#550: Molecular dynamics simulation of seawater pervaporation process with CHC-hydrophilic gel composite photothermal membrane

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Abstract: Pervaporation technology recently plays an important role in seawater desalination and water purification. Carbon honeycomb (CHC) is a novel carbon allotrope, which combines the advantages of graphene and carbon nanotubes. It exhibits excellent photothermal absorption characteristics and a porous structure, making it highly promising for seawater desalination. However, current research on CHC desalination technology mainly focuses on reverse osmosis desalination, with most studies limited to the mechanisms of single CHC membrane materials. On the other way, the application of coupling CHC materials with other functional nanomaterials in seawater photothermal membrane pervaporation remains unexplored. The relevant microscale water molecules and salt ion transport mechanisms also need further clarification. This work uses molecular dynamics analysis and establishes a CHC-hydrophilic gel composite pervaporation membrane structure for seawater desalination, utilizing hydrogen bonding of the hydrophilic gel to enhance CHC water transport. Meanwhile, this work examines the influence of temperature on the water molecule and salt ion transport properties of the composite membrane. Additionally, this work also compares the pervaporation water flux of composite membranes and single membrane under different temperature conditions. The results indicate that increasing temperature boosts the interaction strength between hydrophilic gel and the water molecules within CHC pores, thereby intensifying the water molecule transport process. However, excessively high temperatures can lead to the formation of larger hydrated ion clusters, limiting water molecule transport. In this work, under moderate-temperature conditions, hydrophilic gel significantly enhances the water flux in pervaporation (about 128%). Moreover, ion clusters do not block membrane pores, demonstrating good desalination performance and self-cleaning properties. These findings provide insights into designing new efficient photothermal pervaporation devices.

Keywords: Seawater Desalination, Pervaporation, Carbon Honeycomb, Hydrophilic Gel, Molecular Dynamics Simulation

1. INTRODUCTION

Recently, water shortage has become a global issue. Due to climate changes and environmental pollution, this is antici - pated to intensify even more in the coming years (Mohammed, Aburabie and Hashaikeh, 2023). Pervaporation technology, an advanced seawater treatment method, offers potential advantages over the reverse osmosis process for desalinating high-salinity water (Liang *et al*., 2015). However, current research on functional nanomaterials in the field of pervaporation is still relatively scarce. There is still a need for comprehensive pervaporation membranes that combine high water flux, and high salt retention rates and are both energy-efficient and environmentally friendly (Li *et al*., 2023).

Carbon materials and their derivatives have recently become one of the research hotspots in the field of pervaporation due to their excellent photothermal absorption properties (Tao *et al*., 2018). Most current research in this field is concentrated on two main directions: graphene and its derivatives (Ni *et al*., 2016), as well as carbon nanotubes (Son *et al*., 2015). In contrast, there is relatively less research on the mechanisms of novel carbon materials like CHC in photothermal pervaporation (Yang *et al*., 2023). CHC combines the advantages of graphene and carbon nanotubes, presenting significant research potential (Krainyukova *et al*., 2016). Moreover, the breakthrough applications of hydrophilic gels in desalination (Sharshir *et al*., 2020) provide promising ideas for the composite design and modification treatment of CHC. Current research on CHC desalination technology mainly focuses on reverse osmosis, with most studies examining the mechanisms of single membrane materials. The coupling of CHC materials with functional nanomaterials such as hydrophilic gels in photothermal pervaporation has not yet been explored, and the related water molecule and salt ion transport mechanisms remain to be clarified. Additionally, the effects of environmental factors such as temperature and salinity on the pervaporation characteristics of CHC composite membranes have not yet been revealed.

Therefore, this work employs molecular dynamics (MD) methods to conduct a dynamic simulation analysis of the seawater pervaporation process through CHC-hydrophilic gel composite photothermal membranes, studying the micro-mechanisms of water molecule and salt ion transport during the pervaporation process under different environmental factors. This work provides a theoretical basis for designing new and efficient pervaporation devices.

