

综述与专论

DOI: 10.11949/0438-1157.20241307

金属有机骨架膜应用于海水提铀研究进展

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摘要: 海洋中约有45亿吨铀, 能够满足全球核工业生产千年以上的可持续生产需求, 因此海水提铀被认为是改变世界的化学分离技术之一; 膜分离因效率高、能耗低、无污染等特点, 被广泛用于海水提铀。金属有机骨架(MOF)由于其可变的孔道结构、丰富的活性位点、化学修饰多样性, 作为膜材料在海水提铀应用领域前景广阔。综述了将膜分离技术应用于海水提铀的最新研究进展与未来发展方向, 系统总结了采用MOF膜实现海水提铀的分离机理与面临的挑战。

关键词: 海水提铀; 金属有机骨架; 膜分离; 吸附; 过滤; 膜

中图分类号: TQ 028.3

文献标志码: A

文章编号: 0438-1157 (2025) 05-2087-14

Recent progress on metal-organic framework membranes towards uranium separation from seawater

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Abstract: The oceans hold *ca.* 4.5 billion tons of uranium, which will provide sustainable production for the global nuclear industry more than thousands of years. Therefore, uranium extraction from seawater is considered as one of the world-changing chemical separation technologies. Membrane separation is widely used for uranium extraction from seawater because of its high efficiency, low energy consumption, and non-pollution. Metal-organic framework (MOF) holds great potential for seawater uranium extraction with membrane technology due to the tunable pore size, rich functionality, and diverse post-modification protocols. This paper reviews the latest research progress and future development direction of membrane separation technology in uranium extraction from seawater, and especially systematically summarizes the separation mechanism and challenges of uranium extraction from seawater using MOF membranes.

Key words: uranium extraction; metal-organic framework (MOF); membrane separation; adsorption; filtration; membrane

收稿日期: 2024-11-15 修回日期: 2025-02-03

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基金项目: 国家自然科学基金面上项目(22478056), 中核集团星原计划(CNPE-8208)

引用本文: 张越, 刘佳鑫, 马敬, 刘毅. 金属有机骨架膜应用于海水提铀研究进展[J]. 化工学报, 2025, 76(5): 2087–2100

Citation: ZHANG Yue, LIU Jiaxin, MA Jing, LIU Yi. Recent progress on metal-organic framework membranes towards uranium separation from seawater[J]. CIESC Journal, 2025, 76(5): 2087–2100

引 言

核能作为一种高效、清洁的能源,正逐渐成为我国调整能源结构、优化产业结构、促进经济发展的重要保障^[1-2],因此备受各行各业的关注(图1)。预计截至2030年全球核工业产能将增长56%,而陆基铀燃料(约630万吨)将在不到一百年内出现严重短缺,因此日益增长的核工业需求和常规铀资源的稀缺将会是核工业发展的障碍(图2)^[3-6]。同时,我国作为世界第三核电大国,每年需要进口约80%的铀资源,并且随着核工业的快速发展,预计至2030年,我国铀资源缺口将达到约90%^[7-8]。因此,有效解决铀资源短缺现状将是亟须克服的难题。

海洋中的铀资源约为45亿吨,是地球矿石等传统资源的1000倍^[9-10]。如能够开采和利用海洋中的铀资源,预期将满足核工业1000年以上的可持续生产需求,因此开发高效节能的海水提铀(UES)技术,被认为是将改变世界的化学分离技术之一。目前吸附^[11-15]、光催化^[15,16-22]、离子交换^[23-25]、溶剂萃取^[26-28]和电化学沉淀^[29-31]等多种方法已被尝试用于海水提铀^[32-33]。然而由于海洋系统的复杂性,包括超低铀浓度(约3.3 mg/t)、多种竞争金属离子共存以及严重

