Review

Adsorption and separation technologies based on supramolecular macrocycles for water treatment

Qian Lin [a,b,1], Xiaolong Ding [a,1], Yuansheng Hou [c], Wajahat Ali [d], Zichen Li [b], Xinya Han [a,*], Zhen Meng [e,*], Yue Sun [b,*], Yi Liu [b]

[a] School of Chemistry and Chemical Engineering, Anhui University of Technology, Maanshan 243002, China
[b] State Key Laboratory of Separation Membrane and Membrane Process, School of Chemistry, Tiangong University, Tianjin 300387, China
[c] QingHai Salt Lake Industry Co. Ltd., Golmud 816099, China
[d] Department of Chemistry, University of Baltistan, Skardu 16100, Pakistan
[e] School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210023, China

ARTICLE INFO

ABSTRACT

The escalating challenges in water treatment, exacerbated by climate change, have catalyzed the emergence of innovative solutions. Novel adsorption separation and membrane filtration methodologies, achieved through molecular structure manipulation, are gaining traction in the environmental and energy sectors. Separation technologies, integral to both the chemical industry and everyday life, encompass concentration and purification processes. Macrocycles, recognized as porous materials, have been prevalent in water treatment due to their inherent benefits: stability, adaptability, and facile modification. These structures typically exhibit high selectivity and reversibility for specific ions or molecules, enhancing their efficacy in water purification processes. The progression of purification methods utilizing macrocyclic frameworks holds promise for improved adsorption separations, membrane filtrations, resource utilization, and broader water treatment applications. This review encapsulates the latest breakthroughs in macrocyclic host-guest chemistry, with a focus on adsorptive and membrane separations. The aim is to spotlight strategies for optimizing macrocycle designs and their subsequent implementation in environmental and energy endeavors, including desalination, elemental extraction, seawater energy harnessing, and sustainable extraction. Hopefully, this review can guide the design and functionality of macrocycles, offering a significantly promising pathway for pollutant removal and resource utilization.

1. Introduction

The dual pressures of population growth and climatic fluctuations intensify global water shortages [1–5]. Concurrently, there is a rising concern regarding micropollutants in potable water sources, stemming from municipal, industrial, and agricultural effluents [6]. These micropollutants, encompassing hormones, pharmaceuticals, pesticides, and industrial agents, pose threats even in minimal concentrations. Given the economic and environmental impacts of conventional water treatment materials, the shift toward affordable, eco-friendly nanostructured alternatives without compromising key physicochemical attributes has become paramount [7]. The quest for innovative and sustainable methodologies to access nonconventional water sources [8], such as seawater [9–11], brackish groundwater [12], and wastewater [13], is crucial to supplementing the available water from natural hydrological cycles.

Leveraging inherent porosity, nonthermal adsorptive separation emerges as a cost-efficient and energy-conservative solution. Furthermore, the rising emphasis on membrane separation technologies, with their potential to address energy and environmental constraints, is noteworthy [14, 15]. Membrane bioreactors are gradually being used for the treatment of urban and industrial wastewater. The ideal membranes should have the following advantages: low cost, easy to obtain, anti-pollution, high reuse rate, and excellent separation performance. Zhang et al. [16] improved the filtration performance by adding activated carbon and laccase-immobilized activated carbon. Meanwhile, a bionic dynamic membrane was prepared by physical adsorption and filtration of carbon nanotubes and laccase for the advanced treatment of dye wastewater [17]. Notably, Zhang et al. studied the membrane fouling mechanism of aerobic granular sludge, which provided sufficient theoretical basis for further understanding of the membrane fouling mechanism of AGS in membrane

filtration [18,19]. Chemists further improved the membrane performance by preparing high-precision functional coatings. Geng et al. used Metal−phenolic networks to modify the surface [20]. The membranes can purify industrial wastewater by removing trace organic pollutants and heavy metals. Likewise, Yang et al. [21,22] used atomic layer deposition/sequential osmosis synthesis engineering strategies for building functional materials. It is imperative to distinguish the objectives when utilizing membrane processes for solute extraction and water production, as the underlying separation aims differ. Ultimately, the role of molecular structures in determining water treatment characteristics is undeniable.

Macrocyclic structures along with related functional materials, such as crown ethers [23,24], cyclodextrins (CDs) [25–28], calix[n]arenes (CA [n]s) [29,30], and pillar[n]arenes (PA[n]s) [24–26], have been extensively studied for applications in separation, adsorption, catalysis, and drug transport. Tian et al. [27] summarized the work on supramolecular macrocyclic structures for intelligent stimulation-responsive drug delivery systems. Zhang et al. [30] summarized the selective sensing and transport of ions and chiral objects in supramolecular macrocyclic structures. In commercial chiral columns on the market, cyclodextrin and crown ether are used as chiral separation media to prepare the chiral separation column [31]. A detailed evolution of these supramolecular macrocycles is illustrated in Fig. 1. These entities, with their structurally consistent frameworks and modifiable sizes, can encapsulate various guest molecules through interactions like van der Waals forces, electrostatic associations, and hydrogen bonds. Notably, these macrocyclic entities, with their innate ability for molecular recognition and binding, exhibit remarkable adsorptive efficacy for organic micropollutants in water. Moreover, when used as foundational units, they offer prospective materials for membrane development characterized by high selectivity and reversibility. Previous research has explored a range of responsive interfacial materials by integrating these macrocyclic structures with reactive features [32–39]. To date, multiple research groups have documented the amalgamation of host-guest systems to craft biomimetic gateways [38,39,40–44]. With the synergistic and directional attributes of noncovalent interactions, membranes rooted in host-guest chemistry amalgamate the best of both worlds, finding their niche in membrane and adsorptive separation techniques.

This review underscores the latest advancements in the application of supramolecular macrocycles for water treatment. Initial discussions center on the characteristics of supramolecular macrocycles. Attention is then drawn to diverse regulatory behaviors and mechanisms observed in macrocyclic adsorption and membrane separations. While membrane filtration is a staple in water treatment, its potential for selective solute separation and resource recovery is gaining traction as a research frontier. Hence, advancements in membranes based on macrocyclic hosts, especially in industrial wastewater treatment and resource extraction, are further explored. The concluding section projects future trajectories in macrocyclic host-guest chemistry. This review aims to inspire novel approaches and insights within the realm of adsorption and membrane separation technologies.

2. Characteristics of supramolecular macrocycles

Supramolecular macrocycles are renowned for their inherent cavities and distinct properties, which enable them to selectively bind and recognize guest molecules. This section delves into the structural attributes of macrocycles frequently employed in separation tasks. CDs, composed of 6–12 D-glucopyranose units, are sourced from common plant starches like wheat, corn, and potato [41]. These molecules, featuring their hydrophilic exteriors and hydrophobic cavities, can encapsulate various entities, ranging from organic molecules to inorganic ions and gases. Notably, the annular pores within CDs are rich in primary and secondary hydroxyl groups, serving as chelation and nucleophilic sites and facilitating precise molecular interactions [45–48]. Cucurbit[n] urils (CB[n]s), where n ranges from 5 to 8 and 10, are symmetrical structures derived from glyburide and formaldehyde condensation [49]. Exhibiting stability and organic solvent insolubility, CB[n]s possess inner cavities adept at complexing with metal ions or organic ammonium ions. The interactions involve hydrophobicity, ionic-dipolar forces, or hydrogen bonds between CB[n]s and guest entities. CA[n]s, introduced by Gutsche et al. in the 1970s, draw their name from their resemblance to a Greek chalice [50]. Constructed from methylene-bridged phenol units, CA[n]s offer greater structural flexibility than crown ethers and CDs. This adaptability, combined with a propensity for conformational shifts, allows them to interact with both ions and neutral molecules [51].

Subsequently, PA[n]s were introduced by Ogoshi et al. [52]. Structurally, PA[n]s are composed of hydroquinone or hydroquinone ether, bridged with para-methylene, creating a symmetrical columnar configuration. Their internal cavity is characterized by hydrophobic π-properties, and their adaptable peripheries facilitate binding to neutral or
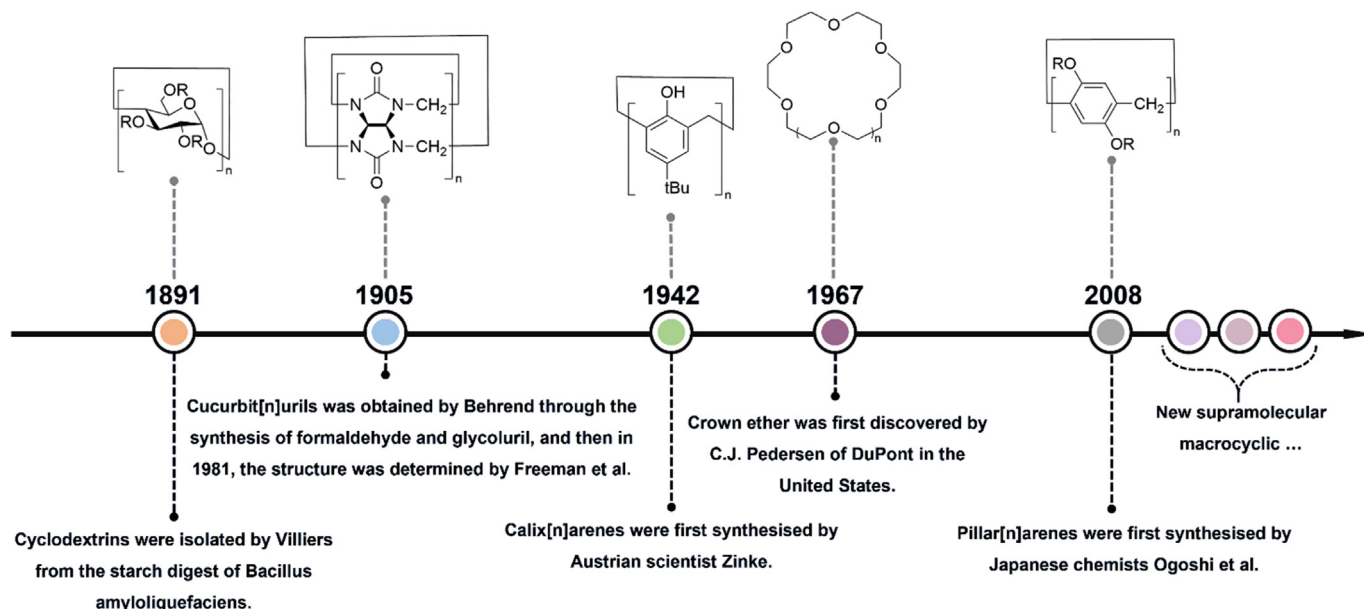