2. MODEL DEVELOPMENT

Polyethylene Oxide (PEO) hydrophilic gel can capture water through a polymer network formed by cross-linked polymer chains and establish strong interactions with it, directly transferring the absorbed energy to the water molecules (Zhu *et al*., 2022). Therefore, this work selects PEO hydrophilic gel as the water-absorbing layer and PVDF as the support layer in the composite membrane.

Based on the foundational theory of MD and the CHC membrane constructed by Yang *et al*. (2023), this work constructs a CHC-PEO hydrophilic gel composite pervaporation membrane, as shown in Figure 1. Given the dynamic non-equilibrium nature of the pervaporation process, this work employs periodic boundary conditions (Shirts, Burt and Johnson, 2006) for simulation and the Nosé-Hoover method to control the pervaporation temperature during the ensemble calculations (Evans and Holian, 1985). This system contains 4500 water molecules, 50 Na^+ and 50 Cl^- ions, used to simulate 3.5 wt% seawater.

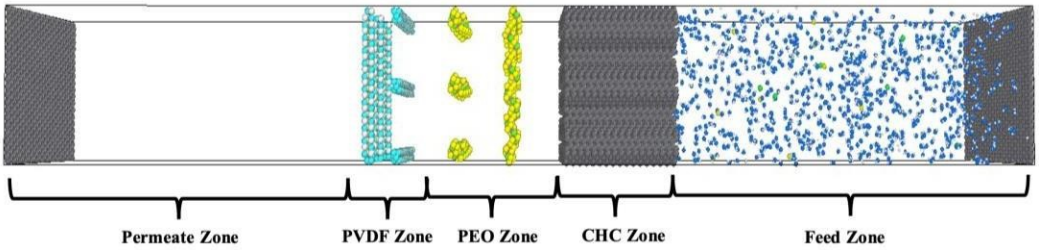

Figure 1: The CHC-PEO-PVDF composite pervaporation membrane (Color codes: Na^+ and Cl^- ions, yellow and green) (Divides the entire system from right to left into the 'Feed Zone', 'CHC Zone', 'PEO Zone', 'PVDF Zone', and the 'Permeate Zone')

2.1. Molecular force field selection

This work employs the open-source Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) to perform MD simulations of the pervaporation process (Plimpton, 1995). The CHC molecule is modeled using the AIREBO force field (O'connor, Andzelm and Robbins, 2015), while H_2O molecules are modeled using the TIP3P force field (Jorgensen *et al*., 1983). The PEO and PVDF molecules are modeled using the OPLS-aa force field (Byutner and Smith, 2000). The non-bonded interactions between atoms like water molecules, salt ions, PEO and PVDF molecules and CHC membrane atoms are described by the 12-6 Lennard-Jones (LJ) and Coulombic potentials. The calculation formula is given as following (Hollingsworth and Dror, 2018):

$$U(r_{ij}) = \sum 4\varepsilon_{ij}[(\frac{\sigma_{ij}}{r_{ij}})^{12} - (\frac{\sigma_{ij}}{r_{ij}})^{6}] + \sum \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} \quad (1)$$

where σ_{ij} and ε_{ij} are zero-crossing distance and potential well depth of the LJ potential. q_i is the charge of the atom, r_{ij} is the distance between two atoms, and ε_0 is the vacuum permittivity. Some force field parameters are listed in Table 1.

In order to accelerate the simulation process, the SHAKE algorithm is employed to control the O-H bond length and bond angle of water molecules to remain constant in this simulation (Miyamoto and Kollman, 1992). Additionally, the mean square displacement (MSD) analysis (Frenkel and Smit, 2023) and average density analysis (Tinnacher *et al*., 2016) methods are mainly employed to judge and predict the trends of particle motion under different pervaporation conditions.

