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Review

Application of Nanofiltration Membrane Based on Metal-Organic Frameworks (MOFs) in the Separation of Magnesium and Lithium from Salt Lakes

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Abstract: With the increasing demand for lithium, the shortage of resources has become increasingly apparent. In order to conserve resources and to improve recovery, the extraction of lithium from salt lakes has become mandatory for sustainable development. Porous metal-organic framework (MOF) materials have attracted extensive attention due to their high/tunable porosity, pore function, multiple pore structures/compositions, and open metal sites. Moreover, MOFs combine the advantages of other porous materials and have a wide range of applications, which have received significant interest from the scientific community. Therefore, the selection of MOFs materials, the optimization of preparation methods, and the research of lithium separators are key directions to improve the total yield of lithium resources in salt lakes in China. This study aims to improve the comprehensive utilization of resources after lithium extraction and strengthen the engineering technology research of lithium extraction from salt lakes. This study can help to achieve the goal of efficient, integrated, and sustainable utilization of salt lake resources. An attempt has been made to summarize the types and preparation methods of MOFs materials, as well as the separation mechanism of MOFs nanofiltration membranes, with reference to its application in lithium extraction from salt lake brine. Finally, the future development of MOFs nanofiltration membranes for lithium extraction from salt lakes is also proposed.

Keywords: MOFs nanofiltration membrane; separation mechanism; salt lake brine; lithium extraction

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1. Introduction

Lithium resources are a vital strategic resource as lithium plays a pivotal role in energy storage devices and other energy applications. The global lithium demand is estimated to grow at the rate of 6% per annum, with the annual total consumption expected to be 95,000 tons in 2025 [1,2]. China's total proven lithium resources are estimated to be 5.1 million tons, of which "salt lake type" lithium resources account for 69%. At present, lithium is extracted from ores and salt lake brine. However, the extraction of lithium from ores has problems pertaining to low recovery rates and difficult mining. China's lithium resources are mainly distributed in the Qinghai-Tibet Plateau. Most of the salt lakes in these locations are of chloride and magnesium sulfate subtype, with a high magnesium-lithium ratio and low lithium content. The challenge of the successful utilization of these sources highly depends on efficient separation of Li^+/Mg^{2+} in brine; hence, different technologies have been created by the scientific community to attempt to improve the separation.

Membrane separation is a well-known and developed separation technology that is established for ease of operation [3], is environmentally benign, and has low energy consumption suitably employed in different industries, which include chemical, pharmaceutical, and other fields [4,5]. Membrane technology is broadly classified as electrodialysis, reverse osmosis, and nanofiltration. Nanofiltration (NF) is a pressure-driven membrane separation process between ultrafiltration (UF) and reverse osmosis (RO) [1]. Nanofiltration has higher water permeability and solute retention at lower operating pressures than RO. Although significant improvements in the types and characteristics of nanofiltration membranes have been made, their application is restricted due to high selectivity/low permeability, and vice versa [2]. Due to low permeability of commercially available membranes, it is imperative to develop membranes with high permeability and selectivity in order to improve its utility [6]. Recent studies have developed a nanofilm with nanoparticles (NPs) added to the functional layer, which form water channels between the hydrophilic surface that significantly increase the water permeability [7]. However, inorganic nanoparticles easily aggregate, which causes pore blockage. Furthermore, rigid nanoparticles are incompatible with the polymer matrix, leading to non-selective porosity generation, which reduces selectivity [8]. The above problems seriously affect the utility of nanofiltration membranes, and necessitate further development.

In recent years, inorganic crystalline materials with excellent stability and regular pore structures have attracted extensive attention from the international community. As a new type of porous material, metal-organic framework materials have the characteristics of variable pore structures and compositions, having the selective permeation of specific ions. Moreover, these materials are low in density, have a high specific surface area, good thermal stability, and are easy to synthesize. The development of membranes based on metal-organic framework materials could provide a broad spectrum of membranes suitable for varied applications. MOF materials are composed of metal ions or ion clusters, and organic ligands [9]. MOFs are crystalline materials with intramolecular pores, also known as porous coordination polymers (PCPs) [10]. The high crystallinity, microporosity, and tunable functional groups of MOFs facilitate the tailoring of chemical properties, pore structures, and can optimize membrane performance [11]. Membranes based on MOFs are usually prepared with Zn, Co, Fe, Cr, Ni, Mn, and mace elements in order to understand the pore design, filtration performance, and separation mechanisms of the membrane transfer process [12]. Therefore, MOF nanofiltration membranes offer great potential for efficient separation of magnesium and lithium in salt lake brine.

2. Metal-Organic Frameworks (MOFs)

MOFs offer significant advantages in the preparation of nanofiltration membranes compared with other inorganic nanomaterials [13]. The pore structure of MOFs can be tuned to form unique nanopores that provide solvent migration channels in transmembrane separation [14]; organic ligands and polymer matrices can enhance the controllability of interfacial interactions with compatibility. According to the theory of coordination chemistry, metal ion nodes and organic ligands are connected through coordination bonds, building material molecular units to form coordination polymers with dimensions [15]. The dimensions of MOFs can be either two or three-dimensional, determined by the number of empty orbitals contained in metal ions and the number of organic ligand teeth. In summary, MOF materials can potentially serve to prepare a new generation of membrane materials, replacing traditional nanoparticles.