Fig. 1. Structural representations of macrocyclic host molecules.

electron-deficient entities [53,54]. Previously, a collection of responsive interfacial materials was constructed by anchoring these macrocyclic hosts with reactive features. With the evolution of macrocyclic chemistry, contemporary macrocyclic structures like resorcinarenes, cyclotriveratrylene, and cyclotetrabenzoin have emerged [55], paving the way for the development of advanced membrane materials.

3. Molecular adsorption and membrane filtration technologies

Various contaminants, such as heavy metal ions, dyes, organic micropollutants like antibiotics, and viruses, differ in size, as illustrated in Fig. 2a. Water pollutant treatments primarily rely on adsorption and membrane filtration strategies. Molecular adsorption refers to the uptake of molecules or ions by a material from its surrounding environment (Fig. 2b). This process is based on the principle that adsorption minimizes interfacial energy. The efficacy of adsorption correlates with the available surface area. Based on the nature of intermolecular forces between the adsorbate and the adsorbent, adsorption can be categorized into physical, chemical, and ion exchange types [56,57]. Physical adsorption arises from weak interactions, including van der Waals forces, hydrogen bonding, and electrostatic attractions. Since no chemical reactions occur, the associated forces are relatively feeble, the adsorption heat is minimal, and desorption occurs with relative ease. Conversely, chemical adsorption results from the establishment of new chemical bonds between the adsorbate and adsorbent, rendering most adsorption in this category irreversible and accompanied by significant adsorption heat. The predominant interactions governing the relationship between adsorbents and adsorbates encompass hydrophobic effects, electrostatic interactions, covalent bonds, surface complexation, hydrogen bonding, π-π interactions, and dipole interactions [58].

Membrane separation is a favored technique in wastewater treatment, attributed to its cost-effectiveness, energy efficiency, eco-friendliness, and scalability. The addition of supramolecular macrocycles with innate cavities can bolster membrane stability and selectivity. Membrane separations can be divided into two primary mechanisms: size sieving [59] and electrostatic interaction, also known as Donnan exclusion [60] (Fig. 2b). Size sieving retains substances exceeding the molecular weight cutoff (MWCO) of the membrane. When a membrane retains over 90% of a specific substance, the molecular weight of that substance is indicative of the membrane's retention capacity. The Donnan effect, or the membrane's charge effect, denotes the electrostatic interaction between ions and the membrane's inherent charge. Electrostatic interactions, particularly for multivalent ions, are crucial when the membrane surface is charged [61]. While uncharged-molecule filtration predominantly operates through size sieving, charged-molecule filtration is driven by the charge effect. Various techniques are employed in membrane fabrication, including interfacial polymerization, vacuum-assisted self-assembly, dip-coating, spin-coating, squeegee-coating, and thermally-induced phase separation. The chosen method significantly influences membrane performance. Consequently, selecting the optimal preparation technique, considering the membrane's material characteristics and intended application, ensures enhanced efficacy and efficiency.

4. Macrocyclic adsorption in water treatment

4.1. Ionic pollutant removal

Heavy metals, owing to their persistence and nondegradability, have long posed significant environmental and health risks [62]. The notorious Minamata disease, attributed to mercury ion contamination of water and marine ecosystems, exemplifies the gravity of such threats. Particularly, Pb^{2+}, an extremely hazardous heavy metal, has been linked to Alzheimer's disease, dementia, neurodegenerative disorders, renal impairment, stunted bone growth, and behavioral anomalies, emphasizing the urgency of heavy metal extraction and removal research.

Li et al. [63] introduced a chitosan-functionalized CB[8], which displayed robust Pb^{2+} adsorption, attributed to the coordination between the CB[8] carbonyl group and the chitosan amino group [64]. Furthermore, two novel covalent organic frameworks (COFs) with strong crystallinity and stability were synthesized for alkali metal separation, utilizing either 18-crown-6 or 24-crown-8 units as the core (Fig. 3a) [65]. Calculations revealed pronounced K^+ binding to Py-B$_{18}$C$_6$–COF and Cs^+ affinity for Py-B$_{24}$C$_8$–COF. Significantly, Shetty et al. [62] introduced a meticulously crafted thioether-crown-rich mesoporous polymer, S-CX4P, based on calix[4]arene for mercury (Hg^{2+}) extraction from water (Fig. 3b). This polymer demonstrated remarkable Hg^{2+} uptake efficiency (1,686 mg/g) and a rapid initial adsorption rate [278 mg/(g·min)]. S-CX4P effectively reduced high Hg^{2+} concentrations from 5 ppm to drinking water-acceptable levels of 2 ppb or lower. Moreover, the polymer showcased facile regeneration at ambient conditions and sustained multiple usage cycles.

4.2. Removal of small molecules pollutants and biomacromolecules

The release of organic micropollutants in wastewater has dire environmental, freshwater scarcity, and public health implications. Reactive dyes, prevalent in textile the and dyeing sectors, offer benefits such as vibrant hues, ease of application, robust color fixation, and cost-effectiveness. In addition, the insecticide chlordecone (CLD), notable for its persistence and low water solubility, was once extensively deployed in the French West Indies, triggering a widespread public health crisis [66]. Even with discontinued production and usage, CLD contamination lingers. Levalois–Grützmacher et al. augmented the adsorptive capacity of activated carbon through chemical surface modifications, endorsing the synergy of activated carbon support and CD as the active site for CLD selective adsorption, fostering stable inclusion (Fig. 4a). γ-CD's proficiency as a chelating agent for CLD removal from
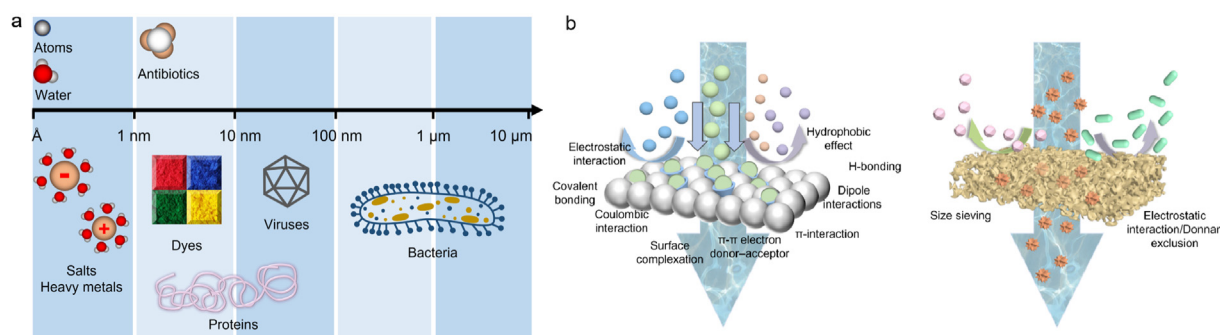

