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The influence of the radius of curvature on water desalination across the nanoporous penta-graphene

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Abstract. In the present study, the water desalination across the penta-graphene has been explored by using molecular dynamics simulation. The penta-graphene, a new carbon allotrope, introduced theoretically in 2015. It was shown that this carbon nanostructure is slightly stiffer against buckling in comparison with the graphene nanoribbons. The effect of radius of curvature (ROC) of the membrane, pore size, and applied pressure, on water flow rate, and salt rejection is investigated. It is shown that salt rejection, and the shape of the oxygen density distribution inside the pore can be influenced by the ROC of membrane. Finally, it is shown that the ROC, and pore size of 2D membranes, play an important role in the salt rejection.

Keywords: water desalination; penta-graphene membrane; radius of curvature; molecular dynamics simulation

1. Introduction

There are a number of desalination techniques, i.e., pressure differences (Dickey and Paskin 1969), reverse osmosis (Elimelech and Phillip 2011, Pontiéa *et al*. 2013), driving electric field (Sint *et al*. 2008), to remove the dissolved salt in saltwater. Moreover, in recent years, a number of computational and experimental works have focused on the *2D* carbon nanostructures, as the desalination membranes (Dickey and Paskin 1969, Corry 2008, Garaj *et al*. 2010, Suk and Aluru 2010, Elimelech and Phillip 2011, Cohen-Tanugi and Grossman 2012, Nair *et al*. 2012, Severin *et al*. 2012, Wang and Karnik 2012, Konatham *et al*. 2013, Pontiéa *et al*. 2013, Xue *et al*. 2013, Zhu *et al*. 2013, Cohen-Tanugi and Grossman 2014, O'Hern *et al*. 2014, Zhu *et al*. 2014, Azamat *et al*. 2015,Azamat *et al*. 2015, Goh and Ismail 2015, Cohen-Tanugi *et al*. 2016), because of their optimized physical and mechanical properties, i.e., extremely thin, extremely strong, and can be chemically modified (Lee *et al*. 2008, Girit *et al*. 2009).

By using molecular dynamics (MD) simulations, it was shown that the pore diameter of graphene can play important role in allowing or blocking salt ions across the membrane (Cohen-Tanugi and Grossman 2012). Cohen-Tanugi and Grossman (Cohen-Tanugi and Grossman 2012), by using MD simulation, found a critical pore diameter, 5.5 A, which beyond this diameter the salt

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ions are able to pass through the graphene membrane. Zhu *et al*. (2013), found that for γ-graphyne-4 sheet, the salt rejection is 100%. Furthermore, recent reports show that for nanopores smaller than about 15 Å, in contrast to the conventional continuum theoretical models, the relationship between the pore area and water flow rate is nonlinear (Xue *et al*. 2013, Zhu *et al*. 2013, Zhu *et al*. 2014). The author, in the previous work (Ebrahimi 2016), by employing a set of MD simulations, investigated water desalination across the fixed and unfixed graphene membranes with Si-passivated nanopore. The results showed that the membrane curvature reduces water flux and increases salt rejection through pore rim (Ebrahimi 2016). The author, in the previous work, investigated the water desalination across Si-passivated nanopours graphene for the systems with unfixed membranes. It was shown that membrane curvature reduces salt passing through pore rim. That study did not investigate the effect of the different radius of curvature (ROC) size on the flux, and salt rejection.

The penta-graphene, with a single layer of carbon pentagons, was introduced theoretically in 2015 (Zhang *et al*. 2015). Penta-graphene has sp^3 and sp^2 hybridized C atoms. It was reported that penta-graphene is thermally, dynamically, and mechanically stable. Currently, there are limited theoretical and numerical works on its structural, mechanical, thermal and electronic properties (Chien *et al*. 2011, Xu *et al*. 2015, Zhang *et al*. 2015, Ebrahimi 2016, Einollahzadeh *et al*. 2016, Li *et al*. 2016). Zhang *et al*. (2015) showed that penta-graphene possesses a negative Poisson's ratio, and is strong under biaxial tensile loading. Furthermore, Li *et al*. (2016) reported that by functionalizing it with adatoms, the electronic and mechanical properties of penta-graphene can be tuned. The author, reported that, this new carbon allotrope is slightly stiffer against buckling in comparison with the graphene nanoribbons (Ebrahimi 2016). Furthermore, it was demonstrated that the fewer collective phonon excitations, and the lower phonon group velocities lead to remarkably lower thermal conductivity of penta-graphene in comparison with graphene (Xu *et al*. 2015). To the best of the author knowledge, there are no theoretical, numerical, and experimental reports on the desalination across penta-graphene membranes. In addition, limited studies focused on the effect of the radius of curvature (ROC) of *2D* membranes on water fluxes and salt rejection (Ebrahimi 2016).