2.1. MOFs Classification

MOFs can be broadly classified into IRMOFs, CuBTC, MIL, ZIFs, and UiO series, and their general characteristics are detailed in Table 1. As can be seen from Figure 1, the different MOF structures have unique channel structures. According to the popular synthesis procedure and the relevant literature summarized in Table 2, it can be concluded that the pore structures of MOFs efficiently transport ions by reducing the resistance across the membrane [16].

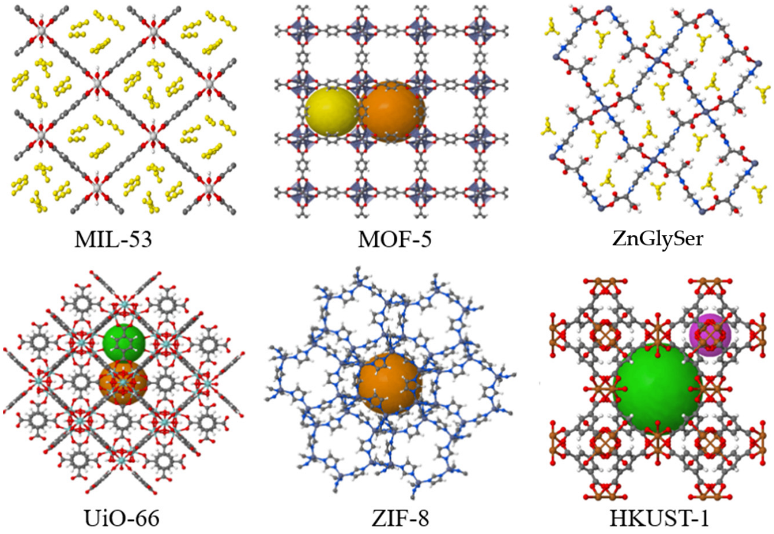

Figure 1. Structure of common MOFs.

According to the literature, the pore size of the IRMOF series is significantly higher than that of the four primary hydrated metal ions (Li^+, Mg^{2+}, K^+, Na^+) in salt lake brine. In general, a pore size of 1.29 nm can easily facilitate the transport of these ions through the membrane. Among them, the pore size of the HKUST series is about 0.82 nm, close to the hydrated ion diameter of Mg^{2+} that can effectively trap hydrated Mg^{2+}. On the other hand, the UiO series has a pore size of about 0.60 nm, which is smaller than the diameter of all hydrated ions. Ions with lower hydration energy are more likely to lose their hydration shell [17] that finds the shortest migration path, with lower migration resistance facilitating better mass transfer and separation.

Li^+ has lower hydration energy than Mg^{2+}; as a result, it will lose its hydration shell more easily than Mg^{2+} and would diffuse faster than the hydrated Mg^{2+}. Although the unhydrated Mg^{2+} is smaller than Li^+, the UiO series NF films exhibit preferential migration of Li^+. The pore size of the ZIF series is about 0.47 nm, and so offers a better particle size sieving effect than the UiO series. The migration order of metal ion in brine in the UiO series NF film is in the order of $Li^+ < Na^+ < K^+ < Mg^{2+}$.

The separation performance of MOFs largely depends on pore size and structure [18]. The metal ions with different hydration diameters are known to exhibit different separation effects (Figure 2a) [19,20]. With loss of the Li^+ hydration shell, the proportions of Li^+/Na^+, Li^+/K^+, and Li^+/Mg^{2+} in the ZIF series are significantly larger than that in the UiO series. The pore size of MOFs plays an essential role in separating magnesium and lithium in brine, and MOFs with smaller pore sizes are more favorable in terms of the selective separation on the membrane surface (Figure 2b).

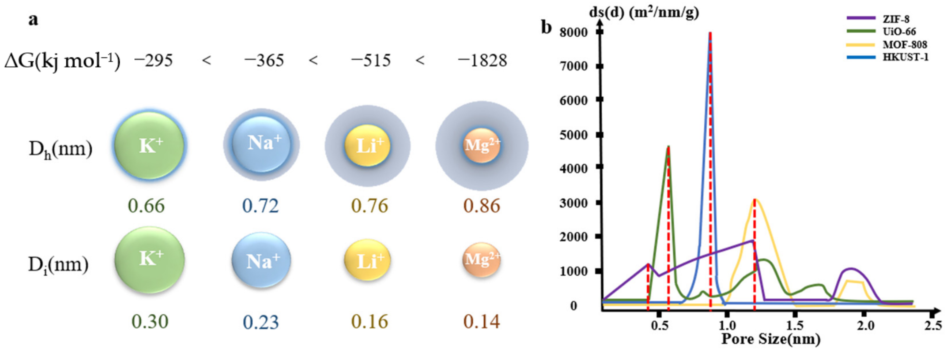

Figure 2. (**a**) Hydration free energy (ΔG), hydrated ionic diameter (Dh), and ionic diameter (Di) of different metal ions [19]; (**b**) pore size distribution of MOFs.

Table 1. The classic types of metal-organic framework materials.

