Study on boron removal performance of covalent organic skeleton membrane by hydroxyl groups

Yan Xing 1, Qiang Lyu 1, Songqing Hu 1, and Shuangqing Sun 1*

1 Schools of Materials Science and Engineering, China University of Petroleum Huadong – Qingdao Campus, Qingdao 266580, P.R. China

Abstract. Growing demand for water desalination promoted the vigorous development of reverse osmosis (RO) membrane. How to effectively remove boron from seawater is the key problem to be solved by RO membrane. It is important to select suitable membrane materials for experimental design before complicated and expensive experimental attempts. In this paper, we demonstrate that pore chemistry plays a key role in boron removal capability of RO membranes via nonequilibrium molecular dynamics simulations. This study shows that the introduction of hydroxyl (-OH) groups into the Covalent organic frameworks (COFs) pore allows for better boron removal without changing water permeability. The optimal boron rejection of AB-COF membranes is 76.67%, and that of ATFG-COF membranes with hydroxyl groups can achieve 90%. This is caused by the hydrophilic pore of ATFG-COF that will preferentially adsorb water molecules to prevent the passage of boric acid molecules through membrane zone. Additionally, -OH groups on the pore will also adsorb a part of boric acid in the membranes, reducing the amount of boric acid entering into the permeate side. The results obtained in this paper can provide guidance for the rational design of RO membranes to achieve more efficient boron removal.

1. Introduction

As the global economy and the rapid growth of population, the shortage of water resources has always been a threat of survival and progress of human society. Although water resources cover 75% of the earth's surface, 97% of them are seawater which cannot be directly used, and fresh water only accounts for 3% of the total water resources, most of which exist in the form of glaciers or ice and snow [1]. Given the abundance of seawater on the Earth's surface, desalination is an ideal solution to the global shortage of fresh water resources.

One of the most difficult components to remove from seawater is boron [2]. Boron is a kind of inorganic molecules, adequate intake of boron in plants [3], animals and humans [4] is good, but excessive intake will produce adverse effect, lead to serious health [5] and ecological destruction [6]. According to the World Health Organization, the concentration limit for boron in drinking water must be below 2.4 mg/L (WHO, 2011). Boron in saltwater typically has a concentration of 4.6 mg/L [7]. It typically occurs as uncharged boric acid, which may permeate through the RO membrane similarly to water. As a result, removing boron from saltwater is a difficult challenge [8].

The advancement of RO technology largely depends on the development of RO membranes, as membranes play a key role in determining the technical and economic efficiency of the RO process [9]. Covalent organic framework (COF) is a new type of porous material [10], which has attracted special attention due to its advantages of structural diversity, low density, high thermal stability and permanent porosity [11]. Therefore, it is one of the ideal materials for preparing RO membranes. Unfortunately, it remains difficult to manufacture COF package membranes with high crystallinity. It's crucial to comprehend the rejection mechanism in order to screen potential COF materials with superior boric acid selectivity before moving further with time-consuming and expensive experimental endeavors.

In this work, we designed two isomorphic microporous COFs based on water stable acridine bonds as RO membranes for boric acid separation experiments. We examined the impact of adding hydrophilic groups on the water permeability and boric acid rejection of the COF membranes using non-equilibrium molecular dynamics (NEMD) simulations. The results show that the introduction of hydrophilic hydroxyl groups can significantly improve the rejection rate of boric acid without changing water permeability. The results of this work can pave the way for the rational design of microporous COF membranes for RO boron removal, and play a favorable role in promoting the development of seawater desalination boron removal technology.

2. Computational details

To verify the boric acid removal performance of the COF membrane for desalinated brine, we used the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) to perform non-equilibrium molecular dynamics simulations. The simulations were performed at 300 K, with a time step of 1 fs and a simulation time of 10 ns. The boron concentration in the feed solution was set to 4.6 mg/L, and the water flux was set to 20 l/m²/h. The results showed that the optimal boron rejection of AB-COF membranes is 76.67%, and that of ATFG-COF membranes with hydroxyl groups can achieve 90%. This is caused by the hydrophilic pore of ATFG-COF that will preferentially adsorb water molecules to prevent the passage of boric acid molecules through membrane zone. Additionally, -OH groups on the pore will also adsorb a part of boric acid in the membranes, reducing the amount of boric acid entering into the permeate side. The results obtained in this paper can provide guidance for the rational design of RO membranes to achieve more efficient boron removal.
The transport model of B(OH)₃ and water through the COFs membrane is shown in Figure 1e. To avoid membrane displacement in the simulation box, we assume that covalent organic frame membranes are rigid. By applying a force to each atom on the piston so that the piston achieves a certain pressure, the resulting transmembrane pressure (60 MPa) can push the boron solution through the membrane by applying different pressures to the two pistons.

Here, we selected two isomorphic microporous COF based on water-stable azine bonds: Acridine-benzene-COF (AB-COF, see Fig. 1a) and Acridine-trimethylated interphenyltrphenol-COF (ATFG-COF, see Fig. 1c), with pore sizes of 9.69 Å and 9.15 Å, respectively. Extended with periodic boundary conditions for the unit cell, we chose a hole with two AB-COF package (see Fig. 1b) and ATFG-COF package (see Fig. 1d) segment membrane model of molecular dynamics simulation as the following. In addition, the dimensions of AB-COF simulation box is a=25.9982, b=30.020, and the dimensions of ATFG-COF simulation box is a=25.9929, b=30.014. Specifically, the value of c increases with the membrane thickness.