Fig. 2. (a) Size of water pollutants from micrometer to sub-nanometer; (b) schematic representation of adsorption and filtration mechanisms. Reproduced with permission from refs. [58,60], Elsevier.
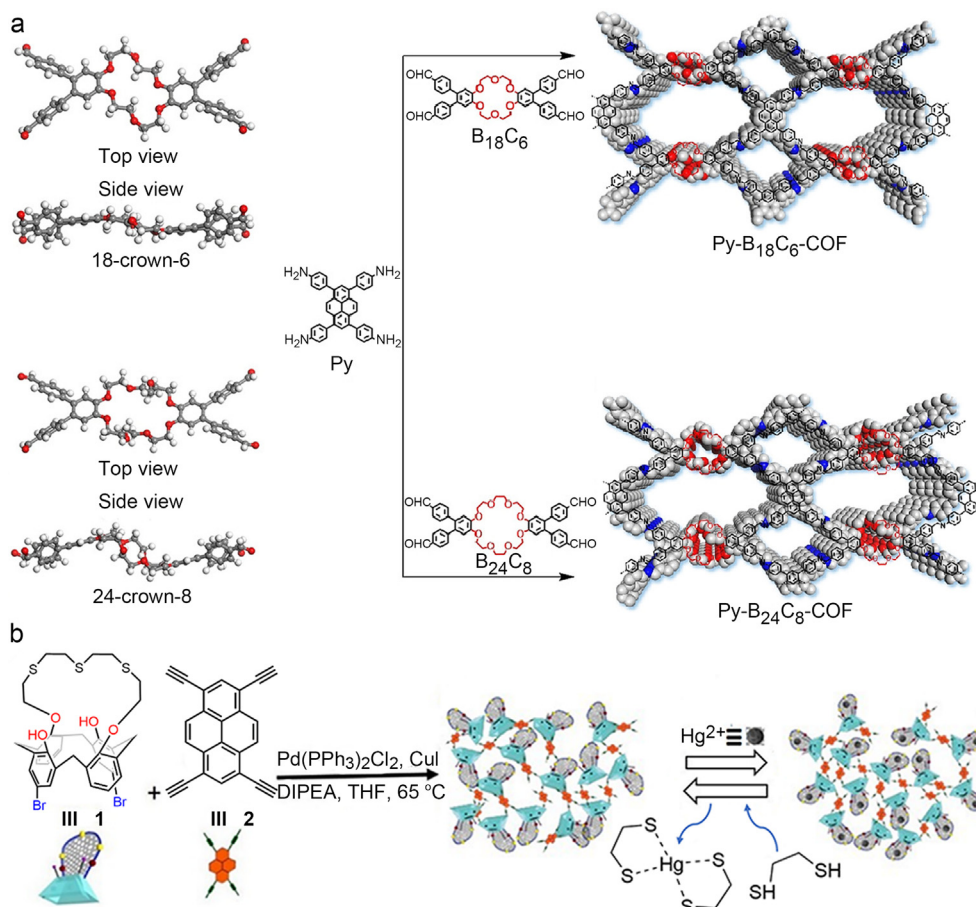
Fig. 3. (a) Synthetic scheme for Py-B$_{18}$C$_6$–COF and Py-B$_{24}$C$_8$–COF. Reproduced with permission from ref. [65], Wiley; (b) Schematic representation of the thioether-crown-rich calix[4]arene porous covalent polymer. Reproduced with permission from ref. [62], American Chemical Society. COF, covalent organic frameworks.

water was affirmed [66] (Fig. 4b). This complex can be effortlessly filtered from water using activated carbon. Ciprofloxacin (CIP) stands out for its remarkable stability and antibiotic efficacy. Cosma's group employed CD-based polymers crosslinked with 1–4 butanediol diglycidyl ether, suggesting recyclable nanosponges for environmentally responsible CIP extraction and recycling from water [67]. The resultant crosslinked polymers, boasting amorphous three-dimensional structures, showcased commendable swelling traits, underscoring predominant interactions between CIP's carboxylic acid groups and the polymers' positively charged surface. Furthermore, effective removal of pharmaceuticals and insecticides like diclofenac, carbendazim, furosemide, and sulfamethoxazole from water was achieved.

Emergent pollutants, such as biological macromolecules including proteins, nucleic acids, and polysaccharides, are now recognized as threats to water systems. The detrimental, persistent, and intricate nature of these pollutants, coupled with their treatment challenges, has heightened concern among both researchers and the public. Schaefer et al. fabricated fibers by integrating a blend of β-CD and polyethersulfone through electrospinning [68] (Fig. 4c). This inclusion of CD augments the fibers' micro-pollutant adsorption capabilities via inclusion complexes. Experimental outcomes revealed that, when augmented with β-CD, the fibers exhibited a 20% increase in E2 adsorption and an 80% uptick in CP adsorption compared to pure nanofibers.

5. Macrocyclic membranes for water treatment

5.1. Filtration of ionic pollutants

Research endeavors continuously focus on innovating strategies and materials for the extraction of heavy metal ions from water. Abdulkadir Sirit and his team developed liquid membranes utilizing the macrocyclic compound p-tert-butylcalix[4]arene 3-diethylaminopropyl diamide derivatives [69]. This method allowed the extraction of chromium (Cr) species in complex forms, efficiently transferring Cr^{6+} from acidic solutions. In the automotive catalyst domain, rhodium (Rh) stands out due to its distinct physicochemical characteristics. Tao et al. devised a strategy to separate Rh^{3+} from concentrated hydrochloric acid, employing a thin-layer oil membrane (TOM) extraction technique with 18C6 crown ether as the extracting agent [70] (Fig. 5a). Optimizing the membrane's thickness and increasing the aqueous phase's flow rate bolstered the flexibility of host molecules. This optimization facilitated enhanced interaction between the interfacial hydrated Rh (III) anion and the 18C6 molecules, alongside water-molecule interactions. Rh^{3+} was selectively isolated from mixed solutions containing Cu^{2+}, Co^{2+}, Ni^{2+}, and Fe^{3+} ions, even at minimal concentrations. Highlighting boron compounds and their potential environmental repercussions in water systems has raised alarms. Excessive human intake can lead to a plethora
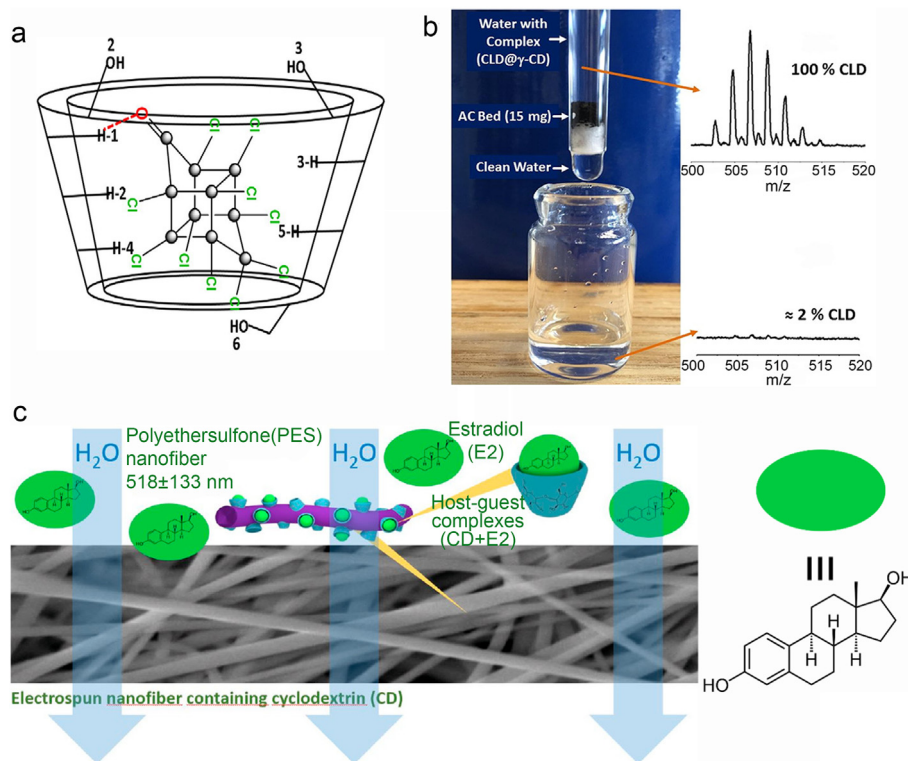
Fig. 4. (a) Proposed conformation of the CLD@γ-CD complex; (b) illustration of an activated carbon bed for water purification. Reproduced with permission from ref. [66], Elsevier; (c) CD-polymer composite designed for micropollutant removal from water. Reproduced with permission from ref. [68], American Chemical Society.

of health issues, ranging from nausea to potential fatalities. Addressing this, Chung et al. [71] utilized CA[*n*]s as a monomer in an aqueous solution, crafting membranes through interfacial polymerization. Serving as molecular sieves, CA[*n*]s offered additional channels within the polymer framework (Fig. 5b). Its hydrophilic sulfonate groups formed ionic bonds with the polyamide selective layer, producing thin-film nanocomposite (TFN) membranes that bolstered water transport while effectively reducing salt migration (Fig. 5c). This research paves the way for advancements in boron-specific treatment membranes.

5.2. Filtration of small molecules pollutants and biomacromolecules

Huang et al. [72] have introduced ultrathin macrocycle membranes, crafted via interfacial polymerization with per-6-amino-β-CD as the monomeric building block (Fig. 6a). These membranes exhibit permeability and shape-selectivity, attributed to their minimal thickness, regulated microporosity, and stratified macrocyclic architecture. Likewise, Liu's group [36] employed CDs to modify the exterior of MXene substrates, forming composite membranes through a vacuum-assisted self-assembly procedure. This membrane showcases remarkable efficacy in segregating dye wastewater. When compared with the native MXene membrane, the modified version demonstrated a permeate flux enhancement by 23.3-fold, achieving a staggering removal rate for methylene blue of over 99.7%. This efficacy is likely due to the membrane's charge effects combined with its size-selective sieving ability. Furthermore, pillararenes, characterized by their rigid and symmetrical framework, have been employed as innovative supramolecular hosts to modify the surface of MXene [35] (Fig. 6b). These structures regulate the interlayer gaps between adjoining nanosheets, introducing a systematically parallel, slit-like membrane architecture. This design addresses the typical poor water permeability seen in many densely packed two-dimensional membranes. Empirical data validated a substantial enhancement in antibiotic separation, driven by the size sieving mechanism coupled with electrostatic interactions between the membranes and antibiotic molecules. This innovative approach, focusing on the crafting of sub-nanochannels and

nanochannels on functional $Ti_3C_2T_x$ membranes, promises to pave the way for layered membrane applications in areas like seawater desalination and comprehensive wastewater management.