MOF Type	Comment	Advantage
IRMOFs	Microporous crystal materials with cubic network structure produced by connecting aromatic carboxylic acid organic ligands with inorganic ion cluster structural units.	• Large specific surface area • Regular channel structure
CuBTC	It is produced by the coordination reaction between copper nitrate solution and benzoic acid (BTC). It has a three-dimensional cross channel structure.	• Strong interaction with gas molecules • Large adsorption heat for unsaturated hydrocarbons
MIL	It is formed by coordination of trivalent metal with organic ligands terephthalic acid and metabenzoic acid, and the pore structure is planar diamond [21].	• The pore breathing effect
ZIFs	It is produced by the coordination connection of metal ions and imidazole ligands, and has a cage like pore structure.	• High thermal stability • Good separation performance of metal ions
UiO	It is formed by the coordination connection of octahedral secondary structural unit Zr, and has a three-dimensional hole structure.	• Excellent thermal • chemical stability

Table 2. Summary of MOFs that have been synthesized in larger amounts.

MOF	Comment
ZIF-8	$Zn(NO_3)_2 \cdot 6H_2O$ and 2-methylimidazole (Hmim) are dissolved separately in MeOH. The latter is poured into the former after stirring with a magnetic bar. Then stir well and let stand for 24 h. Next, the solid and the milky colloids are separated by washing and centrifugation with methanol, and repeated three times. Finally, dry at room temperature and low pressure [22].
UiO-66	$ZrCl_4$ and terephthalic acid are dissolved in DMF to form a crystallization mother liquor. Statically crystallize at 120 °C for 24 h. After washing and drying, add benzoic acid or acetic acid as a conditioner. UiO-66 single crystal is obtained on the conical flask wall by solvent evaporation [23].
Cu-THQ	Cu-THQ MOFs are synthesized by dissolving $Cu(NO_3)_2 \cdot 2.5H_2O$ in degassed water and adding ethylenediamine. The above solution is then vigorously stirred and transferred to a degassed aqueous solution and stirred at room temperature for 12 h. The final centrifugation is followed by three washes with deionized water and acetone. Finally, the obtained Cu-THQ MOFs are dried in an oven at 80 °C for 24 h [24,25].

2.2. Preparation of MOFs Film

Metal-organic framework polycrystalline films are divided into two types, namely supported and unsupported. Among the two, supported metal-organic framework polycrystalline films are the most widely used, with carriers such as metal oxides, inorganic compounds, alloys, and organic polymers. Among the different base materials, polymer materials are preferred due to low cost, availability, flexibility, and favorable mechanical and chemical properties. The common MOFs nanofiltration polymer substrate materials are classified into different types, which include polyvinylidene fluoride, polysulfone, polyethersulfone, polyimide, and polyacrylonitrile.

The current up-to-date MOFs nanofiltration membrane preparation includes in situ growth [26], blending [27], and interfacial polymerization [28]. Table 3 describes the popular process utilized for preparation utilizing different techniques, while the schematic of synthesis process is shown in Figure 3. Among them, the interfacial polymerization method has attracted much attention due to its fast kinetics, ease of operation, thin film thickness, and dense film pores. The preparation method of the MOFs nanofiltration membrane plays an important role in the membrane performance, and hence, the selection of the right method plays an important role in defining the efficiency of the nanofiltration process.

Table 3. Preparation method of MOFs.

Preparation	Process
In Situ Growth (ISG)	In situ growth (ISG) refers to immersing the polyvinyl support film into nanoparticles and then pouring it into the mixed solution of organic phase monomer or water phase monomer.
Blending	There are two preparation methods: the first is to directly mix the MOFs particles with the polymer matrix through L-S phase inversion; the second is to mix the MOFs particles with a cross-linking agent (modified polymer).
Interfacial Polymerization	Refers to immersing the polyvinyl support film into the mixed solution of nanoparticles and organic phase monomer or aqueous phase monomer [29].
Phase Inversion	Refers to the mass transfer of solvent and non-solvent in the homogeneous polymer solution in the surrounding environment and changing the thermodynamic state of the solution by a particular physical method.

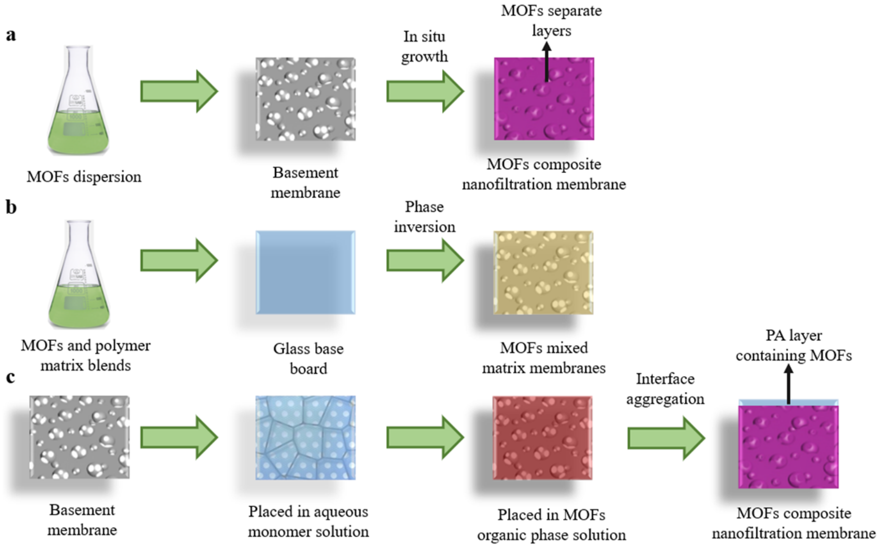

Figure 3. (**a**) Hydration and preparation of MOFs nanofiltration membrane by in situ growth. (**b**) Preparation of MOFs nanofiltration membrane by blending. (**c**) Preparation of MOFs nanofiltration membrane by interfacial polymerization.