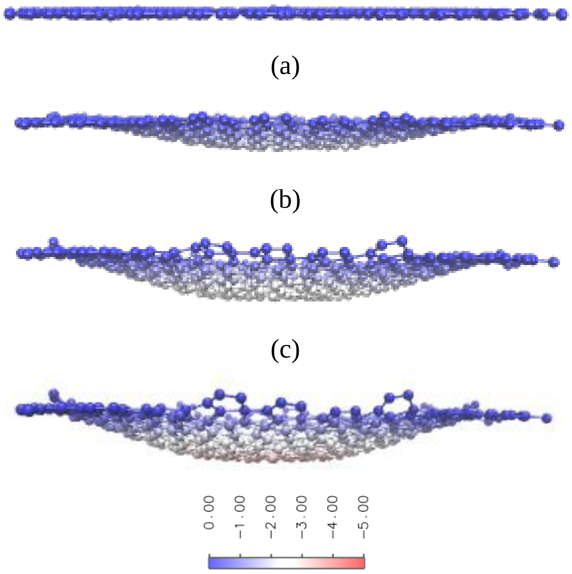
In this study, the water desalination across the penta-geaphene has been reported by using molecular dynamics simulations. The effect of the ROC of membrane, pore size, and applied pressure as the driving force on the permeate salinity have been investigated. We have found that by increasing the ROC of membrane, water flux slightly increases, and salt rejection decreases.

2. Materials and methods

The simulation system consists the penta-graphene membrane sheet of length 3.0 nm in *x* and width 3.0 nm in *y* directions with a pore in a center with the diameter in the range of 5.0-8.5 Å. The 1240 water molecules presented on the both sides (each side has 620 molecules) of the penta-graphene membrane, and the 8 Sodium (Na^+) ions, and 8 Chloride (Cl^-) ions, which yields a concentration of ~0.5M, were randomly placed within the input side. The osmotic pressure difference between the two regions is obtained around the 25 atm, which is almost close to that of ocean water (~27 atm). Simulations were conducted using the LAMMPS software package (Pilmpton 1995). The Tersoff potential (Tersoff 1988) was used to model membrane atoms interactions. The water molecules were modeled using the SPC/E model (Berendsen *et al*. 1987), and the SHAKE algorithm (Miyamoto and Kollman 1992, Lee and Rasaiah 1996) applied to

Table 1 LJ and charge parameters of ions (Cl^-, Na^+) , water molecules, and penta-graphene carbon atoms which considered in the current work (Ebrahimi 2015)

Atom	σ (Å)	ε (kcal/mol)	q (e)
Cl^-	5.165	0.0117	-1.0
Na^+	2.258	0.1684	1.0
O_W	3.166	0.1627	-0.8476
H_W	0.0	0.0	0.4238
C	3.399	0.0859	0.0



(d)

Fig. 1 The side view of penta-graphene membrane with the ROC of *r*=0.0 (a), *r*=2.1 (b), *r*=3.5 (c), and *r*= 4.9 Å (d). The colorbars shows the displacement of membrane atoms

constraint bond length and angles in water. The Lennard-Jones (LJ) potential, and electrostatic forces were used for nonbonded interactions. The LJ and charge parameters implemented in the current simulations are presented in Table 1.

In order to understand the effect of geometry shape, and pore size of membrane on water desalination and salt ions rejection, a series of simulations with different ROC's in the range of 0.0-4.9 Å were carried out. The flat, and curved geometries of penta-graphene membrane with a pore diameter of *d*=6.0 Å , are shown in Fig. 1. In the all systems, the periodic boundary conditions are imposed in all three dimensions. By using the conjugate gradient algorithm, the energy minimizations of all systems were performed. Following minimization, the membranes were fixed, and the systems were equilibrated for 100 ps within an NPT ensemble at a room temperature (300K) to find the optimized volume of the simulation cell. Finally, a constant force, $f = \frac{A\Delta P}{n}$ (Zhu *et al*. 2002), related to the driving force, is applied in the -*z* (*z*) direction to a rigid feed