Dong et al. [73] pioneered an innovative affinity membrane, specifically designed to efficiently eliminate steroid hormones from water systems. The initial polymerization was conducted using 2-hydroxyethyl methacrylate (HEMA) and ethylene dimethylacrylate (EDMA) monomers in tandem with inert porogens. Subsequent to this, an affinity membrane was fabricated by tethering the β-CD ligand to the foundational poly(HEMA-co-EDMA) membrane via photodynamic disulfide linkages (Fig. 6c). Notably, this β-CD-enhanced affinity membrane exhibited a 30% elevation in E2 adsorption compared to the primary membrane. This improved performance is credited to the inception of inclusion-host–guest complexes. An intriguing feature of this development is the photodynamic nature of the disulfide bonds. This allows the affinity membrane to undergo UV-triggered regeneration of its inherent β-CD ligands after each adsorption cycle, thereby restoring its original affinity attributes. The novel approach of employing dynamic covalent bonds for tethering affinity ligands onto membranes introduces the potential to renew the adsorption capabilities of such membranes via photodynamic exchange. The biomimetic catalytic membranes exhibit powerful in situ regeneration efficacy as well as minimal fouling during oil-in-water emulsion separation. These new findings pave the way for energy-efficient applications in tackling energy and environmental issues [74]. In summary, macrocyclic molecular-structured materials demonstrate exceptional separation specificity, positioning them as ideal candidates for addressing a broad spectrum of pollutants present in industrial wastewater.

6. Exploiting macrocycles in seawater and salt lake resource management

Seawater and salt lake resource development is a crucial strategy for addressing challenges like water scarcity and the extraction of chemical resources. Several innovative approaches utilizing macrocyclic molecules have been recently explored. Chung et al. [75] pioneered pressure
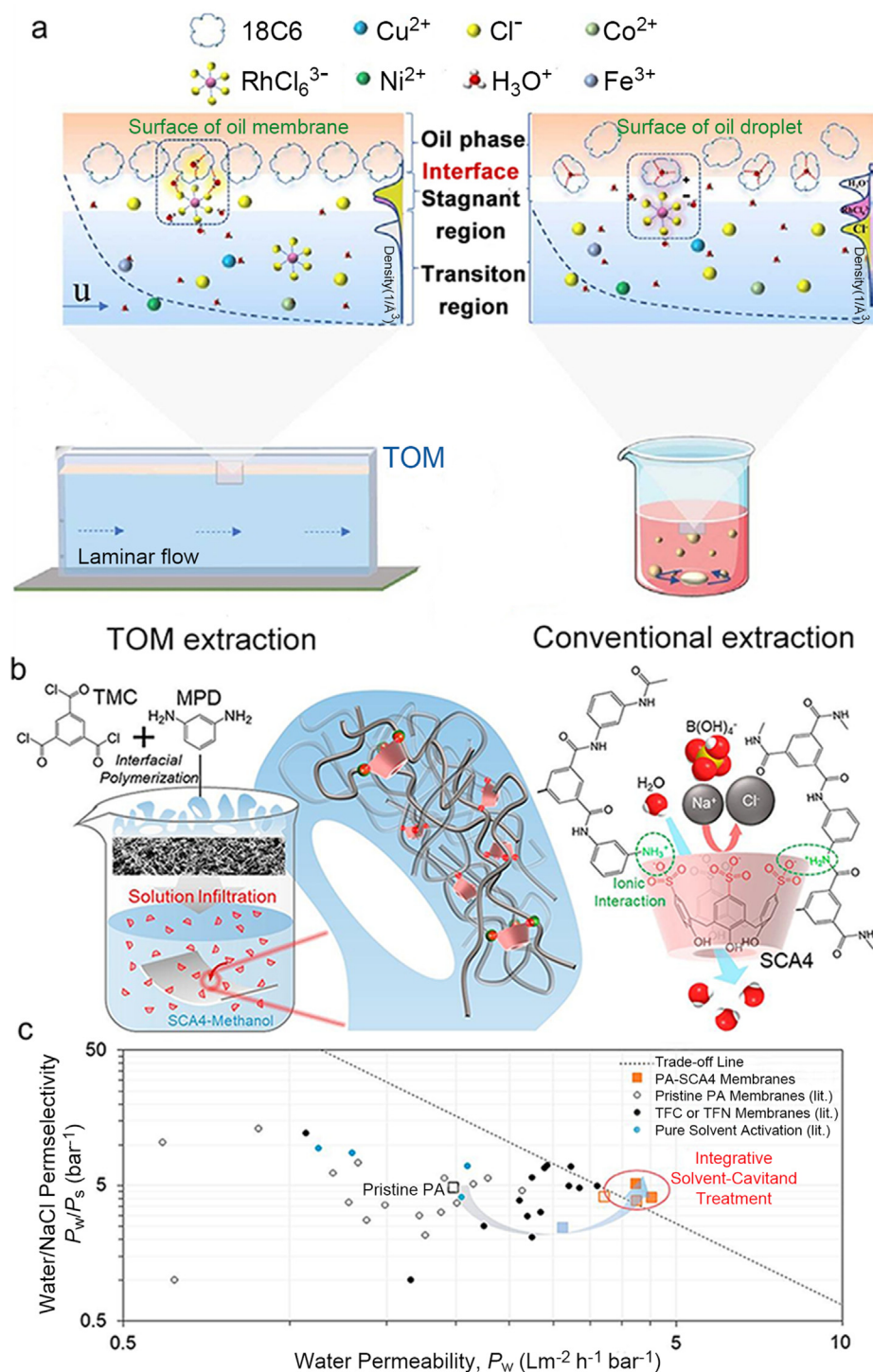
Fig. 5. (a) Mechanism diagrams of TOM extraction and conventional extraction. Reproduced with permission from ref. [70], Elsevier; (b) schematic illustration of an integrative solvent-cavitand treatment system; (c) comparison of permeability and selectivity across different membranes. Reproduced with permission from ref. [71], Elsevier. TOM, thin-layer oil membrane.

retarded osmosis (PRO) membrane technology to harness osmotic energy. Two variants of calix[*n*]arenes were integrated into the polyamide matrix and then solubilized in an m-phenylenediamine (MPD) solution via interfacial polymerization. This enhanced the selectivity of the resultant membranes due to the distinctive macrocyclic molecular structure and heightened molecular sieving capability. Drawing inspiration from the notable adhesion properties of octopus tentacles (Fig. 7a), Zhang et al. [76] incorporated cucurbit[5]uril into the two-dimensional MXene material to fabricate a membrane. Through a combination of size