Carlos et al. [30] utilized liquid-phase crystallization to prepare continuous MOF layers on hollow fiber scaffolds (Figure 4a). The synthesis of bilayer polyamide-MOF membrane was affected by interfacial polymerization technique. Based on different advanced characterization methods, the permeability and selectivity were reported to be improved when compared with the conventional TFC membrane (without an MOF layer). The water permeability was reported to have improved from 0.06 ± 0.01 to 0.24 ± 0.09 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$, while the metal ion rejection improved from 88 ± 2 to 98 ± 1%. Wang et al. [31] utilized polyether alum ultrafiltration membrane materials with different layer thicknesses to construct the organic-inorganic hybrid modifier Co-MOF. The ZIF-67 modified polyether alum membranes were prepared by blending and phase inversion method (Figure 4b). They reported that the ZIF-67 modified polyether alum membrane had excellent permeability and separation efficiency. At 4 wt% ZIF-67 content, the water flux was reported to be

55.696 L·m^{-2}·h^{-1}, with a 98% rejection of metal ions. Mokhtar et al. [32] prepared magnetically modified metal-organic framework nanoparticle NF membranes by a traditional phase inversion method (MOF@Fe_3O_4). The synthesized nanoparticles were characterized using advanced analytical methods and reported improved thermal stability of the modified MOF@Fe_3O_4 membrane. At a pH of three and a temperature of 25 °C, the metal ions removal was 88.31 ± 2.1%. Yao et al. [33] used Cu_2O nanoparticles with PVDF microfiltration as the base membrane (Figure 4c). The structure of PVDF/i-Cu-TCPP/PA film was prepared by interfacial polymerization. They reported the permeability to be four times higher than the PVDF/PA membrane (up to 1.93 L·m^{-2}·h^{-1}·bar^{-1}) without affecting the rejection (>96%).

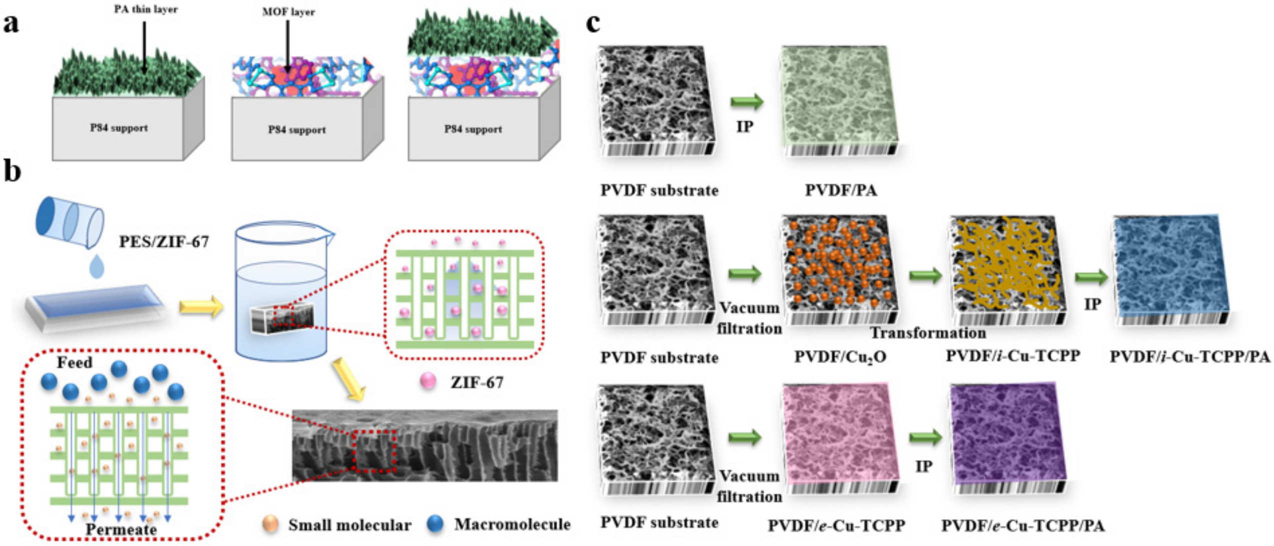

Figure 4. (**a**) Structures of the three membranes synthesized: the TFC membrane, composed by the polyimide P84® support, and the PA thin film [30]. (**b**) Schematic diagram of membrane preparation process and mass transfer mechanism diagram [31]. (**c**) Schematic illustration of the fabrication processes of the three TFC membranes based on commercial PVDF microfiltration substrate [33].

2.3. Separation Mechanisms of MOFs Membrane

During the membrane separation process, the separation medium exerts a driving force on both sides of the membrane so that the components on the raw material side can selectively permeate the membrane to affect the separation and purification. The metal-organic framework materials, as a new type of porous material, possess excellent crystallization effect and surface chemical composition, and have been reported to offer excellent separation efficiency for liquid molecules.