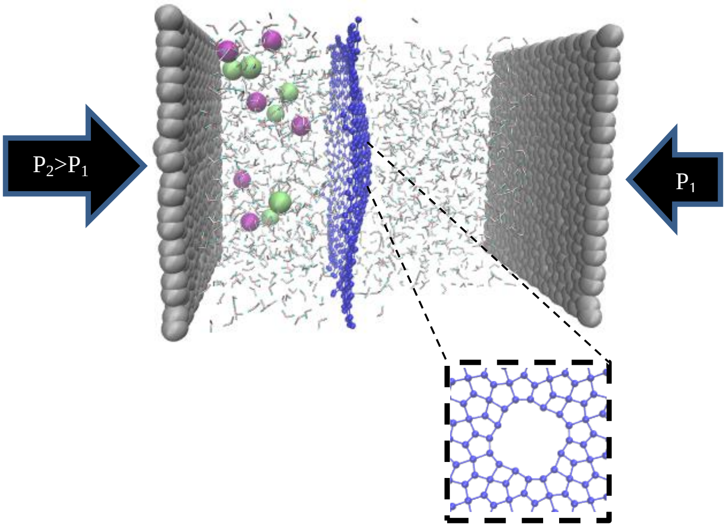


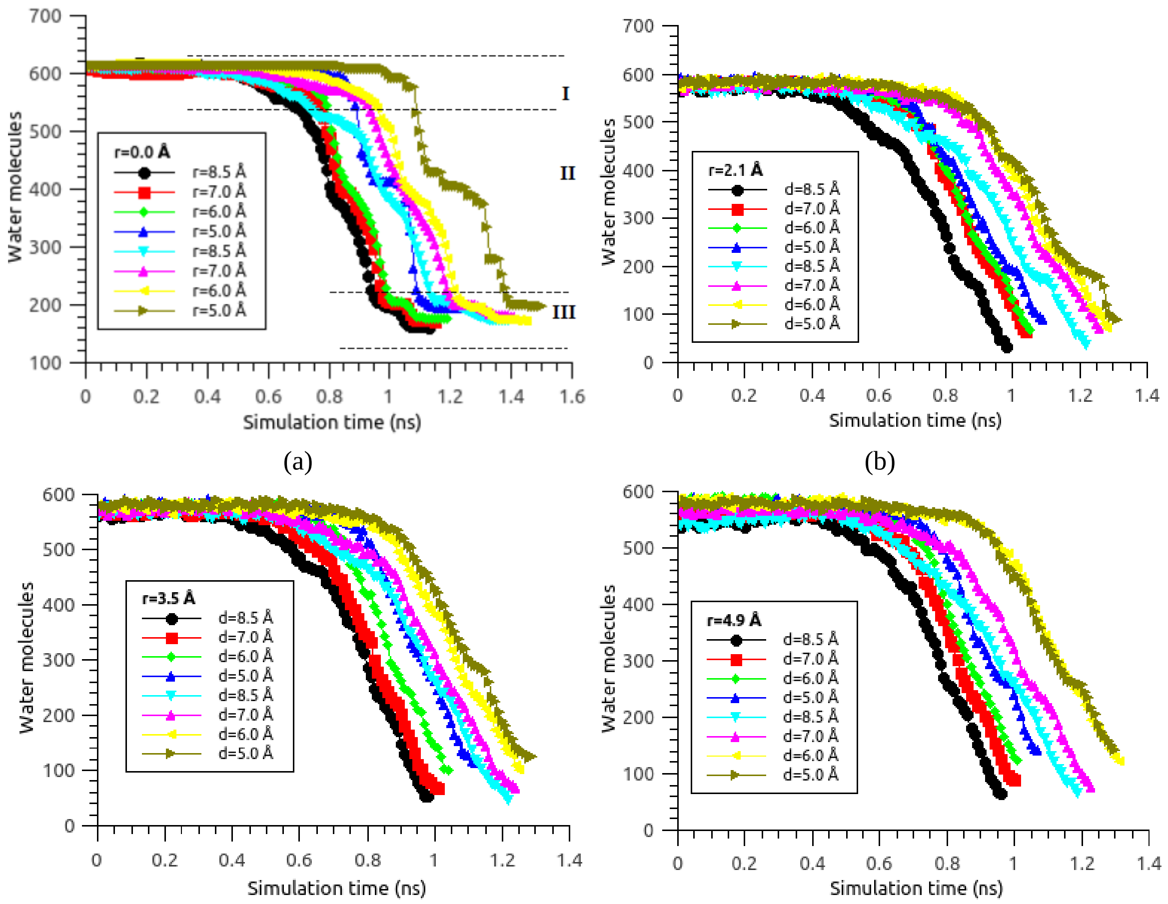
Fig. 2 Snapshot of the computational system with the membrane ROC of (r=4.9Å), and, the pore diameter of d=6.0 Å (bottom figure shows the top view of the membrane pore). The membrane atoms are presented in blue, and sodium and chloride ions are shown as violet and green spheres, respectively. Two rigid pistons which applied ΔP between feed and permeate sides, are shown as gray. The driving pressure P_2 is applied to the left piston