Table 1: Partial 12-6 LJ potential parameters and charges in this work

Atom types	σ (Å)	ε (eV)	$q(e)$	description
C	3.2200	0.0025	0.0000	The C atom in CHC (O'connor, Andzelm, Robbins, 2015)
H	0.4000	0.0020	0.4170	The H atom in H_2O (Jorgensen *et al*., 1983)
O	3.1500	0.0066	-0.8340	The O atom in H_2O
Na^+	2.4300	0.0020	1.0000	MacKerell Jr *et al*., 1998
Cl^-	4.0400	0.0065	-1.0000	MacKerell Jr *et al*., 1998
C	3.5000	0.0029	0.1400	The C atom in PEO (Byutner and Smith, 2000)
H	2.5000	0.0013	0.0300	The H atom in PEO
C	3.5000	0.0029	-0.6500	The C atom in PVDF (Byutner and Smith, 2000)
F	2.9830	0.0026	-0.2830	Byutner and Smith, 2000

2.2. Relaxation and simulation

During the energy minimization phase, the system is relaxed for 60 ps under the microcanonical ensemble (NVE) to prevent atomic overlap caused by overly dense water molecules generated in the 'Feed Zone'. This work employs the Particle−Particle Particle−Mesh (PPPM) method to calculate the long-range Coulombic forces, with an accuracy of 10^{-4}. And the cutoff distance of LJ potential is 15 Å. The constraint method for water molecules employs the SHAKE algorithm. The system coordinates and other relevant information are periodically output and saved to trajectory files. Subsequently, the system undergoes molecular dynamics simulation for 10 ns under the canonical ensemble (NVT), utilizing the Nosé -Hoover thermostat method for temperature control, with system energy periodically recorded.

3. RESULTS AND DISCUSSION

3.1. Model construction and validation

Based on molecular dynamics theory, this work first constructs a CHC pervaporation membrane and compares the water flux J_w with the CHC pervaporation membrane designed by Yang *et al*. (2023) for validation, which can be estimated as:

$$J_w = N_w / (A \cdot t) \tag{2}$$

where N_w is the final number of water molecules passing through the CHC membrane by pervaporation, *t* is the pervaporation time, as well as *A* is the cross-sectional area of the CHC membrane. The comparison results of the pervaporation water flux for the two groups at different temperatures are shown in Figure 2.

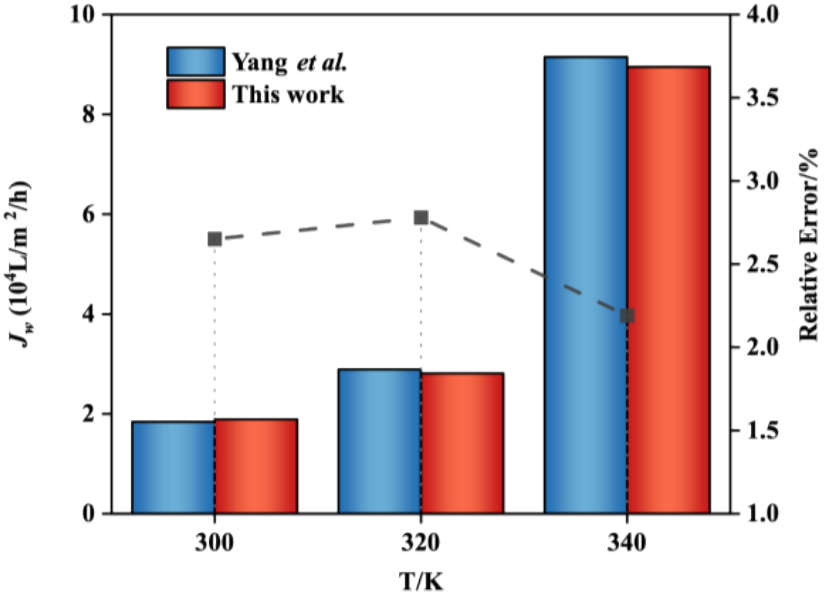

Figure 2: Comparison results of pervaporation water flux

The analysis indicates that the pervaporation water flux of this work is in good agreement with those of the structure used by Yang *et al*. (2023), with relative error not exceeding 3.0%. This confirms that the force field parameters for the CHC molecule, the Na^+ and Cl^- ions, and the water molecules, as well as the ensemble settings, are correct, proving the reliability of this membrane. It provides a model basis for conducting research on the water molecule and salt ion characteristics of the CHC-hydrophilic gel composite photothermal membrane in the seawater pervaporation process.