Metal-organic frameworks are classified as polycrystalline and mixed matrix films. The separation process relies on the pores in the dense polycrystalline films and follows a dissolution-diffusion mechanism. Figure 5 shows that the solvent and solute do not interact, and penetrate the cortex through molecular diffusion. Simultaneously, the polycrystalline film can also adsorb certain impurities in the solution. Therefore, selective adsorption and molecular sieving often coexist in most nanofiltration separation processes; known as selective adsorption-molecular sieving process. Mixed matrix membranes (MMMs) (Figure 6) are formed by metal-organic framework nanocrystals uniformly embedded in an organic polymer matrix. The principle is to use the difference in the dissolution and diffusion rates in the membrane to achieve separation under the pressure difference between the two phases.

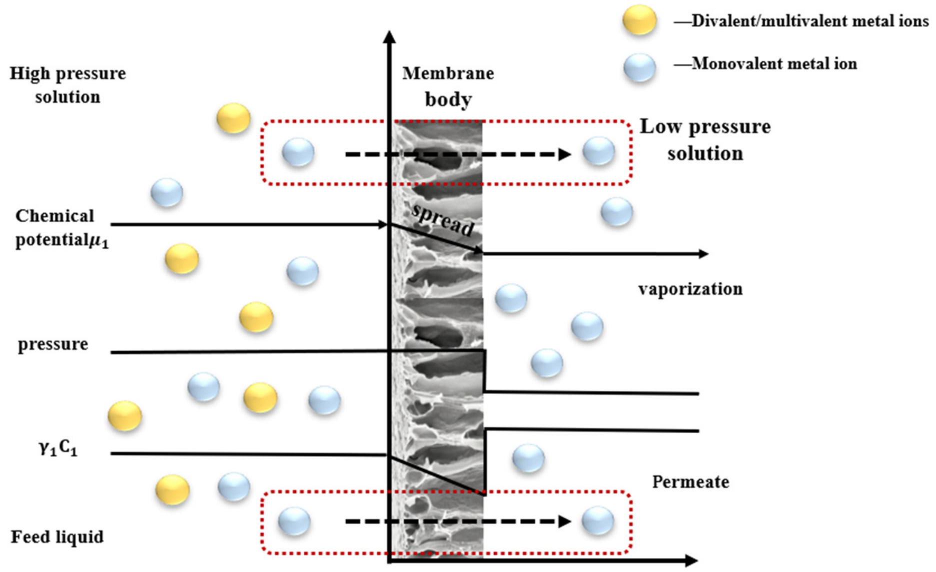

Figure 5. Solution-diffusion model.

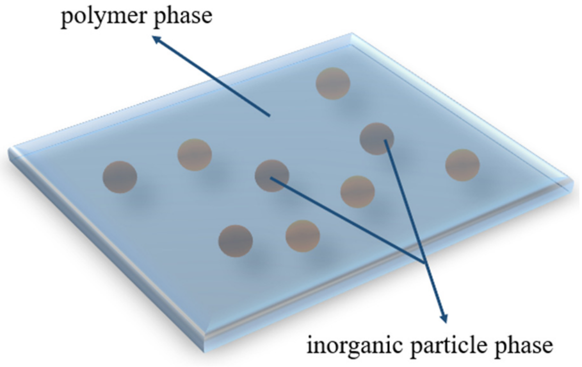

Figure 6. Structure of MMMs.

The ZIF-7-copolymerized silicone rubber (PebaxW) mixed matrix membrane prepared by Li et al. [34] had excellent separation performance for CO/CH$_4$ and CO/N$_2$. The separation selectivity of the PebaxR membrane was improved by more than double due to the highly efficient molecular sieving in the pores, due to the incorporation of ZIF-7 (pore window diameter of 0.29 nm) nanoparticles. Bae et al. [35] prepared a ZIF-90-polyimide (6FDA-DAM) mixed matrix membrane, which had significantly improved separation compared to polymer membranes, which closely compared with the selective adsorption-molecular sieving process of ZIF-90. Zornoza et al. [36] prepared a polymerized matrix membrane based on a flexible NHz-MIL-53 crystal. They observed an increase in separation selectivity with an increase in pressure within a certain range. This phenomenon was reported to be on the basis of the pore breathing of the flexible materials.

In summary, MOF nanocrystals have narrow sieving channels and preferentially adsorb permeable components. According to the adsorption-diffusion mechanism, the nanocrystals transfer molecules in a selective adsorption-molecular sieving process, offering a significantly improved separation performance of the mixed matrix membranes.

3. Application of MOFs Nanofiltration Membrane in Salt Lake

It is well known that natural seawater and salt lake brines are rich in lithium [37,38]. The following section attempts to present an update on the application of the MOF nanofiltration method for separation from lithium resources.

3.1. Technology Review on Lithium Extraction Method from Salt Lake

Figure 7 presents a thorough analysis of the literature pertaining to applications of various technologies for the separation of magnesium and lithium from brine: the solar cell method, precipitation method [39,40], ion exchange adsorption method, calcination leaching method [41], solvent extraction method, and membrane method [42]. Table 4 summarizes and compares the merits and demerits of the different technologies specific to its application to the separation of magnesium and lithium from salt lake brine [43,44].