(permeate) piston during simulations, where n is the number of solvate atoms, A is the cross sectional area of the penta-graphene, and ΔP is the desired pressure difference. The computational system of the current work for a system with the ROC of r=4.9 Å, and pore diameter of d=6.0 Å is shown in Fig. 2. Initial velocities were sampled from a Maxwell-Boltzmann distribution. The Nosè-Hoover thermostat (Hoover 1985) was implemented to control the temperature during the simulations, and the velocity-Verl*et al*gorithm (Allen and Tildesley 1986) with the simulation time-step set at δt=2.0 fs was utilized to integrate the equations of motion. The choice of this time-step provided a good balance between accuracy and computational costs.

3. Results and discussion

To examine the effect of curvature on desalination, the water desalination across fixed penta-graphene membranes with different ROC's, and pore sizes, have been investigated by using molecular dynamics simulations.

Fig. 3 shows a number of water molecules on the input side (feed side) as a function of simulation time for the flat membrane (3a), and curved membrane with the radius of curvature of r=2.1 (3b), r=3.5 (3c), and r=4.9 Å (3d). As can be seen from this figure, the water flow almost divided by the three regimes for all systems. The regimes, I, II, and III (Fig. 3(a)), represent the equilibrium regime, close to linear, and plateau curves, respectively. As can be seen from Fig. 3, the linear portion of the curves (second regime) was more developed, by increasing ROC, and the pore size of the membrane. In addition, for all systems, by increasing applied pressure, pore size, and ROC, water flux increases. The water flux for all simulations obtained in the range of 350-

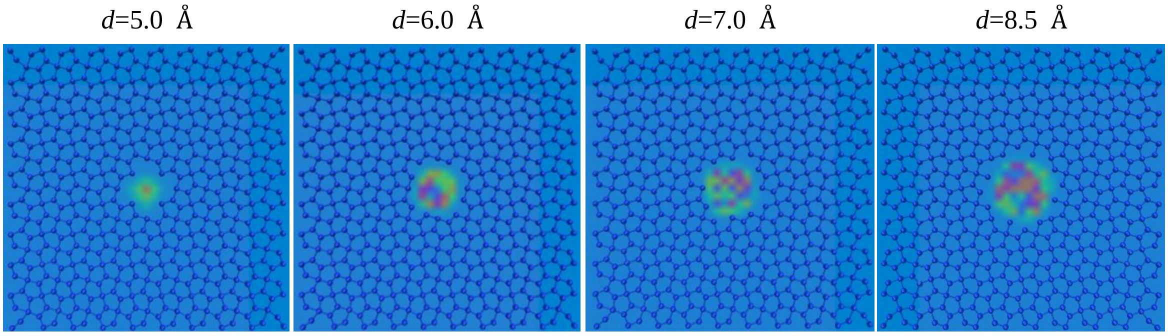


(a) (b)

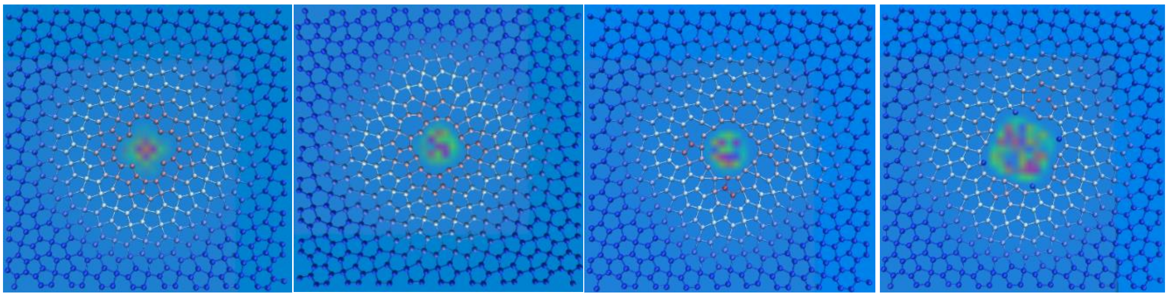
(c) (d)