的生物污垢等,严重阻碍了海水提铀(UES)技术的快速发展与工业应用^[4-5,34]。相较而言,膜分离技术具有操作简单、能耗低、效率高、环境友好等特点^[35],近期在海水提铀研究中备受关注。具体而言,第一,膜分离过程简单易行,无须复杂烦琐的操作步骤。第二,膜分离过程能耗相对较低,契合当下节能环保的发展理念。第三,无论是基于吸附筛分机理还是尺寸筛分机理,膜材料对海水中铀的截留率均能达到90%以上,可大幅提升铀资源的回收效率。此外,膜分离过程不会对环境造成显著破坏和污染,充分保障了生态系统的平衡与稳定,便于兼顾资源高效利用与生态有效保护。但目前工业上主流的膜产品是聚合物膜,其分离性能常常受trade-off效应制约^[36-37]。为突破上述效应,亟须开发新型高性能膜材料。

金属有机骨架(MOF)是一类由金属离子和有机配体组成的多孔晶体材料。金属离子构成的节点(次级结构单元,SBU)与有机配体的多样性连接构型,赋予了MOF材料这种微孔物质高孔隙率、高度有序、高比表面积、孔径可调和多样拓扑结构等特点^[4,35],并且MOF材料作为一种微孔物质,其具备的化学功能性(即可通过在MOF膜上修饰合适的功能基团调控其优先吸附性)、可剪裁性(即可通过选