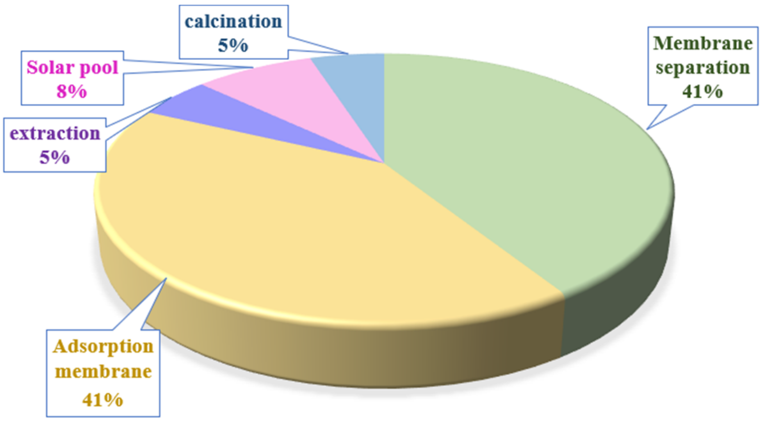

Figure 7. Proportion of actual capacity of lithium carbonate in magnesium lithium separation technology.

Table 4. Preparation method of MOFs [45].

Method	Type	Advantage	Disadvantage
Extraction method	• Organic extraction • Ionic liquid extraction	• Good selectivity • Environment friendly	• Higher cost • serious pollution • Complex preparation
Adsorption method	• Manganese ion sieve • Titanium ion sieve • Aluminum adsorbent	• Stable reaction • Larger capacity • Good selectivity	• Serious pollution • Easier agglomeration • Capacity attenuation
Reaction/separation coupling		• Mild conditions • Higher utilization	• Sodium salt
Membrane method	• Nanofiltration • Electrodialysis	• Simple process • Good selectivity • Low consumption	• Complex processing
Electrochemical method		• Good stability • Environment friendly	• Higher consumption • Higher requirements

Based on the review, it can be determined that the utilization of electrodialysis and electrochemical methods are energy intensive, and are suitable for salt lake brine with a low Mg^{2+}/Li^{+} ratio. The precipitation/calcination method produces large amounts of waste residue high in salt content, as well as being energy intensive. The extraction process utilizes organic solvents and ionic liquids as extractants, with high separation efficiency and yield. However, it is also affected by severe equipment swelling, solvent loss, and atmospheric pollution. The Mg^{2+}/Li^{+} ratio in salt lake brines in China is above 50. At that high ratio, selective lithium extraction is challenging, as both Mg^{2+} and Li^{+} show very similar ionic properties in aqueous solutions.

3.2. Current Status of MOF NF Membranes in Brine Applications

The section below provides experimental and theoretical references for developing MOFs-based membrane materials for lithium extraction from salt lakes. In recent years, nanofiltration technology has been widely used as an emerging and environmentally friendly membrane separation technology to deal with high Mg^{2+}/Li^+ ratio salt lake brine. Affected by steric hindrance and membrane pore sieving, the NF membrane retains more divalent/multivalent ions and passes more monovalent ions (Figure 8). Nanofiltration membranes based on MOFs have been widely used for metal ion separation in salt solutions [46], due to their ordered pore structure, tunable pore size, and modifiable functions [47,48]. With lithium being such an important mineral for sustainable development, extraction from salt lake brine utilizing MOFs nanofiltration membranes demonstrates excellent future prospects.

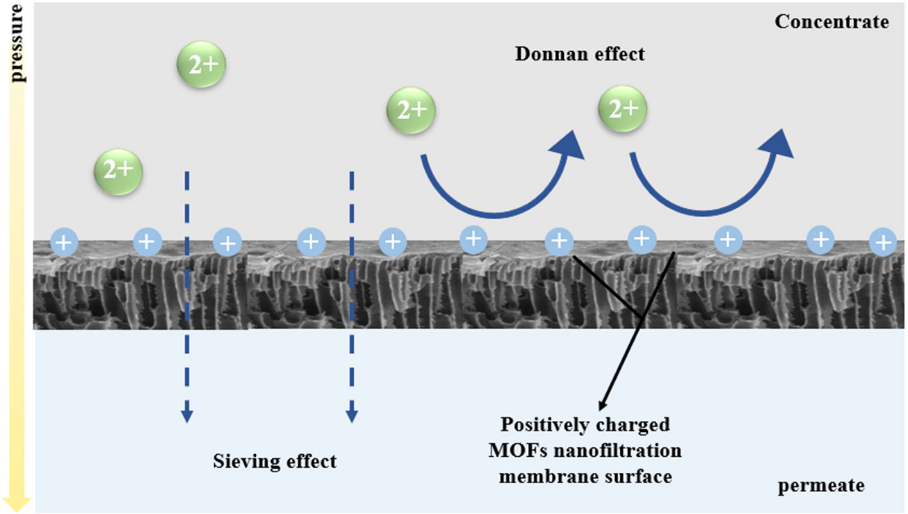

Figure 8. Separation process of MOFs nanofiltration membrane.