Fig. 3 Shows the water molecules on the input side via simulation time for the flat (a), and curved membranes with the ROC of r=2.1 (b), r=3.5 (c), and r= 4.9 Å (d), under 150, and 200 MPa applied pressures. The dashed lines in 3-a, show the borders of the different regimes of the systems

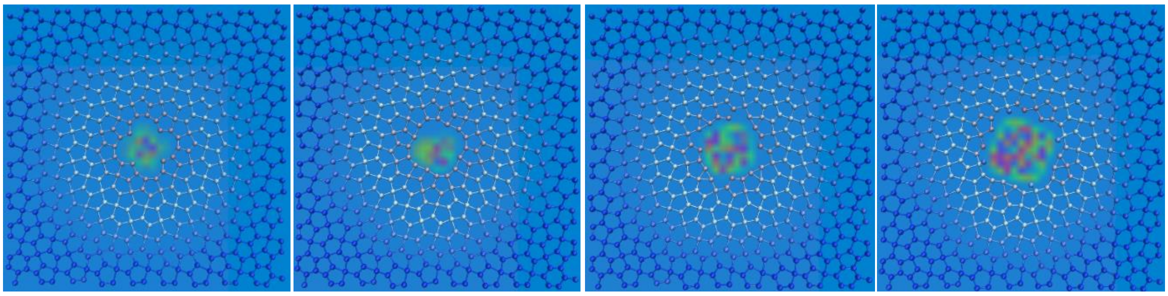
1300 ns^{-1}. In the previous works water flux obtained for graphene membrane in the range of 10-2000 ns^{-1} by using different methods (Cohen-Tanugi and Grossman 2014, Nicolaı *et al*. 2014, Zhu *et al*. 2014, Chen and Yang 2015, Ebrahimi 2016). The current results demonstrate that the water flux of flat, and curved penta-graphene membrane with different ROC is in the range of the graphene membrane. The oxygen density map, which creates a map of the weighted atomic density at each gridpoint (Humphrey *et al*. 1996), inside the membrane pore has calculated and shown in Fig. 4. This figure represents the symmetry of the shape of density surface, for all systems with the smallest pore size (d=5.0 Å). By increasing the pore size, the asymmetrical shapes are developed, and by increasing ROC, the distribution area of oxygen map increases, too. From Figs. 3, and 4, it can be concluded that, the symmetric shape of the oxygen density in the pore, leads to the almost nonlinear behaviour of water flow rate. Moreover, Fig. 4 may demonstrate that, by decreasing the pore size, the mobility of water molecules inside the nanopore, reduces, and eventually, the symmetrical shape of the water density surface inside the nanopore



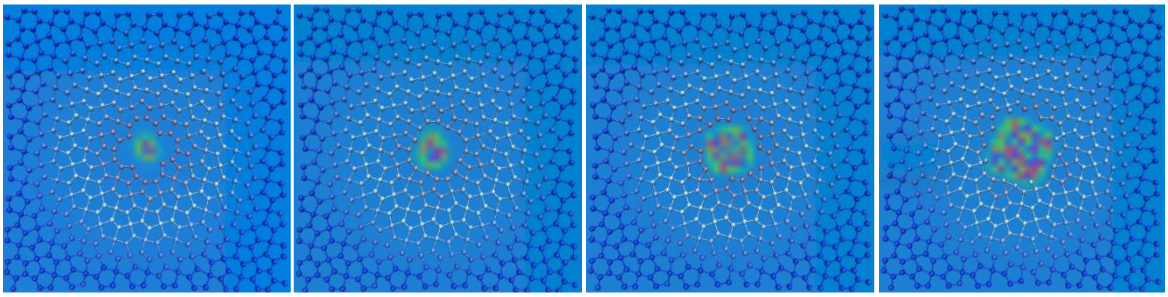
(a) *r*=0.0 Å



(b) *r*=2.1 Å



(c) *r*=3.5 Å



(d) *r*=4.9 Å

Fig. 4 Oxygen density map inside the flat (a), and curved membrane with the ROC of *r*=2.1 (b), *r*=3.5 (c), and *r*=4.9 Å (d). The pore diameter from left to right is *d*=5.0, 6.0, 7.0, and 8.5 Å, respectively. Blue indicates the region without oxygen atoms, red indicates the highest probability of finding oxygen atoms