3.2. Impact of temperature on the pervaporation performance of CHC-PEO composite membranes

During the pervaporation process, the partial pressure difference across the CHC composite membrane drives the permeation process. Temperature changes affect the kinetic energy of particles in the system, which alter their diffusion capabilities and may also impact the physicochemical properties of the membrane material, ultimately affecting the pervaporation efficiency. This work investigates the transport characteristics of water molecules and salt ions through CHC -PEO hydrophilic gel composite membranes under three temperature conditions: 300K, 320K, and 340K.

The average density analysis and MSD analysis of water molecules with temperatures are shown in Figures 3(a) and 3(b). The results reveal that, with temperature increasing, the diffusion capability of water molecules increases, and the water molecules lingering in the pores of the CHC membrane pass through, and are extensively adsorbed in the 'PEO Zone', demonstrating that the water absorption performance of PEO hydrophilic gel improves as the temperature rises.

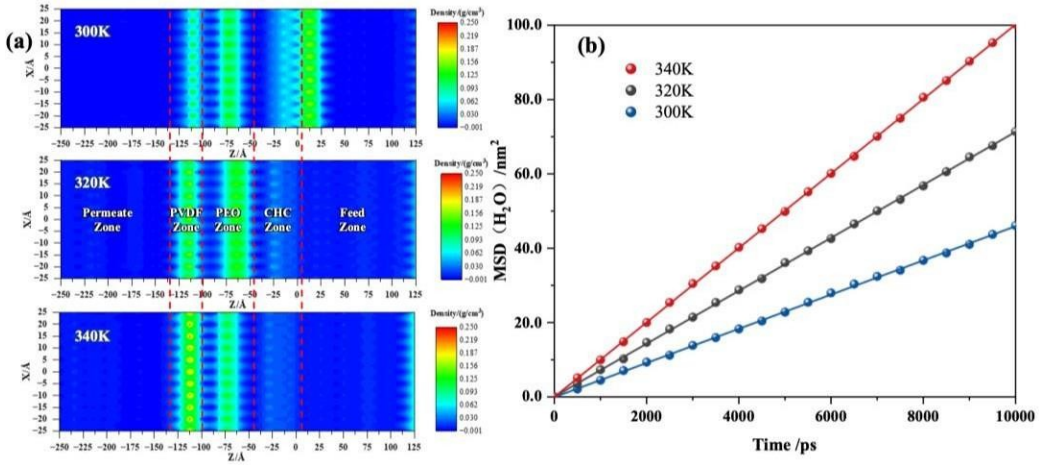

Figure 3: (a) Cloud diagram of density distribution of water molecules with temperatures; (b) MSD of water molecules with temperatures

By analyzing the average density distribution of salt ions along the z-axis, the desalination performance of the CHC-PEO hydrophilic gel composite membrane is tested. Figure 4(a) shows the average density of two ions and Figure 4(b) shows the MSDs of ions at different temperatures. Ionic aggregation was observed at the surface of the CHC in the later stage of simulation under both 300K and 320K conditions. As the temperature increases, the ion density and water molecule density at the CHC entrance decreases, while the ion concentration far from the membrane increases, and the diffusion capability of ions increases. Prove that after increasing the temperature, the mobility of ions is enhanced, forming larger hydrated ion clusters that drift further away. On the other hand, the adsorption capability of PEO hydrophilic gel on the water molecules in the pores is enhanced after the temperature increases, thereby mitigating pore blocking.