sieving and charge effects, this membrane selectively concentrated uranyl carbonate from seawater, achieving this even in high-salinity environments due to potent interactions with the hydroxyl groups on the MXene surface (Fig. 7b). Furthering the research on uranium (U) extraction, Shao et al. [77] devised a cost-effective and straightforward technique for efficient U(VI) extraction. Their composite, a blend of cucurbit[6]uril and Fe ions with graphene oxide, exhibited substantial U(VI) adsorption capacity. This capability arises from the plethora of oxygen-rich functional groups within the composite. Similarly, Sun et al.
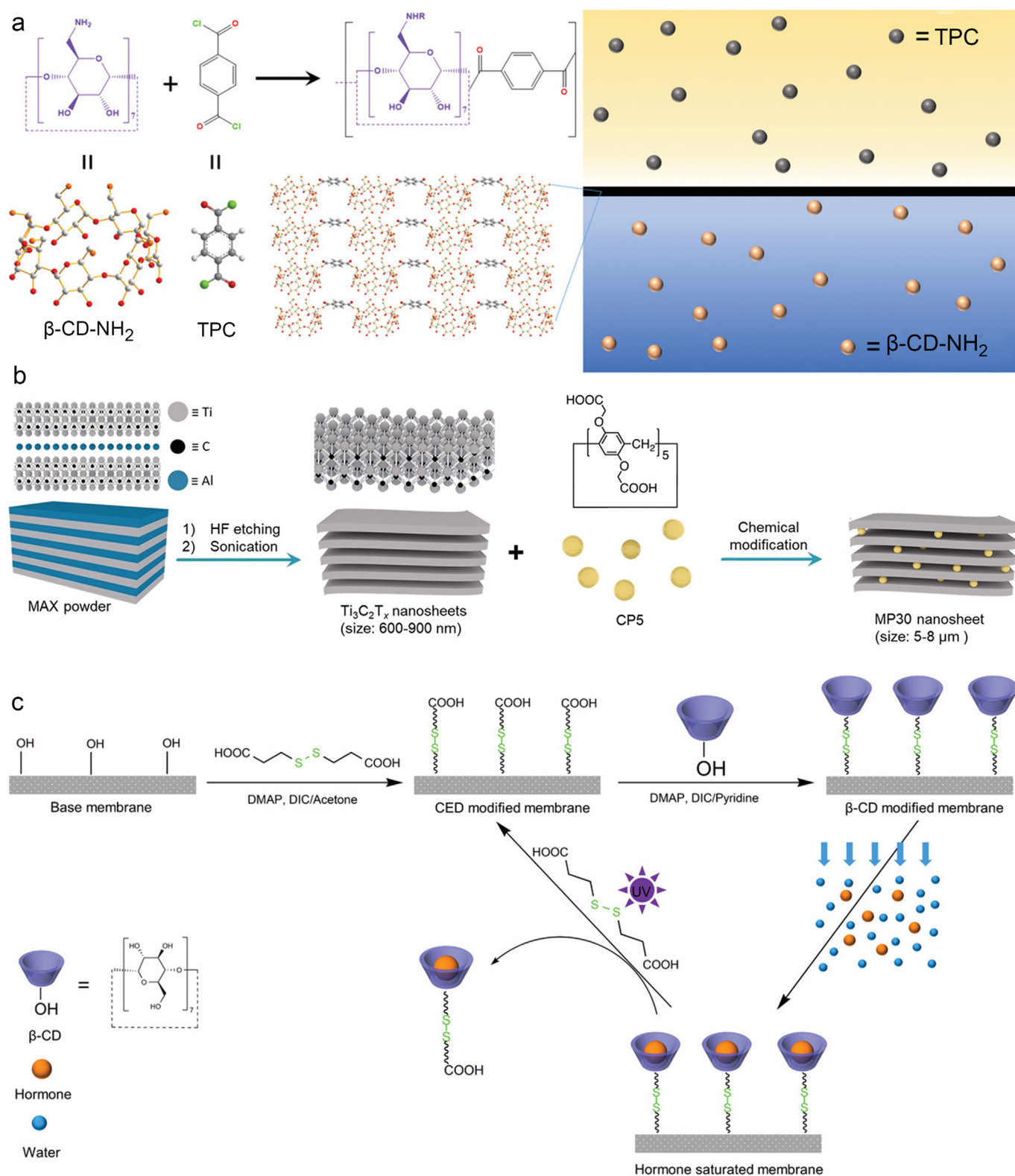
Fig. 6. (a) Synthesis process of the polyamide-CD membrane via interfacial polymerization. Reproduced with permission from ref. [72], Wiley; (b) Schematic preparation of MXene- pillararenes (MP) nanosheet, MP membrane. Reproduced with permission from ref. [35], Wiley; (c) representation of polymer membrane using disulfide linkage and photodynamic regeneration of β-CD. Reproduced with permission from ref. [73], Wiley. CD, cyclodextrin.

[78] developed cucurbit[6]uril-based membranes that showcased enhanced uranyl ion adsorption, facilitated by the formation of expansive cavities and residual nitrogen atoms (Fig. 7c).

Additionally, membrane technologies have shown great promise in advancing sustainable, cost-effective, and eco-friendly methods for extracting lithium from seawater and salt lakes. A primary challenge in
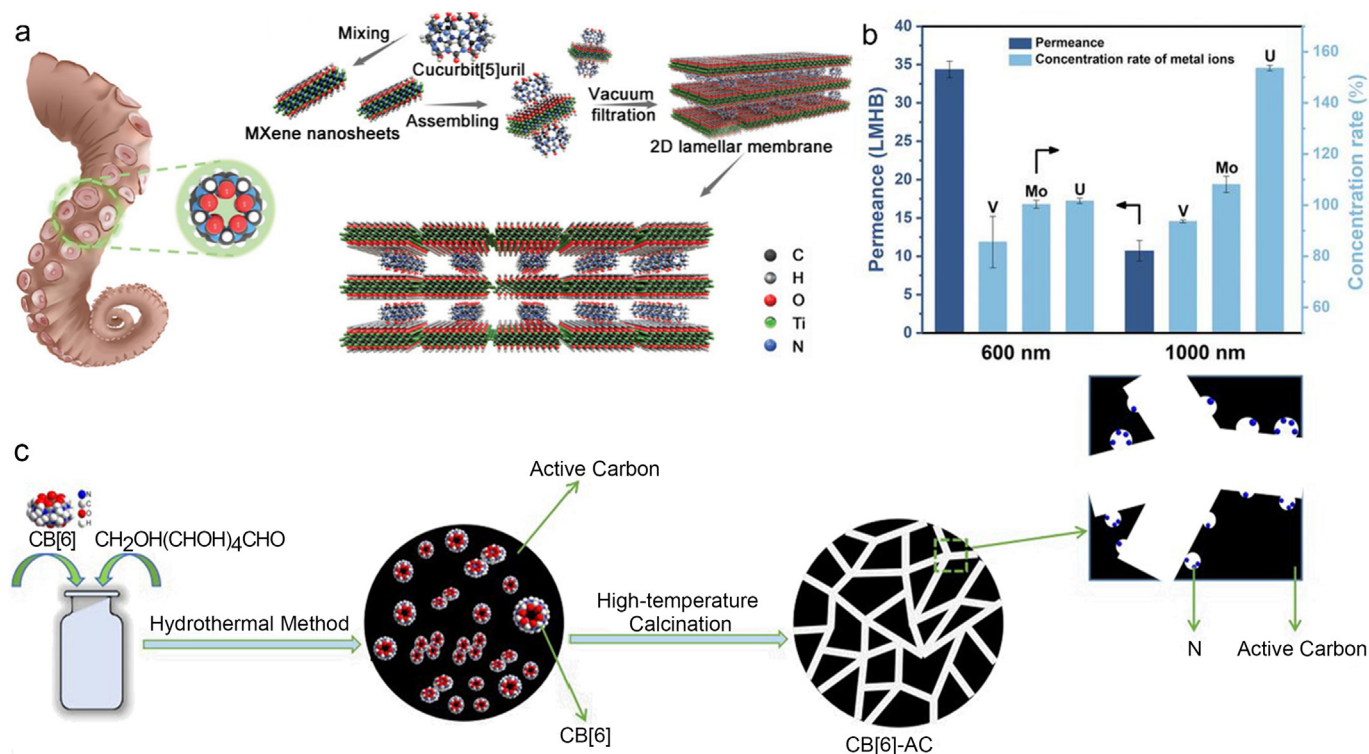
Fig. 7. (a) Illustration of CB5-supported Ti$_3$C$_2$T$_x$ membrane fabrication; (b) V/Mo/U separation in natural seawater using Ti$_3$C$_2$T$_x$/ cucurbit[5]uril membranes (TBM). Reproduced with permission from ref. [76], Wiley; (c) Sysnthesis procedure of macroporous carbon material for U(VI) adsorption. Reproduced with permission from ref. [78], Elsevier.

this extraction process is the separation of lithium ions from prevalent impurity metal ions like Mg^{2+}, Na$^+$, and K$^+$. Kazemabad et al. [79] introduced crown ether into polycation polyethylenimine (PEI), subsequently forming polyelectrolyte multilayer membranes (PEMMs) through a layer-by-layer deposition process. These membranes demonstrated pronounced Li$^+$/K$^+$ selectivity. This selectivity arises because the membrane's polymeric architecture restricts the formation of 2:1 potassium-crown ether complexes. Taking a different approach, Yoon's team integrated crown ether molecules into graphene-poly(ether sulfone) (PES)-based nanofiber membranes (CGPNFs) [80]. The inclusion of graphene nanosheets enhanced the nanofiber's stability while also augmenting its surface roughness and hydrophilicity. PES functioned as a foundational unit, bolstering the membrane's mechanical robustness. Additionally, crown ethers have been covalently linked to cellulose acetate backbones, forming adsorptive units within polyethylene membranes stabilized through intermolecular hydrogen bonding [81]. These innovative membranes achieved the efficient separation of Li$^+$ from larger cations, capitalizing on ionic-dipolar interactions.

Ruan et al. [82] introduced a mechanically interlocked three-dimensional porous organic framework utilizing crown ether (Crown-POF). This was further developed into porous thin-film nanocomposite membranes. Within this structure, four crown atoms alongside a single Ntert-amine atom function as adsorption sites, offering specific recognition and binding of Li$^+$ ions. Subsequently, Mao et al. [83] synthesized a distinctive polyamide membrane (14C4 PA) using the nonsolvent-induced phase separation (NIPS) technique, demonstrating the potential for efficient lithium ion capture. Similarly, Wang et al. designed nanofiltration membranes with elevated permeability by incorporating 1,4,7,10-tetraazacyclodecane (Cyclen). This design strategically leverages Cyclen's properties to achieve a high rejection of divalent ions, ensuring optimal lithium ion selectivity.

7. Conclusion and prospect

This review offers a synopsis of the advancements in macrocycle-based adsorption materials and membranes for water treatment, with an emphasis on their utilization in seawater and salt lake resources. The research posits that separation and purification technologies, leveraging supramolecular macrocycles characterized by robust structures and facile functionalization, hold promise for real-world applications. While supramolecular chemistry has seen significant exploration, applications involving macrocyclic hosts in separation and purification are still nascent. Momentum in this domain should prioritize understanding the relationship between structure and efficacy, encompassing molecular design, synthesis, and performance assessment. Key considerations include:

(i) Laboratory-based adsorption separation technologies often operate under idealized conditions. However, real-world industrial water sources present a vast array of pollutants in substantial quantities. The durability, reusability, and contamination resistance of macrocyclic hosts will be pivotal in determining their feasibility for large-scale applications. Controllably obtaining ultra-thin, defect-free large macrocyclic porous composite films/membranes is one of the key factors affecting film performance.

