside (7, 7) to (10, 10) CNTs, two or more spiral water chains were present, which subsequently allows ions to be hydrated closer to the hydration conformation in a bulk solution.

3.3. Desalination potential: CNT membrane vs. polymeric RO membrane

To demonstrate the feasibility of using CNTs as a promising membrane material for desalination, it must first be compared with a standard polymeric RO membrane that is used for SWRO membrane desalination. Lab experiments were conducted using a cross-flow membrane filtration test unit (SEPA CF, Osmonics, Inc., USA) at a constant temperature of 25˚C. An RE8040-SHN400 RO membrane (Woongjin Chemical Co., Ltd, Korea) having an effective membrane area of 140 cm^2 was used for all lab experiments. Seawater solution, consisting of NaCl crystals dissolved in deionized water, had a concentration of 35,000 ppm. RO was performed by subjecting the seawater solution to a constant pressure of 55 bar. For the pilot-plant experiments, a seawater solution of 35,000 ppm concentration was used. Using a FILMTEC SW30-4040 membrane (Dow Chemical Company, USA), RO experiments were conducted at 25˚C using two RO modules having a total effective area of 14.8 m^2. The permeate flow rate and concentration data for both lab and pilot SWRO experiments were subsequently recorded.

The desalination capabilities of the conventional polymeric membranes and CNT membranes are compared in Fig. 6. To compare the water production capacity of the two membranes, the study obtained the normalized flux values from both simulations and experiments. In this study, the normalized flux instead of the standard water flux was selected as the basis of the comparison for water production capacity, as the RO experiments and CNT simulations were performed under different pressures. It was found that the CNT membrane could enable a water flux that is 3–4 orders of magnitude higher than the flux allowed by conventional polymeric RO membranes.

Ion rejection of polymeric membranes during lab and pilot experiments were high, with averages of 99.82 and 98.20%, respectively. Among the model CNT membranes, only the (6, 6) membranes were able to achieve salt rejection comparable to polymeric membranes. In the best case, the ion rejection of the (6, 6) CNT membranes subjected to applied pressures of 5,000 and 7,500 bar was 100%. Rejection for the (6, 6) membrane during RO simulation at applied pressures of 10,000 and 12,500 bar was also quite high, at 95 and 87.5%, respectively. Even though the simulations were conducted at very high pressures, however, it follows that decreasing the pressure down to typical RO operating pressures would maintain the ability of (6, 6) CNT membranes to reject 100% of the ions.

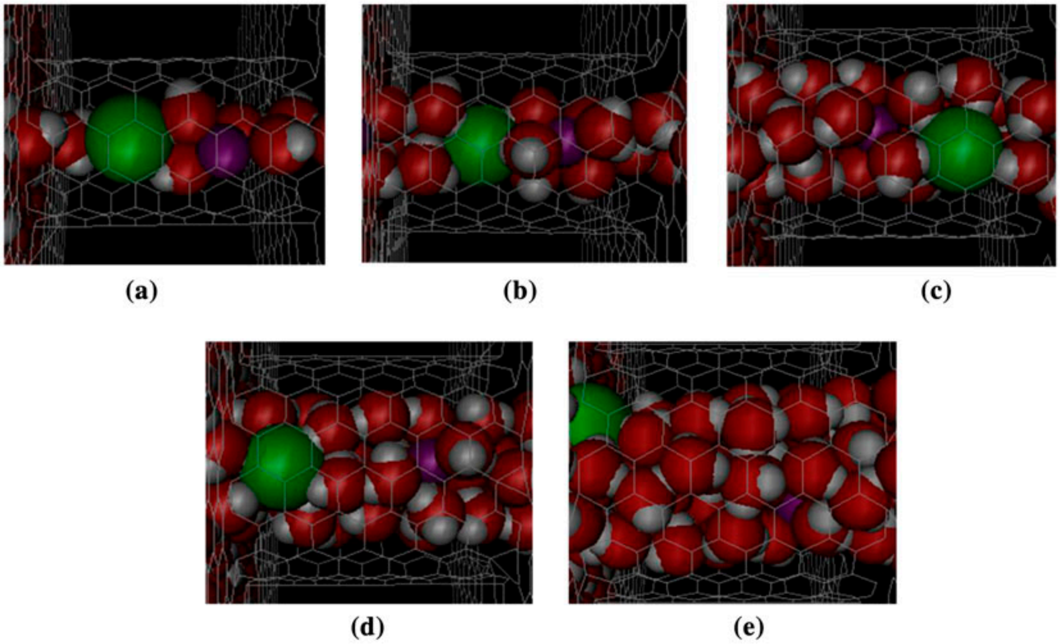

Fig. 5. Snapshots of ion permeation during different simulations used to visualize the typical coordination numbers of sodium (purple) and chlorine (green) ions with hydrating water molecules (red/white) inside the CNT pore: (a) (6, 6) CNT, 25000 bar, (b) (7, 7) CNT 7500 bar, (c) (8, 8) CNT, 7500 bar, (d) (9, 9) CNT, 7500 bar, and (e) (10, 10) CNT, 7500 bar.