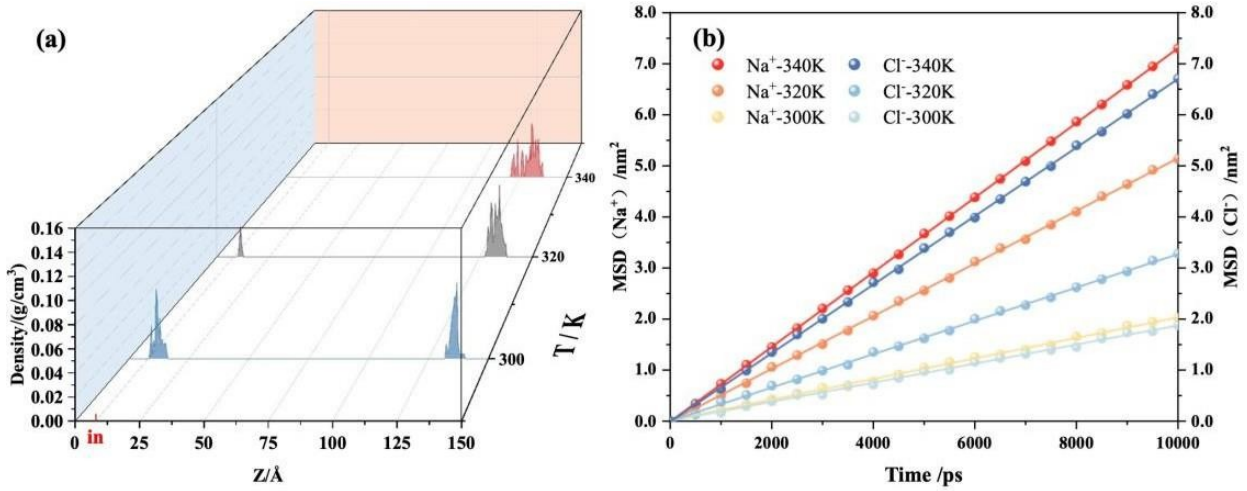

Figure 4: (a) The average density distribution of ions with temperatures; (b) MSDs of Na+ and Cl- with temperatures

Under all three temperature conditions, ions did not permeate into the CHC membrane layer, confirming that the CHC-PEO composite membrane possesses good desalination performance. Additionally, the observed ion accumulation at a distance from the membrane also suggests that the PEO composite membrane system has a self-cleaning function.

The diffusion coefficient of particles can be calculated by the slope of the MSD image, which describes the diffusion capability and motion mode of particles. Therefore, in the process of pervaporation, the larger the slope of the MSD fitting curve, the larger the diffusion coefficient, indicating that the molecular diffusion capability is stronger. For three-dimensional space, the diffusion coefficient can be described as follows (Frenkel and Smit, 2023):

$$D_\alpha = \frac{1}{6N_\alpha}\lim_{t\to\infty}\frac{\mathrm{d}}{\mathrm{d}t}\sum_{i=1}^{N_\alpha}\left\langle\left|\boldsymbol{x}^{(i)}(t)-\boldsymbol{x}^{(i)}(0)\right|^2\right\rangle \tag{3}$$

Where D_α is the diffusion coefficient ($cm^2 \cdot s^{-1}$). The diffusion coefficients of water molecules and salt ions in the composite system at different temperatures are shown in Table 2:

Table 2: The diffusion coefficients of water molecules and salt ions with temperatures

T/K	$H_2O/\times10^{-5}cm^2\cdot s^{-1}$	$Na^+/\times10^{-6}cm^2\cdot s^{-1}$	$Cl^-/\times10^{-6}cm^2\cdot s^{-1}$
300	4.6000	2.0114	1.8679
320	7.1200	5.1536	3.2644
340	10.0200	7.3135	6.7116

Figure 5(a) shows the dynamic number of water molecules in the hydrophilic gel region. The comparison result of pervaporation water flux between the single membrane and the CHC-PEO composite membrane with temperature is shown in Figure 5(b). Compared to the CHC single membrane, the CHC-PEO composite membrane shows better permeability. In this simulation, it performs best under moderate-temperature conditions, with a water flux increase of approximately 128.11% compared to the single membrane. While under high-temperature conditions, the efficiency of the composite membrane is similar to that of the single membrane.