(ii) Membrane technologies tailored for water treatment face challenges related to scalability and fabrication techniques. This is particularly salient for emerging membrane materials, which currently hinder their extensive deployment in large-scale water treatment operations.

(iii) Given the strides in computational science, simulations are invaluable for assessing membrane separation performance. Molecular dynamics simulations, which track molecular temporal evolution, are crucial for forecasting material transport within constrained environments. A thorough grasp of the interplay between the thermodynamics

and kinetics of supramolecular macrocycles in separation processes is vital. Machine learning and artificial intelligence are considered powerful approaches to overcome the shortcomings of experimental methods. They may predict the effective receptor structures based on the associated data-driven calculations. Consequently, with the increased investigation on how macrocycle-based adsorbent/separation materials interact at the molecular level, optimal macrocyclic receptors for the desired separations will be created with the guidance of various machine learning and artificial intelligence programs.

Generally, innovations in macrocyclic supramolecular chemistry are anticipated to catalyze progress not only in environmental spheres like water treatment and lithium extraction from salt lakes but also in broader areas such as metal extraction and recycling. We also believe that challenges with macrocycle-based adsorption materials and membranes can be properly addressed in the future with the development of emerging synthesis and characterization techniques, especially for high-performance macrocycle-based materials. Such advancements are poised to invigorate associated disciplines and even foster novel fields of study.

CrediT authorship contribution statement

Q.L.: writing–original draft, writing–original revise. X.L.D. and Z.C.L.: investigation, writing–original draft. Y.S.H., W.A., and Y.L.: supervision, writing–review. X.Y.H., Z.M., and Y.S.: conceptualization, writing–review & editing.

Declaration of competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

References

[1] M. Elimelech, The global challenge for adequate and safe water, J. Water Supply Res. Technol. - Aqua 55 (2006) 3–10, https://doi.org/10.2166/aqua.2005.064.

[2] X. Wang, P.L. McCarty, J. Liu, N.Q. Ren, D.J. Lee, H.Q. Yu, Y. Qian, J. Qu, Probabilistic evaluation of integrating resource recovery into wastewater treatment to improve environmental sustainability, Proc. Natl. Acad. Sci. USA 112 (2015) 1630–1635, https://doi.org/10.1073/pnas.1410715112.

[3] C.M. Sales, P.K.H. Lee, Resource recovery from wastewater: application of meta-omics to phosphorus and carbon management, Curr. Opin. Biotechnol. 33 (2015) 260–267, https://doi.org/10.1016/j.copbio.2015.03.003.

[4] J.Y.M. Tang, F. Busetti, J.W.A. Charrois, B.I. Escher, Which chemicals drive biological effects in wastewater and recycled water? Water Res. 60 (2014) 289–299, https://doi.org/10.1016/j.watres.2014.04.043.

[5] R. Das, C.D. Vecitis, A. Schulze, B. Cao, A.F. Ismail, X. Lu, J. Chen, S. Ramakrishna, Recent advances in nanomaterials for water protection and monitoring, Chem. Soc. Rev. 46 (2017) 6946–7020, https://doi.org/10.1039/c6cs00921b.

[6] A. Alsbaiee, B.J. Smith, L. Xiao, Y. Ling, D.E. Helbling, W.R. Dichtel, Rapid removal of organic micropollutants from water by a porous β-cyclodextrin polymer, Nature 529 (2015) 190–194, https://doi.org/10.1038/nature16185.

[7] M.A. Shannon, P.W. Bohn, M. Elimelech, J.G. Georgiadis, B.J. Mariñas, A.M. Mayes, Science and technology for water purification in the coming decades, Nature 452 (2008) 301–310, https://doi.org/10.1038/nature06599.

[8] Y.J. Lim, K. Goh, R. Wang, The coming of age of water channels for separation membranes: from biological to biomimetic to synthetic, Chem. Soc. Rev. 51 (2022) 4537–4582, https://doi.org/10.1039/d1cs01061a.

[9] W. Zhang, Y. Zhu, X. Liu, D. Wang, J. Li, L. Jiang, J. Jin, Salt-induced fabrication of superhydrophilic and underwater superoleophobic PAA-g-PVDF membranes for effective separation of oil-in-water emulsions, Angew. Chem. Int. Ed. 53 (2013) 856–860, https://doi.org/10.1002/anie.201308183.

[10] B. Meng, G. Liu, Y. Mao, F. Liang, G. Liu, W. Jin, Fabrication of surface-charged MXene membrane and its application for water desalination, J. Membr. Sci. 623 (2021) 119076, https://doi.org/10.1016/j.memsci.2021.119076.

[11] W. Xian, X. Zuo, C. Zhu, Q. Guo, Q.-W. Meng, X. Zhu, S. Wang, S. Ma, et al., Anomalous thermo-osmotic conversion performance of ionic covalent-organic-framework membranes in response to charge variations, Nat. Commun. 13 (2022) 3386, https://doi.org/10.1038/s41467-022-31183-w.

[12] L. Ding, L. Li, Y. Liu, Y. Wu, Z. Lu, J. Deng, Y. Wei, J. Caro, et al., Effective ion sieving with Ti₃C₂Tₓ MXene membranes for production of drinking water from seawater, Nat. Sustain. 3 (2020) 296–302, https://doi.org/10.1038/s41893-020-0474-0.

[13] N.K. Khanzada, M.U. Farid, J.A. Kharraz, J. Choi, C.Y. Tang, L.D. Nghiem, A. Jang, A.K. An, Removal of organic micropollutants using advanced membrane-based water and wastewater treatment: a review, J. Membr. Sci. 598 (2020) 117672, https://doi.org/10.1016/j.memsci.2019.117672.

[14] C.Y. Tang, Z. Yang, H. Guo, J.J. Wen, L.D. Nghiem, E. Cornelissen, Potable water reuse through advanced membrane technology, Environ. Sci. Technol. 52 (2018) 10215–10223, https://doi.org/10.1021/acs.est.8b00562.

[15] R.P. Lively, D.S. Sholl, From water to organics in membrane separations, Nat. Mater. 16 (2017) 276–279, https://doi.org/10.1038/nmat4860.

[16] W. Zhang, W. Liang, Z. Zhang, Dynamic scouring of multifunctional granular material enhances filtration performance in membrane bioreactor: mechanism and modeling, J. Membr. Sci. 663 (2022) 120979, https://doi.org/10.1016/j.memsci.2022.120979.

[17] W. Chen, J. Mo, X. Du, Z. Zhang, W. Zhang, Biomimetic dynamic membrane for aquatic dye removal, Water Res. 151 (2019) 243–251, https://doi.org/10.1016/j.watres.2018.11.078.

[18] W. Zhang, W. Liang, Z. Zhang, T. Hao, Aerobic granular sludge (AGS) scouring to mitigate membrane fouling: performance, hydrodynamic mechanism and contribution quantification model, Water Res. 188 (2021) 116518, https://doi.org/10.1016/j.watres.2020.116518.

[19] W. Zhang, F. Jiang, Membrane fouling in aerobic granular sludge (AGS)-membrane bioreactor (MBR): effect of AGS size, Water Res. 157 (2019) 445–453, https://doi.org/10.1016/j.watres.2018.07.069.

[20] H. Geng, Q.Z. Zhong, J. Li, Z. Lin, J. Cui, F. Caruso, J. Hao, Metal ion-directed functional metal-phenolic materials, Chem. Rev. 122 (2022) 11432–11473, https://doi.org/10.1021/acs.chemrev.1c01042.

[21] X. Yang, A.B.F. Martinson, J.W. Elam, L. Shao, S.B. Darling, Water treatment based on atomically engineered materials: atomic layer deposition and beyond, Matter 4 (2021) 3515–3548, https://doi.org/10.1016/j.matt.2021.09.005.

[22] X. Yang, P. Sun, Y. Wen, A.U. Mane, J.W. Elam, J. Ma, S. Liu, S.B. Darling, et al., Protein-activated atomic layer deposition for robust crude-oil-repellent hierarchical nano-armored membranes, Sci. Bull. (2023) 218–226, https://doi.org/10.1016/j.scib.2023.12.001.

[23] X. Yang, Q. Zhang, Y. Liu, M. Nian, M. Xie, S. Xie, Q. Yang, S. Wang, et al., Metal-organic framework nanoparticles with universal dispersibility through crown ether surface coordination for phase-transfer catalysis and separation membranes, Angew. Chem. Int. Ed. 62 (2023) e202303280, https://doi.org/10.1002/anie.202303280.

[24] T. Yan, S. Liu, C. Li, J. Xu, S. Yu, T. Wang, H. Sun, J. Liu, Flexible single-chain-heteropolymer-derived transmembrane ion channels with high K⁺ selectivity and tunable pH-gated characteristics, Angew. Chem. Int. Ed. 61 (2022) e202210214, https://doi.org/10.1002/anie.202210214.