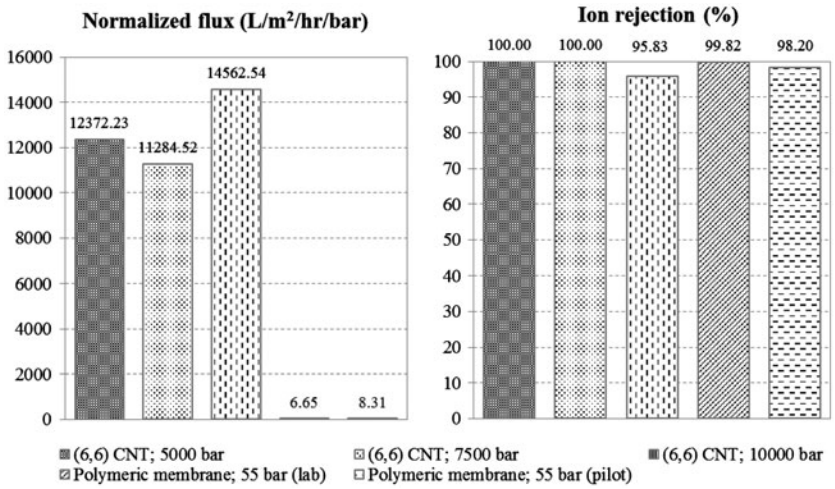

Fig. 6. Comparison of ion rejection, normalized flux, and price per effective membrane area of (6, 6) CNT membrane and conventional polymeric membranes.

The difference between the ability to desalinate effectively is dictated by the mechanism of water and ion transport inside the polyamide and CNT membranes. It could be recalled that water, in contrast to ions, can easily pass through the CNT membrane because there is a lower energy barrier to water flow compared to ion conductance. Of the two models for membrane transport during RO, transport through the CNT is closer to the pore flow model because the CNT membrane can be considered a porous membrane having small nanopores [23]. On the other hand, in a conventional polymeric RO membrane, the transport mechanism depends on the solubility; the mode of transport in a polyamide RO membrane is dictated by the solution–diffusion model [24]. A previous atomistic simulation of an FT-30 RO membrane showed that the transport of water and ion through a polyamide membrane was affected by the difference in the mobilities of water and ions through the membrane [25]. Because the modes of transport through the CNT and polymeric membranes are different, further molecular dynamics investigations into the solution–diffusion model governing polymeric RO membranes should be made in order to compare the two membranes in terms of energy barrier and to provide more comprehensive information about the transport mechanisms in the two membranes.

4. Conclusion

Using molecular dynamics, a preliminary investigation into the potential for using CNT membranes for SWRO desalination was performed. It was found that a CNT membrane can allow a water flux that is 3–4 orders of magnitude higher than the flux allowed in a typical polymeric RO membrane, which is notably higher than that predicted by Hagen–Poiseuille equation. Flow through CNTs is not entirely covered by classical fluid mechanics because these theories only consider water as a bulk substance and do not take into account molecular interactions and the narrowness of the channel. The high ion rejection ability of the simulated (6, 6) CNT membrane, which was between 95 and 100%, was also comparable to a standard polymeric membrane. Importantly, it should be noted that even though the present study is still in preliminary stages of investigation, it was able to show the usefulness of molecular dynamics in studying membrane processes and even fouling phenomena for novel membranes.

Acknowledgment

This research was supported by a grant (code 14IFIP-B087385-01) from Industrial Facilities & Infrastructure Research Program funded by Ministry of Land, Infrastructure and Transport of Korean government.

References

[1] C. Fritzmann, J. Löwenberg, T. Wintgens, T. Melin, State-of-the-art of reverse osmosis desalination, Desalination 216 (2007) 1–76.

[2] M.E. Suk, A.V. Raghunathan, N.R. Aluru, Fast reverse osmosis using boron nitride and carbon nanotubes, Appl. Phys. Lett. 92(13) (2008) 133120–133123.