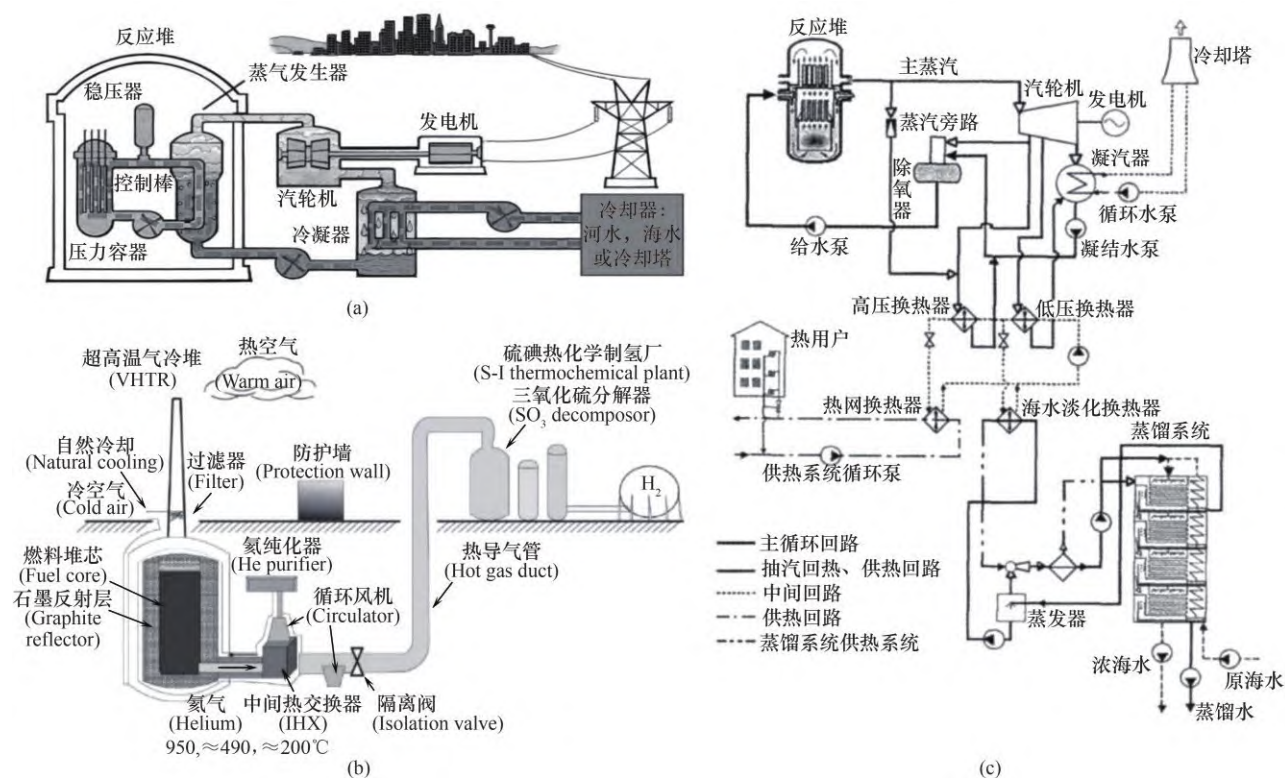


图1 (a)核能发电;(b)核能制氢;(c)核能海水淡化^[3]

Fig.1 (a) Nuclear power for electricity generation; (b) Nuclear power for hydrogen production; (c) Nuclear power for seawater desalination^[3]

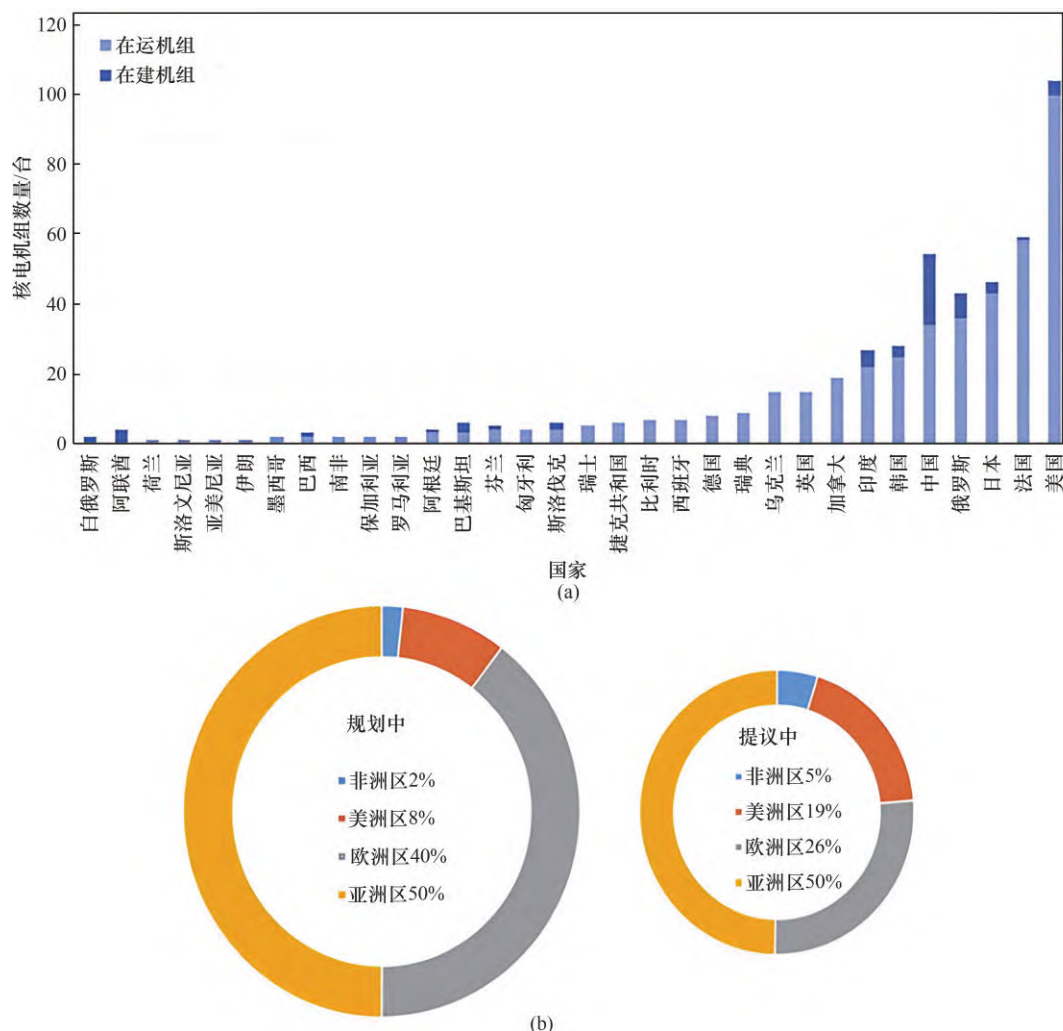


图2 (a)世界核电机组发展需求;(b)世界核电发展需求区域分布^[3]