Guo et al. [49] synthesized a PSS@HKUST-1-6.7 nanofiltration membrane using polystyrene sulfonate (PSS) threads and HKUST-1 MOF using an in situ constraint conversion method. The membrane was anchored by a three-dimensional salt-based network with a Li^+ flux of 6.75 $mol \cdot m^{-2} \cdot h^{-1}$, five orders of magnitude higher than the original HKUST-1 membrane. The ideal selectivities for Li^+/Na^+, Li^+/K^+, and Li^+/Mg^{2+} were 78, 99, and 1815, respectively. Zhang et al. [50] used polyvinyl chloride as a matrix and six different metalorganic frameworks (MOFs@PVC) to separate Li^+ and Mg^{2+} in the solution. The pore size, sieving, and sulfonation effects of MOFs were evaluated by the current-voltage (I-V) method (Figure 9a). The results indicated beneficial effects of smaller pore size and sulfonation of MOFs for the separation of magnesium and lithium. The diffusion coefficient of lithium ions was 2.0×10^{-10} $cm^2 \cdot s^{-1}$, while that of magnesium ions was 4.67×10^{-11} $cm^2 \cdot s^{-1}$. The above work used sulfonated MOFs to improve nanofiltration performance and highlighted the prospects of stable sulfonated zirconium-based MOFs for magnesium-lithium separation, providing a potential option for lithium recovery from salt lake brines. Although highly stable zirconium-based MOF films have recently been developed, fundamental understanding is still in its infancy [51]. Thus, it is imperative to develop MOF nanofiltration membranes with a good interception and water permeability. Cong et al. [52] fabricated continuous MOF-303 aluminum films on α-Al_2O_3 substrates by in situ hydrothermal method based on size sieving and electrostatic repulsion mechanisms (Figure 9b). They reported good divalent ion rejection and permeability, with a $MgCl_2$ rejection of 93.5% and a Na_2SO_4 rejection of 96.0%, at a permeation flux of 3.0 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1} \cdot \mu m$. Liu et al. [53] prepared a hollow-fiber alumina-supported UiO-66 desalination membrane, which repels multivalent ions due to the pore sieving effect. They reported excellent multivalent ion rejection of 86.3% for Ca^{2+} and 98.0% for Mg^{2+}. Water permeability was also reported for MOF nanofiltration membranes prepared with alumina, zirconium, and zeolite. In order to prevent the oxidation of aluminum oxide, anodic aluminum oxide (AAO) has been widely used in separating magnesium and lithium as a supporting membrane in recent years. Wang et al. [54] combined ZIF-8 and UiO-66 to prepare MOF materials using the size-sieving effect. Moreover, MOF nanofiltration membranes were prepared with anodic aluminum oxide (AAO) as support. Recently, Xiao et al. [55] prepared a Uio-66-based bilayer (-$(COOH)_2$ and -NH_2) membrane by in situ growth method for the separation of magnesium and lithium from Qinghai Salt Lake brine. The film is also known as bilayer zirconium-metalorganic framework (MOF-on-MOF) film (Figure 9c). The membrane was reported to have nano-scale cavities, windows, and functional groups, which facilitate Mg^{2+} and Ca^{2+} to selectively transport K^+, Na^+, and Li^+. The membrane had good separation efficiency for magnesium and lithium. The selectivity of Li^+ and Mg^{2+} was as high as 90.8%, and its Mg^{2+}/Li^+ selectivity was 2.93 times higher than that of the UiO-66-NH_2 film.

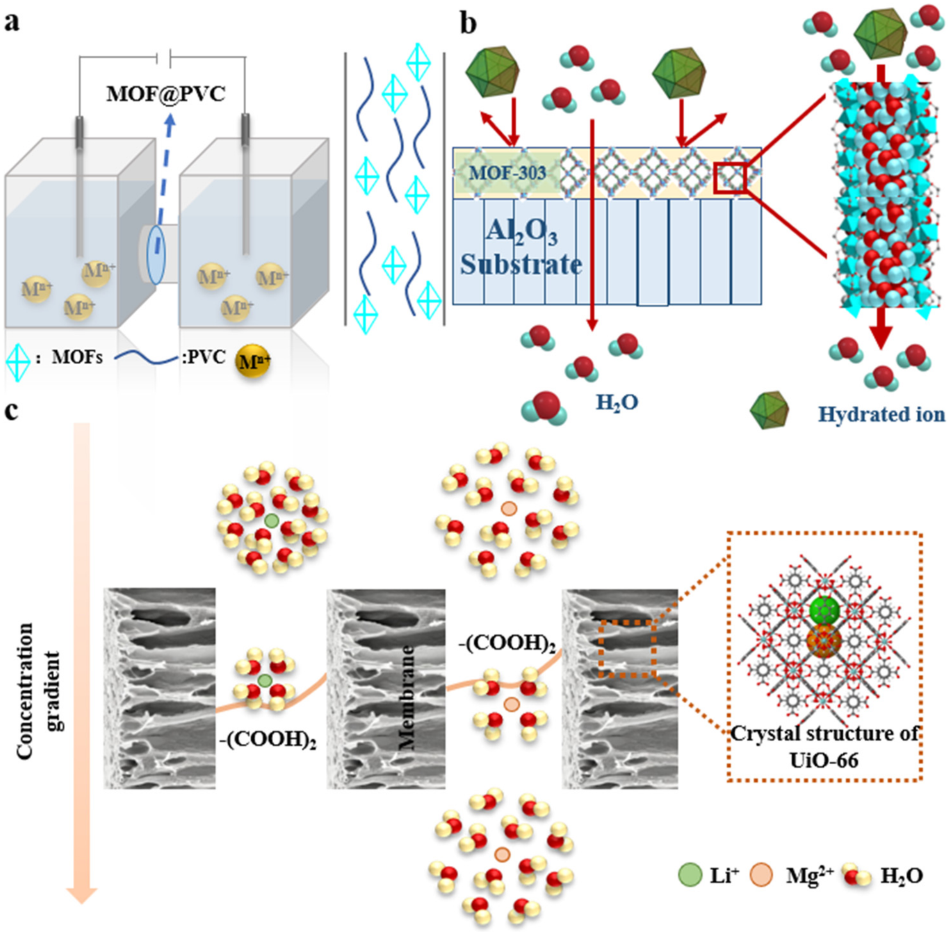

Figure 9. (**a**) The schematic diagram of the test for ion conductivity and the photo of the setup for ion conductivity [50]. (**b**) Schematic representation of water desalination with a metal−organic framework MOF-303 membrane [52]. (**c**) UiO-66-$(COOH)_2$-on-UiO-66-NH_2 membrane for Li^+ recovery [55].