[25] W. Liu, Y. Li, R. Li, H. Xu, X. Lu, W. Dong, Z. Zhang, Y. Wang, Constructing 2D ultrathin graphene oxide membranes with supramolecular-assembled nano-adhesives for enhancing water stability, Nano Res. 16 (2023) 8505–8511, https://doi.org/10.1007/s12274-023-5524-2.

[26] Z. Jiang, R. Dong, A.M. Evans, N. Biere, M.A. Ebrahim, S. Li, D. Anselmetti, W.R. Dichtel, et al., Aligned macrocycle pores in ultrathin films for accurate molecular sieving, Nature 609 (2022) 58–64, https://doi.org/10.1038/s41586-022-05032-1.

[27] B. Tian, Y. Liu, J. Liu, Smart stimuli-responsive drug delivery systems based on cyclodextrin: a review, Carbohydr. Polym. 251 (2021) 116871, https://doi.org/10.1016/j.carbpol.2020.116871.

[28] X.-P. He, R.-H. Li, S. Maisonneuve, Y. Ruan, G.-R. Chen, J. Xie, Fluorogenic supramolecular complexes formed between pyrenyl-β-cyclodextrin and glyco-rhodamine for the selective detection of lectins, Chem. Commun. 50 (2014) 14141–14144, https://doi.org/10.1039/c4cc06356b.

[29] Q.-W. Zhang, J. Zajíček, B.D. Smith, Cyclodextrin rotaxane with switchable pirouetting, Org. Lett. 20 (2018) 2096–2099, https://doi.org/10.1021/acs.orglett.8b00655.

[30] S. Zhang, I. Boussouar, H. Li, Selective sensing and transport in bionic nanochannel based on macrocyclic host-guest chemistry, Chin. Chem. Lett. 32 (2021) 642–648, https://doi.org/10.1016/j.cclet.2020.06.035.

[31] L.Q. Xu, Y.K. Yee, K.-G. Neoh, E.-T. Kang, G.D. Fu, Cyclodextrin-functionalized graphene nanosheets, and their host-guest polymer nanohybrids, Polymer 54 (2013) 2264–2271, https://doi.org/10.1016/j.polymer.2013.02.043.

[32] R.-H. Li, J. Ma, Y. Sun, H. Li, Tailoring two-dimensional surfaces with pillararenes based host–guest chemistry, Chin. Chem. Lett. 31 (2020) 3095–3101, https://doi.org/10.1016/j.cclet.2020.06.041.

[33] S. Zhang, M. Cheng, M.K. Dhinakaran, Y. Sun, H. Li, Enantioselective antiport in Aasymmetric nanochannels, ACS Nano 15 (2021) 13148–13154, https://doi.org/10.1021/acsnano.1c02630.

[34] F. Zhang, J. Ma, Y. Sun, Y. Mei, X. Chen, W. Wang, H. Li, Construction of a switchable nanochannel for protein transport via a pillar[5]arene-based host–guest system, Anal. Chem. 90 (2018) 8270–8275, https://doi.org/10.1021/acs.analchem.8b01948.

[35] Y. Sun, F. Yi, R.H. Li, X. Min, H. Qin, S.Q. Cheng, Y. Liu, Inorganic–organic hybrid membrane based on pillararene-intercalated mxene nanosheets for efficient water purification, Angew. Chem. Int. Ed. 61 (2022) e202200482, https://doi.org/10.1002/anie.202200482.

[36] M.-j. Tao, S.-Q. Cheng, X.-L. Han, F. Yi, R.-H. Li, Y. Rong, Y. Sun, Y. Liu, Alignment of MXene based membranes to enhance water purification, J. Membr. Sci. 662 (2022) 120965, https://doi.org/10.1016/j.memsci.2022.120965.

[37] R.H. Li, Q. Lin, S.L. Li, Y. Sun, Y. Liu, MXenes functionalized with macrocyclic hosts: from molecular design to applications, Chempluschem 88 (2023) e202200423, https://doi.org/10.1002/cplu.202200423.

[38] O. Jovanovic, C.F. Amábile-Cuevas, C. Shang, C. Wang, K.W. Ngai, What water professionals should know about antibiotics and antibiotic resistance: an overview, ACS ES&T Water 1 (2021) 1334–1351, https://doi.org/10.1021/acsestwater.0c00308.

[39] H. Qin, X. Ding, S.-Q. Cheng, S.-Y. Qin, X. Han, Y. Sun, Y. Liu, An H₂S-regulated artificial nanochannel fabricated by a supramolecular coordination strategy, J. Phys. Chem. Lett. 13 (2022) 9232–9237, https://doi.org/10.1021/acs.jpclett.2c02233.

[40] E.M.M. Del Valle, Cyclodextrins and their uses: a review, Process Biochem. 39 (2004) 1033–1046, https://doi.org/10.1016/s0032-9592(03)00258-9.

[41] B. Shi, H. Guan, L. Shangguan, H. Wang, D. Xia, X. Kong, F. Huang, A pillar[5] arene-based 3D network polymer for rapid removal of organic micropollutants from water, J. Mater. Chem. A 5 (2017) 24217–24222, https://doi.org/10.1039/c7ta08894a.

[42] B. Zheng, F. Wang, S. Dong, F. Huang, Supramolecular polymers constructed by crown ether-based molecular recognition, Chem. Soc. Rev. 41 (2012) 1621–1636, https://doi.org/10.1039/c1cs15220c.

[43] M. Stredansky, E. Turco, Z. Feng, R. Costantini, G. Comelli, A. Verdini, L. Floreano, A. Morgante, et al., On-surface trapping of alkali atoms by crown ethers in ultra high vacuum, Nanoscale Adv. 1 (2019) 1721–1725, https://doi.org/10.1039/c9na00014a.

[44] S.-Q. Cheng, Q. Lin, S.-L. Li, Y.-X. Guo, X.-L. Han, Y. Sun, Y. Liu, Recent advancements in supramolecular macrocycles for two-dimensional membranes for separations, Green Chem. 25 (2023) 7026–7040, https://doi.org/10.1039/d3gc01996a.

[45] P. Tang, Q. Sun, L. Zhao, Y. Tang, Y. Liu, H. Pu, N. Gan, Y. Liu, et al., A simple and green method to construct cyclodextrin polymer for the effective and simultaneous estrogen pollutant and metal removal, Chem. Eng. J. 366 (2019) 598–607, https://doi.org/10.1016/j.cej.2019.02.117.

[46] M. Gu, G. Zhang, J. Liu, S. Shen, D. Liu, Y. Hong, Tunable multipurpose separation technology based on crosslinked dialdehyde-β-cyclodextrin and polyethyleneimine coating membrane, Separ. Purif. Technol. 320 (2023) 124077, https://doi.org/10.1016/j.seppur.2023.124077.

[47] J. Yu, Z. Li, M. Xia, L. Zhang, D. Zhao, B. Li, C. Chen, Y. Jiao, et al., Green and edible cyclodextrin metal-organic frameworks modified polyamide thin film nanocomposite nanofiltration membranes for efficient desalination, J. Membr. Sci. 679 (2023) 121714, https://doi.org/10.1016/j.memsci.2023.121714.

[48] M. Jia, W.-H. Zhang, X. Zhang, M.-J. Yin, S. Gu, X. Hu, H. Guo, Hydroxypropyl-β-cyclodextrin-based polyester TFC membrane for efficient antibiotic desalination, Separ. Purif. Technol. 317 (2023) 123884, https://doi.org/10.1016/j.seppur.2023.123884.

[49] F.J. McInnes, N.G. Anthony, A.R. Kennedy, N.J. Wheate, Solid state stabilisation of the orally delivered drugs atenolol, glibenclamide, memantine and paracetamol through their complexation with cucurbit[7]uril, Org. Biomol. Chem. 8 (2010) 765–773, https://doi.org/10.1039/b918372h.

[50] D. Gutsche, Foreword, Supramol. Chem. 26 (2014) 452, https://doi.org/10.1080/10610278.2014.888882.

[51] Y. Ishii, Y. Takenaka, K. Konishi, Porous organic–inorganic assemblies constructed from keggin polyoxometalate anions and calix[4]arene–Na⁺ complexes: structures and guest-sorption profiles, Angew. Chem. 116 (2004) 2756–2759, https://doi.org/10.1002/ange.200453693.

[52] T. Ogoshi, S. Kanai, S. Fujinami, T.-a. Yamagishi, Y. Nakamoto, para-Bridged symmetrical pillar[5]arenes: their lewis acid catalyzed synthesis and host–guest property, J. Am. Chem. Soc. 130 (2008) 5022–5023, https://doi.org/10.1021/ja711260m.

[53] J.-R. Wu, G. Wu, Y.-W. Yang, Pillararene-inspired macrocycles: from extended pillar[n]arenes to geminiarenes, Accounts Chem. Res. 55 (2022) 3191–3204, https://doi.org/10.1021/acs.accounts.2c00555.

[54] W.X. Feng, Z. Sun, M. Barboiu, Pillar[n]arenes for construction of artificial transmembrane channels, Isr. J. Chem. 58 (2018) 1209–1218, https://doi.org/10.1002/ijch.201800017.