Fig.2 (a) World nuclear power unit development requirements; (b) World nuclear power development requirements in the regional distribution^[3]

择适当的配体与金属离子调控 MOF 膜的尺寸筛分性^[38]以及可设计性(即可通过孔道微环境调控、膜微结构优化等方法制备具有多样化结构的 MOF 膜)都使其可针对特定分离体系进行定向设计,从而满足不同条件下海水中的使用要求,使其在海水提铀领域具有广阔的应用前景。本文综述了基于 MOF 膜实现高效海水提铀的最新研究进展,着重介绍了骨架官能团、孔道尺寸、拓扑结构等 MOF 膜孔道微环境对其海水提铀性能的影响,最后在此基础上展望了基于 MOF 膜实现高效海水提铀的应用前景。

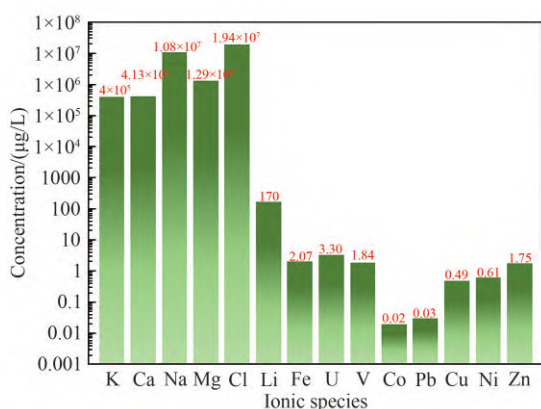
1 MOF 膜海水提铀亟须克服的关键问题概述

海水提铀被认为是解决铀资源短缺的重要方

式^[9, 39]。但极其复杂的海水体系对铀的高效提取造成了巨大的阻碍,其主要原因有:(1)海水复杂的离子共存体系和极低的铀离子浓度;(2)海水变化的 pH 和高盐度;(3)海水温度周期变化与复杂多变的海洋生态系统^[12, 39-41]。

1.1 复杂离子共存体系和极低铀离子浓度

海水中共存金属离子很多,例如浓度较高的 Ca^{2+} 、 Mg^{2+} 、 Na^{+} 、 K^{+} 等碱/碱土金属离子和浓度较低的 V^{5+} 、 Ni^{2+} 、 Cu^{2+} 、 Zn^{2+} 、 Pb^{2+} 等高价态过渡金属离子^[42](图3)。碱/碱土金属中, Ca(II) 和 Mg(II) 等离子会与 U(VI) 络合形成 $\text{CaUO}_2(\text{CO}_3)_3^{2-}$ 和 $\text{MgUO}_2(\text{CO}_3)_3^{2-}$, 使其无法分离出单一 U(VI) ; 而高价态过渡金属中, V(V) 和 Co(II) 等离子则会与 U(VI) 竞争膜表面吸附位点,使其同时从海水中提取出来,从而无法选择性分离出 U(VI) 。此外,海水中的 U(VI) 含量极低(约 3.3 mg/t),必然降低铀酰离子与膜表面的碰撞概

图3 海水中主要离子浓度^[9, 12]Fig.3 Major ion concentrations in seawater^[9, 12]

率和铀酰离子向膜表面的扩散速率^[12, 42-43],进而影响U(VI)的提取效率和选择性。因此,如何克服复杂的离子共存体系和极低的铀离子浓度对U(VI)的选择性提取,是基于MOF膜实现海水提铀所必须克服的严峻挑战。