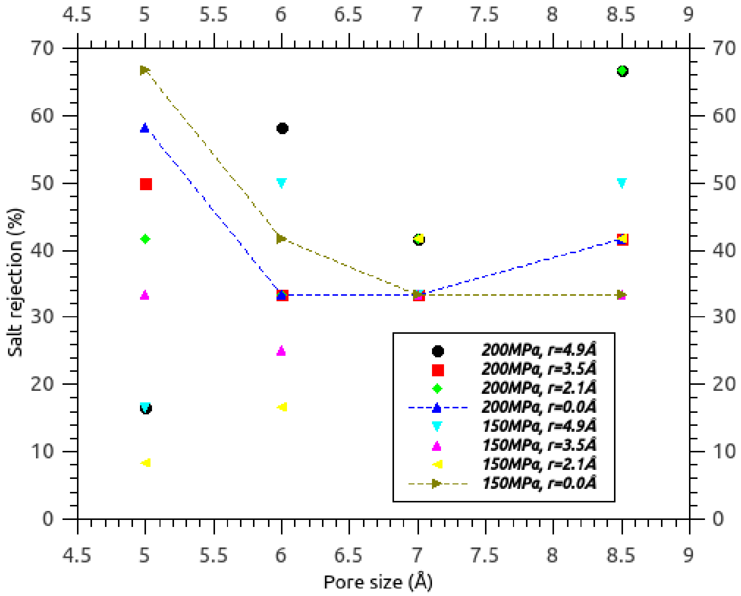


Fig. 5 Shows the salt rejection versus pore diameter. The flat membrane exhibits stronger salt rejection performance than curved membranes for pores with smaller diameters (d<7.0 Å)

more developed. In addition, by increasing the ROC, the number of molecules that are located near the membrane surfaces, increases, and then, the Vander-Waals gap between water molecules increases, and, finally, it leads to the asymmetrical shapes of the water density distribution inside the membrane pore.

The salt rejection for all systems was calculated and shown in Fig. 5. The salt rejection was obtained from the salinity of filtered water at the time when the half the water molecules has flowed through the membrane relative to the initial water salinity (Cohen-Tanugi and Grossman 2012). This figure represents that while, for flat membrane by increasing pore size the salt rejection decreases, for curved shape membranes by increasing pore size, salt rejection increases. Also, salt rejection reaches a maximum of 70%, for both systems, with a flat membrane (and the smallest pore size, d=5.0 Å); and curved shape membrane with the largest ROC (and the largest pore size, d=8.5 Å). Moreover, the salt rejection reaches a minimum of 10% for the curved shape membrane with the pore diameter of d=5.0 Å, and ROC of r=2.1 Å, under the applied pressure of 150MPa. The Fig. 5 indicates that, unlike the systems with the flat membrane, by increasing the ROC, and the pore size, the salt rejection increases. Generally, the present results agree well with the author previous work, which showed that by increasing curvature of graphene membrane with Si-passivated naopore, salt rejection increases (Ebrahimi 2016). Unfortunately, in order to comparison, there is no data for the water desalination across penta-graphene membrane.

Consequently, the ROC, and pore size of *2D* membranes, play an important role in the water flow rate and salt rejection. By increasing the ROC, the mobility of water molecules inside the membrane increases more than salt ions. Finally, by increasing the pore size, and the ROC, the number of water molecules can pass through the membrane before passing salt ions, increases. Our finding shows that, the water flow rate and salt rejection performance are sensitive to the both, pore size and, the ROC of penta-graphene membrane.

4. Conclusions

In summary, the influence of geometric shape and the pore size on water desalination across penta-graphene membrane investigated by employing a set of MD simulations. The results show that the effect of both, pore size and radius of curvature (ROC) of the membrane, on salt rejection is noteworthy. The examination revealed that by increasing the ROC, the flow rate and salt rejection increases. Furthermore, salt ions passage decreases as applied pressure increases. It was shown that, while, by increasing the pore size salt rejection decreases for systems with flat membrane, by increasing the pore size, salt rejection increases for systems with curved membrane. In addition, by increasing the pore size and the ROC; the asymmetrical shape, and distribution area of oxygen density inside the pore more developed.

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