PVC-based membranes were also trialed for the separation of magnesium-lithium from solution. The membrane had strong mechanochemical stability and minimal steric hindrance of transmembrane migration in salt solutions. Furthermore, the attraction between sulfonic acid groups and metal ions was reported to affect the selective migration of Li^+ to Na^+, K^+, and Mg^{2+}. Additionally, the sulfonated MOF nanofiltration membrane could control the pore structure as spongy and enhance membrane retention. The holes and exposed regions of the alumina-supported membrane provide a shortcut for a resistance-free and non-selective transport of metal ions, which are easy to prepare, having good mechanical and chemical stability [56,57].

4. Discussion

The successful use of MOF nanofiltration membranes is due to their unique selectivity among expected isolated species. To achieve the best separation effect, select the appropriate MOF materials based on the different magnesium-lithium ratios of the brine. Based on the advances that have been reviewed in this study, the separation mechanism is the most significant for the research and development of MOF nanofiltration membranes. The mass transfer process was described by selecting the corresponding mathematical model of the MOFs nanofiltration membrane separation process. The calculation of the mass transfer coefficient is conducive to reasonable optimization by changing the external conditions of the MOFs nanofiltration membrane, such as MOFs material selection, its preparation process optimization, and its particle sizes. Internal conditions such as membrane thickness, membrane pore structure, and pore radius can also improve selectivity and permeability. Therefore, establishing and enhancing the mass transfer process based on the reasonable mathematical model is expected to achieve efficient lithium extraction from salt lake brine with a high magnesium-lithium ratio using MOFs nanofiltration membrane, which is beneficial to China's long-term development strategy.

5. Conclusions

5.1. Conclusions

MOF nanofiltration membranes have received considerable attention from the scientific community, owing to its possible separation applications. A number of attempts have been made to assess its effectiveness for the separation of Li^+ from salt water brine. The introduction of MOF materials into nanofiltration membranes has not only expanded its application, but also opened up new directions for preparing nanofiltration membranes. Although a variety of MOF porous base membranes with sub-nanometer pore sizes have been developed for brine solution separation, it is plagued by a number of issues which can be summarized as follows:

(1) Water stability: Most MOF materials are unstable in water, which not only limits the selection of MOF materials to prepare nanofiltration membranes, but also limits the application of MOF nanofiltration membranes for the extraction of lithium from salt lakes.

(2) Dispersion: MOF materials are prone to agglomeration in pure solvents or polymer solvents. Agglomeration mitigation is carried out by stirring or modification of MOFs. However, it is still not conducive to the uniform preparation of MOF nanofiltration membranes.

(3) Particle size: The crystal size of MOFs can be effectively controlled by grinding and modification. However, the internal pore size of some MOF nanofiltration membranes is large, which is not conducive to improving the retention rate of solutes.

(4) Hydrophobicity: The aromatic organic framework in MOFs has a certain hydrophobicity, so it has influence on the water flux of the nanofiltration membrane.

(5) Compatibility: The MOF layer has weak adhesion to the matrix, which may cause perforation and stability problems during filtration.

(6) Low thermal stability and poor solvent resistance: As a result, the polymer substrate cannot be used as a support layer for MOF growth. Instead, inorganic supports are chosen for MOF growth.

In summary, MOF nanofiltration membranes have great potential in intercepting solute ions, and hence, further research should be directed towards overcoming the shortcomings summarized above, to harness the beneficial effects.

5.2. Future Prospects

In salt lake brine with high magnesium-lithium ratio, the generality and specificity of Li^+ transport behavior in the pore structure of nanofiltration membrane should be strengthened in order to significantly improve the separation effect of MOFs nanofiltration membrane. According to the characteristics of ions contained in salt lake brine, it is promising to design MOF nanofiltration membranes with targeted pore morphology and surface charge.

In the future, it will be important to conduct in-depth research on the problems encountered in adding MOFs to nanofiltration membranes. For example, selecting appropriate metal ions, organic ligands, and their modification will optimize the performance of the material. At the same time, compounding with enzymes, metal nanoparticles, and quantum dots will also enhance the relevant properties of the membranes. In the synthesis process of MOFs, the chemical concentration ratio of synthesizing MOFs with smaller particle sizes can improve the particle size and improve the stability of MOFs; modification of MOFs with chemical reagents can improve dispersibility, hydrophilicity, and compatibility of MOFs with polymer substrates; breaking through the limitations of MOFs in the application of nanofiltration membranes, the wide application of MOFs nanofiltration membranes is realized through a novel preparation method of MOFs.

In summary, the performance optimization of metal-organic framework materials should adopt reasonable methods, such as research from the aspects of effect, ease of operation, universality, and economics. Finally, MOF nanofiltration membranes are widely used to solve practical problems and do not only remain in the experimental stage.

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