1.2 水体复杂pH和高盐度

盐度表示溶解在水体中盐的含量,是控制U(VI)存在形式和溶解浓度的重要因素,海水盐度为3.2%~4.0%,是U(VI)含量的 $10^6 \sim 10^7$ 倍^[32, 42, 44]。Ladshaw等^[45]的研究表明,海水中所含的NaCl等高浓度盐类,将在很大程度上降低膜对U(VI)的吸附能力和提取速度,进而降低海水提铀效率。He等^[46]详细研究了0.1~0.44 mol/L NaCl溶质对铀分离去除的影响。实验结果表明,高盐度海水会和U(VI)形成铀酰碳酸盐复合物,进而阻止U(VI)与膜表面的吸附基团进行吸附结合,使膜对U(VI)的吸附能力大幅下降,最终导致U(VI)的提取能力出现明显衰减[图4(a)]。

由于pH可能影响膜吸附机理和U(VI)存在状态,

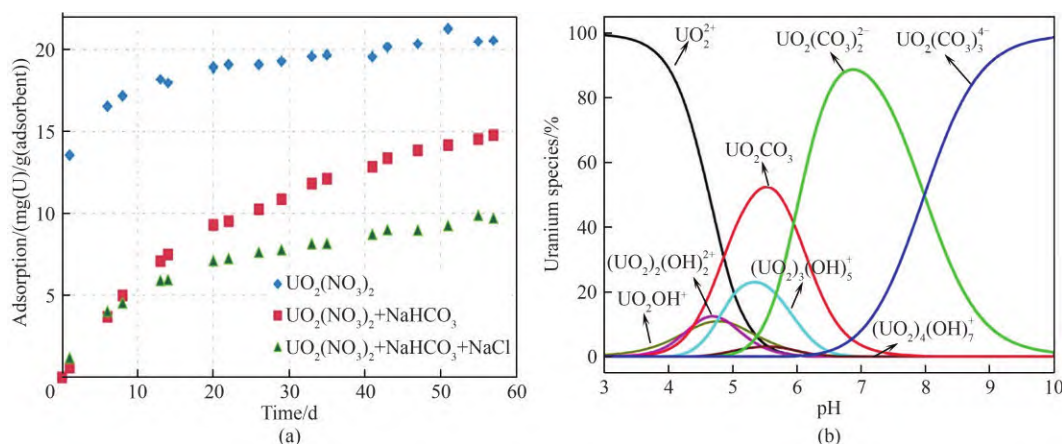
因而也是影响海水提铀回收率的重要因素。Lin等^[47-48]研究了不同pH下U(VI)的存在形式:酸性条件下,U(VI)主要以 UO_2^{2+} 、 $(\text{UO}_2)_2(\text{OH})_2^{2+}$ 、 $(\text{UO}_2)_3(\text{OH})_5^+$ 和 UO_2OH^+ 等阳离子形式存在,随着pH升高,将相继出现 $\text{UO}_2(\text{CO}_3)_2^{2-}$ 和 $\text{UO}_2(\text{CO}_3)_3^{4-}$;当pH接近海水酸碱度(约8.3)时, $\text{UO}_2(\text{CO}_3)_3^{4-}$ 成为海水中U(VI)的主要存在形式[占海水中铀酰碳酸盐的84.9%,图4(b)],而Krestou等^[41]研究发现 $\text{UO}_2(\text{CO}_3)_3^{4-}$ 由于U—C和U—O键键长的相似性以及线性结构,比其他配体更加稳定,无法通过简单的物理方法使其分解为 UO_2^{2+} 等形式,因而增加了海水提铀难度。所以依据海水的实际pH,减小高盐度带来的负面影响,将是基于膜分离实现海水提铀的另一关键所在。