A mechanism analysis based on previous simulation results indicates that, under high-temperature conditions, the water absorption capability of PEO in the composite membrane decreases, reducing its adsorptive effect on water molecules in the CHC pores. Additionally, at high temperatures, hydrated ion clusters move away from the membrane surface, reducing the potential at the entrance and diminishing the influence on water molecules within the pores. Therefore, the final pervaporation water flux difference compared to the single membrane is not significant.

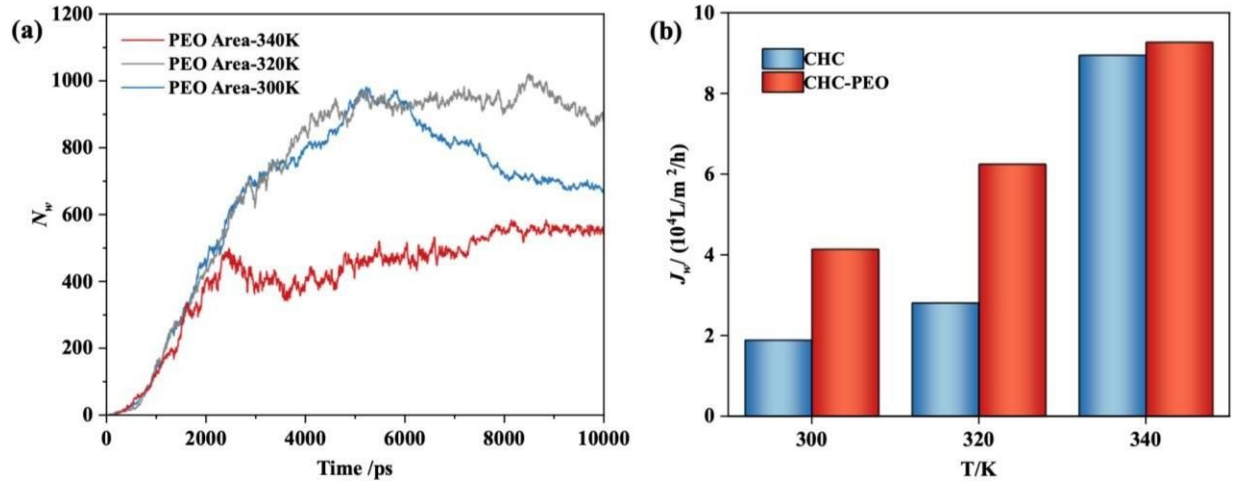

Figure 5: (a)The dynamic number of water molecules in the 'PEO Zone' of the pervaporation process; (b)Comparison of pervaporation water flux J_w of two membranes with temperature

4. CONCLUSION

This work conducts an MD simulation analysis of the seawater pervaporation process using CHC-hydrophilic gel composite photothermal membranes, constructing a CHC-PEO composite membrane to investigate the impacts of temperature on the water molecule and salt ion transport characteristics of the composite membranes. The main conclusions are as follows:

- Temperature affects the hydrophilic gel by increasing the interaction between PEO hydrophilic gel and water molecules as the temperature rises. However, at higher temperatures, the water absorption capability of PEO decreases, altogether, allowing water molecules to directly enter the permeation side, ensuring high pervaporation efficiency.
- Temperature affects the ions by enhancing the diffusion capability of hydrated ion clusters with increasing temperature. Their adsorption capability on water surpasses that of hydrophilic gel. However, excessively high temperaturescan enlarge the volume of hydrated ion clusters, thereby restricting further diffusion of water molecules and salt ions.
- In this work, PEO hydrophilic gel exhibits the best enhancement effect on the water molecule transport process of CHC pervaporation membranes under moderate-temperature conditions. It significantly improves water flux (improved by 128%) in pervaporation and ensures that ion clusters do not block pores but drift away from the membrane, suggesting the CHC-PEO composite membranes have a self-cleaning function and well desalination performance.

5. ACKNOWLEDGEMENT

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