[55] W. Chen, P. Chen, G. Zhang, G. Xing, Y. Feng, Y.-W. Yang, L. Chen, Macrocycle-derived hierarchical porous organic polymers: synthesis and applications, Chem. Soc. Rev. 50 (2021) 11684–11714, https://doi.org/10.1039/d1cs00545f.

[56] A.A. Oladipo, A.O. Ifebajo, R. Vaziri, Green adsorbents for removal of antibiotics, pesticides and endocrine disruptors, Green Adsorbents for Pollutant Removal 19 (2018) 327–351, https://doi.org/10.1007/978-3-319-92162-4_10.

[57] M.E.A. El-sayed, Nanoadsorbents for water and wastewater remediation, Sci. Total Environ. 739 (2020) 139903, https://doi.org/10.1016/j.scitotenv.2020.139903.

[58] J.F. Nure, T.T.I. Nkambule, The recent advances in adsorption and membrane separation and their hybrid technologies for micropollutants removal from wastewater, J. Ind. Eng. Chem. 126 (2023) 92–114, https://doi.org/10.1016/j.jiec.2023.06.034.

[59] H. Yu, M. Liao, W. Zhao, G. Liu, X.J. Zhou, Z. Wei, X. Xu, K. Liu, et al., Wafer-scale growth and transfer of highly-oriented monolayer MoS₂ continuous films, ACS Nano 11 (2017) 12001–12007, https://doi.org/10.1021/acsnano.7b03819.

[60] M.B. Asif, S. Iftekhar, T. Maqbool, B.K. Pramanik, S. Tabraiz, M. Sillanpää, Z. Zhang, Two-dimensional nanoporous and lamellar membranes for water purification: reality or a myth? Chem. Eng. J. 432 (2022) 134335, https://doi.org/10.1016/j.cej.2021.134335.

[61] M. Zhang, K. Guan, Y. Ji, G. Liu, W. Jin, N. Xu, Controllable ion transport by surface-charged graphene oxide membrane, Nat. Commun. 10 (2019), https://doi.org/10.1038/s41467-019-09286-8.

[62] D. Shetty, S. Boutros, A. Eskhan, A.M. De Lena, T. Skorjanc, Z. Asfari, H. Traboulsi, J. Mazher, et al., Thioether-crown-rich calix[4]arene porous polymer for highly efficient removal of mercury from water, ACS Appl. Mater. Interfaces 11 (2019) 12898–12903, https://doi.org/10.1021/acsami.9b02259.

[63] Z. Li, L. Li, D. Hu, C. Gao, J. Xiong, H. Jiang, W. Li, Efficient removal of heavy metal ions and organic dyes with cucurbit [8] uril-functionalized chitosan, J. Colloid Interface Sci. 539 (2019) 400–413, https://doi.org/10.1016/j.jcis.2018.12.078.

[64] C.-F. Chen, Y. Han, Triptycene-derived macrocyclic arenes: from calixarenes to helicarenes, Accounts Chem. Res. 51 (2018) 2093–2106, https://doi.org/10.1021/acs.accounts.8b00268.

[65] S. An, Q. Xu, Z. Ni, J. Hu, C. Peng, L. Zhai, Y. Guo, H. Liu, Construction of covalent organic frameworks with crown ether struts, Angew. Chem. Int. Ed. 60 (2021) 9959–9963, https://doi.org/10.1002/anie.202101163.

[66] V.K. Rana, R. Kissner, S. Gaspard, J. Levalois-Grützmacher, Cyclodextrin as a complexation agent in the removal of chlordecone from water, Chem. Eng. J. 293 (2016) 82–89, https://doi.org/10.1016/j.cej.2016.02.032.

[67] V. Rizzi, J. Gubitosa, R. Signorile, P. Fini, C. Cecone, A. Matencio, F. Trotta, P. Cosma, Cyclodextrin nanosponges as adsorbent material to remove hazardous pollutants from water: the case of ciprofloxacin, Chem. Eng. J. 411 (2021) 128514, https://doi.org/10.1016/j.cej.2021.128514.

[68] A.I. Schäfer, K. Stelzl, M. Faghih, S. Sen Gupta, K.R. Krishnadas, S. Heißler, T. Pradeep, Poly(ether sulfone) nanofibers impregnated with β-cyclodextrin for increased micropollutant removal from water, ACS Sustain. Chem. Eng. 6 (2017) 2942–2953, https://doi.org/10.1021/acssuschemeng.7b02214.

[69] S. Alpaydin, A.Ö. Saf, S. Bozkurt, A. Sirit, Kinetic study on removal of toxic metal Cr(VI) through a bulk liquid membrane containing p-tert-butylcalix[4]arene derivative, Desalination 275 (2011) 166–171, https://doi.org/10.1016/j.desal.2011.02.048.

[70] D. Tao, H. Zhou, K. Cui, L. Xie, K. Huang, Preferential recovery and separation of rhodium in the concentrated hydrochloric acid using thin-layer oil membrane extraction based on laminar flow, Chem. Eng. Res. Des. 192 (2023) 69–81, https://doi.org/10.1016/j.cherd.2023.02.012.

[71] J. Wu, J. Gao, S.-B. Chen, T.-S. Chung, Solvent-activated thin-film nanocomposite membranes molecularly tuned with macrocyclic cavities for efficient water desalination and boron removal, Chem. Eng. J 469 (2023) 143982, https://doi.org/10.1016/j.cej.2023.143982.

[72] T. Huang, T. Puspasari, S.P. Nunes, K.V. Peinemann, Ultrathin 2D-layered cyclodextrin membranes for high- performance organic solvent nanofiltration, Adv. Funct. Mater. 30 (2020) 1906797, https://doi.org/10.1002/adfm.201906797.

[73] Z. Dong, M. Tagliavini, J. Darmadi, V. Trouillet, A.I. Schäfer, P.A. Levkin, Regeneration of β-cyclodextrin based membrane by photodynamic disulfide exchange—steroid hormone removal from water, Adv. Mater. Interfac. 7 (2020) 1902100, https://doi.org/10.1002/admi.201902100.

[74] X. Yang, Y. Wen, Y. Li, L. Yan, C.Y. Tang, J. Ma, S.B. Darling, L. Shao, Engineering in situ catalytic cleaning membrane via prebiotic-chemistry-inspired mineralization, Adv. Mater. 35 (2023) e2306626, https://doi.org/10.1002/adma.202306626.

[75] B. Li, S. Japip, T.-S. Chung, Molecularly tunable thin-film nanocomposite membranes with enhanced molecular sieving for organic solvent forward osmosis, Nat. Commun 11 (2020) 1198, https://doi.org/10.1038/s41467-020-15070-w.

[76] P. Zhang, Y. Zhang, L. Wang, K. Qiu, X. Tang, J.K. Gibson, X. Liu, L. Mei, et al., Bioinspired macrocyclic molecule supported two-dimensional lamellar membrane with robust interlayer structure for high-efficiency nanofiltration, Adv. Sci. 10 (2022) e2206516, https://doi.org/10.1002/advs.202206516.

[77] L. Shao, X. Wang, Y. Ren, S. Wang, J. Zhong, M. Chu, H. Tang, L. Luo, et al., Facile fabrication of magnetic cucurbit[6]uril/graphene oxide composite and application for uranium removal, Chem. Eng. J. 286 (2016) 311–319, https://doi.org/10.1016/j.cej.2015.10.062.

[78] S. Sun, D. Xiong, Y. Zhuang, G. Cheng, L. Shi, Y. Zhang, Facile fabrication of macroporous carbon materials with cucurbit[6]uril as precursor/template and its application for uranium removal, Environ. Technol. Innovat. 28 (2022) 102779, https://doi.org/10.1016/j.eti.2022.102779.

[79] M. Kazemabad, A. Verliefde, E.R. Cornelissen, A. D'Haese, Crown ether containing polyelectrolyte multilayer membranes for lithium recovery, J. Membr. Sci. 595 (2020) 117432, https://doi.org/10.1016/j.memsci.2019.117432.

[80] H. Jo, T.-H. Le, H. Lee, J. Lee, M. Kim, S. Lee, M. Chang, H. Yoon, Macrocyclic ligand-embedded graphene-in-polymer nanofiber membranes for lithium ion recovery, Chem. Eng. J. 452 (2023) 139274, https://doi.org/10.1016/j.cej.2022.139274.

[81] I. Abdulazeez, B. Salhi, N. Baig, A. Al-Saadi, Molecular dynamics simulation of the fractionation of lithium and magnesium-ions on crown ether-grafted cellulose

acetate polyelectrolyte membranes, J. Mol. Liq. 376 (2023) 121475, https://doi.org/10.1016/j.molliq.2023.121475.

[82] X. Ruan, C. Zhang, Y. Zhu, F. Cai, Y. Yang, J. Feng, X. Ma, Y. Zheng, et al., Constructing mechanical shuttles in a three-dimensional (3D) porous architecture for selective transport of lithium ions, Angew. Chem. Int. Ed. 62 (2023) e202216549, https://doi.org/10.1002/anie.202216549.

[83] L. Mao, R. Chen, J. He, H. Pei, B. He, X. Ma, J. Li, Remarkably high Li$^+$ adsorptive separation polyamide membrane by improving the crown ether concentration and electron density, ACS Sustain. Chem. Eng. 10 (2022) 10047–10056, https://doi.org/10.1021/acssuschemeng.2c02950.