1.3 海洋温度和生态环境

海洋温度变化将直接影响MOF膜的U(VI)吸附热力学、吸附动力学和孔道扩散过程。从热力学角度分析,U(VI)的吸附过程是吸热过程,随着操作温度提高,膜对U(VI)的吸附能力也将提升^[50-51]。实验人员在塔拉普尔原子能发电站出入口的相关实验证实了上述理论的合理性。此外,海水温度直接影响海洋动植物与微生物生长,而在长时间U(VI)提取过程中,上述生物可能累积在膜表面与孔道内部,导致膜污染而使分离性能降低^[52-53]。因此,基于MOF膜开展海水提铀,需要控制实验地点和实验温度,以维持膜材料的高分离性能。

2 MOF膜海水提铀的研究进展

前已述及,膜分离因其能耗低、效率高和操作简便等特点,在海水提铀中得到了广泛的研究^[34, 44]。

图4 (a)不同盐度对吸附剂铀吸收量的影响^[42]; (b) U(VI)在不同pH范围内的分布情况^[42, 49]Fig.4 (a) Effect of different salinities on the absorption of uranium by adsorbents^[42]; (b) Distribution of U(VI) in different pH ranges^[42, 49]

其中,MOF材料由于以下特性:(1)通过修饰有机配体,可有效调控孔道尺寸与比表面积^[54]; (2)通过修饰特定官能团或功能化金属节点,可赋予MOF材料特定功能^[55]; (3)通过调控骨架缺陷,可丰富MOF材料物理化学性质^[56],引起了科研人员的广泛兴趣(图5)。

2.1 基于优先吸附机理的MOF膜海水提铀

吸附分离是目前基于MOF膜实现海水提铀的主要机理^[58-59],例如Su等^[60]采用ZIF-67膜作为吸附材料,富集模拟海水中的U(VI)。ZIF-67膜对U(VI)表现出超高吸附容量(1683.8 mg/g)和高截留率(>99%; 吸附截留率:一定量吸附剂在一定体积含铀溶液中单次饱和吸附后,溶液去除的铀质量

与原溶液中铀质量之比),主要归因于ZIF-67骨架中Co—OH与U(VI)间的强键合作用(图6)。在此基础上,进一步通过官能团后修饰对MOF膜进行功能改性,增强其对U(VI)的吸附能力,以最终达到高效分离U(VI)的目的。其中,偕胺肟基、氨基、羟基和磷酸基是目前得到最广泛应用的修饰基团。

2.1.1 偕胺肟基(AO) 偕胺肟官能团由于酸性位点肟基氧原子和碱性位点氨基氮原子可与U(VI)形成稳定的螯合物,对U(VI)具有优异的吸附能力^[42]。Chen等^[61]合成了偕胺肟修饰的UiO-66-AO,其在天然海水中U(VI)吸附容量可达2.68 mg/g,并且在2 h截留率高达94.8%。为克服单一MOF材料无法在海

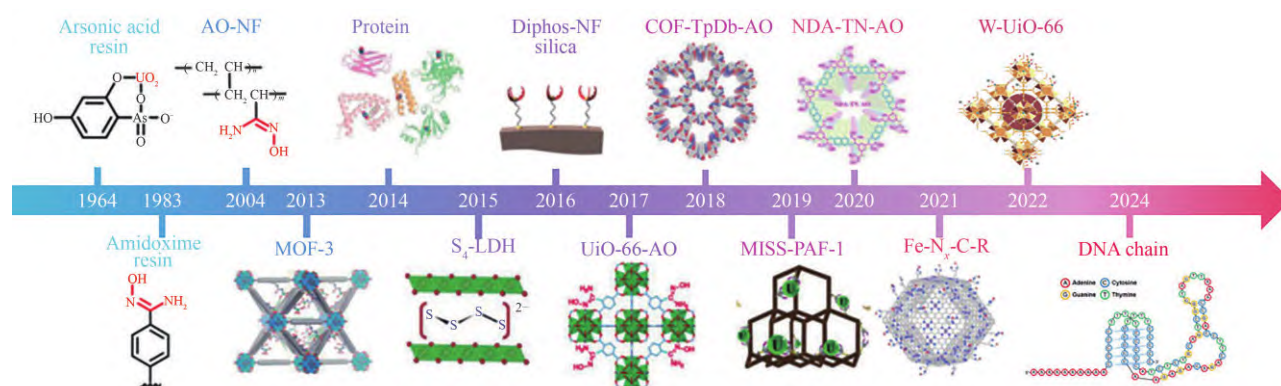


图5 1964年以来曾用于海水提铀的功能材料发展时间线^[20, 39, 57]