Fig. 1. The monomeric unit of AB-COF(a) and ATFG-COF(c). The periodic structure of AB-COF(b) and ATFG-COF (d). The simulation system for the movement of water and B(OH)₃ via COF multilayers is shown in the following diagram (e).

With a Nose-Hoover thermostat of 300 K and a damping value of 100 time steps, a specification (NVT) ensemble was employed throughout the MD simulation. After the initial energy is minimized, the system balances 100 ps in the NVT ensemble, keeping the external piston pressure fixed. Subsequently, 20 ns of data was collected in the NVT ensemble.

3. Results and discussion

3.1. Water permeability

We first studied the water permeability of COF membranes with different thickness. Fig. 2 depicts the relationship between the number of layers and water permeability. It can be seen that whether it is pure water or boron-containing brine, water flux decreases with the increase of membranes thickness. This is because the internal resistance of the channel to water increases with the increase of the membrane thickness. MD simulation results show that when boron-containing brine passes through the COF membranes (see Fig. 2a), as the number of membrane layers increases from 1 to 8, the permeability of AB-COF membrane decreases sharply from 375.44 L m⁻² h⁻¹ bar⁻¹ (LMHB) to 94.29 LMHB, and that of ATFG-COF membranes decreases sharply from 364.41 LMHB to 90.53 LMHB. Then, with the further increase of the number of layers to 20, the permeability of AB-COF membrane gradually decreased to 41.01 LMHB, and that of ATFG-COF membrane gradually decreased to 42.51 LMHB. In this process, the permeability of AB-COF and ATFG-COF membranes vary with the number of layers almost the same.

Due to the presence of -OH in the pore, it is easy for ATFG-COF to form hydrogen bonds with H atoms in aqueous solution. Therefore, the hydrophilicity of ATFG-COF is much higher than that of AB-COF, which is consistent with the results of the density distribution diagram (Fig. 2c, 2e). However, as mentioned above, the water fluxes of ATFG-COF membrane and AB-COF membrane are basically the same when simulating the separation of pure water and boron-containing brine. It can be seen that the presence of hydrophilic -OH does not affect the number of water molecules passing through the membrane region. We believe that, on the one hand, oxygen atoms in the ATFG-COF pore will make the pore wall absorb more water molecules, and attract the water molecules in the feeding zone into the membrane zone. On the other hand, the adsorbed water molecules in the pore wall will prevent other water molecules from passing through the membrane region and entering the permeable region. When the attraction and obstruction are basically the same, the influence of oxygen atoms on the pore wall on the water flux can be ignored, so the water flux of ATFG-COF membrane can be consistent with that of AB-COF.
3.2. Rejection mechanism of boric acid

Fig. 3 shows the function of boron repulsion with the number of COF film layers. Obviously, the boric acid retention rate increased with the increase of film thickness and finally leveled off. When the number of film layers reached 20, the boric acid interception rate reached the maximum. At this time, the boric acid interception rate of AB-COF film was 76.67%, and the boric acid interception rate of ATFG-COF film was 90%. Studies have shown that water molecules will preferentially adsorb through hydrogen bonding interactions in a stable imine-linked covalent organic framework, and water molecules occupying pore walls will block the passage of B(OH)₃ [12]. Therefore, with the increase of membrane thickness, the amount of water molecules adsorbed by COF membrane also increases, and boric acid molecules are prevented from passing through the membrane region. The retention rate of boric acid molecules increased with the increase of membrane thickness. When the membrane thickness reaches a certain value, the amount of water molecules adsorbed by COF membrane reaches a maximum, and the obstruction to B(OH)₃ also reaches a maximum. After that, the interception rate of boric acid molecules will remain constant.

It can be seen from Fig. 3 that the boron repulsion of ATFG-COF is always greater than that of AB-COF when the number of film layers is greater than 1. Combined with the density distribution diagram of boric acid molecules in COF channel (Fig. 2d and 2f), it can be seen that the absorption of water and boric acid in ATFG-COF channel is higher than that of AB-COF channel. This is because the -OH group on the ATFG-COF pore channel easily forms hydrogen bonds with water and boric acid molecules, which prevents boric acid molecules from passing through the COF membrane. The boron reactance of AB-COF (23.33%) was greater than that of ATFG-COF (12.86%) when the film number was 1. We believe that under the action of hydrogen bond, ATFG-COF membrane preferentially adsorbs more boric acid molecules into the membrane. Due to the thin membrane layer, the adsorbed boric acid molecules will pass through the membrane and enter the osmotic side under the action of pressure difference. At this time, the boron resistance of ATFG-COF films is lower than that of AB-COF films.
4. Conclusion

In conclusion, the transport state of boric acid solution on isomorphic microporous COF membrane is simulated by non-equilibrium molecular dynamics. By introducing -OH into the COF pore, higher boron removal rate can be obtained without affecting the permeability of the COF membrane. The maximum boric acid retention rate of AB-COF membrane was 76.67%, and the maximum boric acid retention rate of ATFG-COF membrane containing -OH could reach 90%. After analyzing the molecular details, it was found that the -OH group plays a key role in boron removal. It could not only adsorb water molecules to block the boric acid passing, but also adsorb part of boric acid in the membrane region, thus reducing the boric acid passing rate. The results of this work illustrate the key role of hydrophilic groups in the design of boron removal membranes for desalination. Although the present work uses two isomorphic COFs as the model system, we suggest that the influence of hydrophilic groups may also play a role in the boron removal of other COFs desalination membranes.

References