[3] B. Corry, Designing carbon nanotube membranes for efficient water desalination, J. Phys. Chem. B 112(5) (2008) 1427–1434.

[4] F.M. Garakani, R. Kalantarinejad, A molecular dynamics simulation of water transport through C and SiC nanotubes: Application for desalination, Int. J. Nano Dimen. 2(3) (2012) 151–157.

[5] J.M. Haile, Molecular Dynamics Simulation: Elementary Methods, John Wiley & Sons, Canada, 1992.

[6] H. Ebro, Y.M. Kim, J.H. Kim, Molecular dynamics simulations in membrane-based water treatment processes: A systematic overview, J. Membr. Sci. 438 (2013) 112–125.

[7] S. Plimpton, Fast parallel algorithms for short-range molecular dynamics, J. Comput. Phys. 117(1) (1995) 1–19.

[8] G. Hummer, J.C. Rasaiah, J.P. Noworyta, Water conduction through the hydrophobic channel of a carbon nanotube, Nature 414(6860) (2001) 188–190.

[9] W.L. Jorgensen, J. Chandrasekhar, J.D. Madura, R.W. Impey, M.L. Klein, Comparison of simple potential functions for simulating liquid water, J. Chem. Phys. 79(2) (1983) 926–935.

[10] I.S. Joung, T.E. Cheatham, Determination of alkali and halide monovalent ion parameters for use in explicitly solvated biomolecular simulations, J. Phys. Chem. B 112(30) (2008) 9020–9041.

[11] M.P. Allen, D.J. Tildesley, Computer Simulation of Liquids, Oxford University Press, New York, NY, 1987.

[12] A. White, Intermolecular potentials of mixed systems: Testing the Lorentz-Berthelot mixing rules with ab initio calculations, DSTO Aeronautical and Maritime Research Laboratory, Australia, 2000.

[13] J.K. Holt, H.G. Park, Y.M. Wang, M. Stadermann, A.B. Artyukhin, C.P. Grigoropoulos, A. Noy, O. Bakajin, Fast mass transport through sub-2-nanometer carbon nanotubes, Science 312(5776) (2006) 1034–1037.

[14] L. Wang, R.S. Dumont, J.M. Dickson, Nonequilibrium molecular dynamics simulation of water transport through carbon nanotube membranes at low pressure, J. Chem. Phys. 137(4) (2012) 44102–44114.

[15] P.K. Kundu, I.M. Cohen, Fluid Mechanics, fourth ed., Elsevier, London, 2008.

[16] A. Kalra, S. Garde, G. Hummer, Osmotic water transport through carbon nanotube membranes, Proc. Nat. Acad. Sci. 100(18) (2003) 10175–10180.

[17] C.H. Ahn, Y. Baek, C. Lee, S.O. Kim, S. Kim, S. Lee, S.-H. Kim, S.S. Bae, J. Park, J. Yoon, Carbon nanotube-based membranes: Fabrication and application to desalination, J. Ind. Eng. Chem. 18(5) (2012) 1551–1559.

[18] J.A. Thomas, A.J.H. McGaughey, Water flow in carbon nanotubes: Transition to subcontinuum transport, Phys. Rev. Lett. 102(18) (2009) 184502.

[19] R. Shannon, Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides, Acta Crystallogr. Sect. A 32(5) (1976) 751–767.

[20] T.A. Hilder, D. Gordon, S.H. Chung, Salt rejection and water transport through boron nitride nanotubes, Small 5(19) (2009) 2183–2190.

[21] A.L. Van Geet, Hydration number of sodium ions determined by sodium magnetic resonance, J. ACS 94 (16) (1972) 5583–5587.

[22] D. Hugh Powell, A.C. Barnes, J.E. Enderby, G.W. Nelson, P.S. Salmon, The hydration structure around chloride ions in aqueous solution, Faraday Discuss. Chem. Soc. 85 (1988) 137–146.

[23] B.J. Bucior, D.L. Chen, J. Liu, J.K. Johnson, Porous carbon nanotube membranes for separation of H_2/CH_4 and CO_2/CH_4 mixtures, J. Phys. Chem. C 116(49) (2012) 25904–25910.

[24] J.G. Wijmans, R.W. Baker, The solution-diffusion model: A review, J. Membr. Sci. 107 (1995) 1–21.

[25] M.J. Kotelyanskii, N.J. Wagner, M.E. Paulaitis, Atomistic simulation of water and salt transport in the reverse osmosis membrane FT-30, J. Membr. Sci. 139 (1998) 1–16.