Fig.5 Timeline of the development of functional materials that have been used in seawater separation of uranium since 1964^[20, 39, 57]

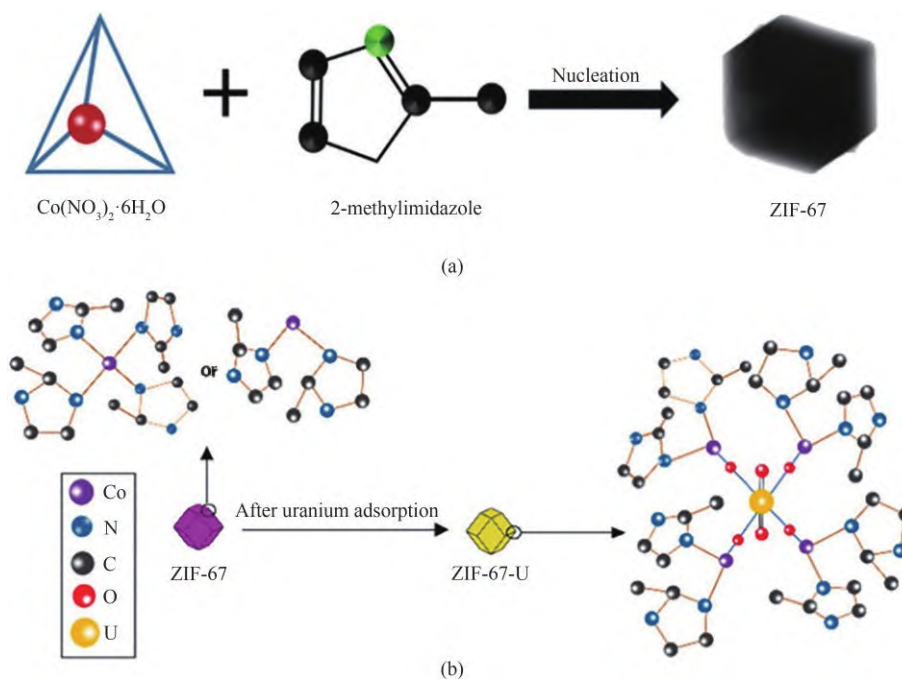


图6 (a)ZIF-67合成;(b) ZIF-67吸附分离U(VI)的机理示意图^[60]

Fig.6 (a) Synthesis of ZIF-67; (b) Schematic of the mechanism for U(VI) separation by ZIF-67 adsorption^[60]

水提铀过程中实现高效回收利用等问题,Chen 等^[62]通过联合使用双轴拉伸法和酰胺脲化修饰,制备了酰胺脲化聚丙烯腈纳米纤维膜(AO-PAN NFM),其在 24 h 内 U(VI)截留率高达 56.52%;Wang 等^[63-64]通过聚丙烯腈接枝和酰胺脲化,合成了酰胺脲化纤维素纤维膜(PAO-CFM),其对天然海水中 U(VI)的吸附容量保持在 1.22 mg/g,不仅具有良好的吸附能力,还具备良好的重复使用性能(>5 次);Yu 等^[65-66]通过更换膜材料,将重复循环使用次数提升至 10 次以上,吸附容量超过 7 mg/g;Wang 等^[67]通过简单抽滤法制备了 UiO-66-PAO 棉纤维复合膜,在天然海水中的 U(VI)截留率提高至 80.6%,并且可重复循环使用 50 次以上,从而极大提升了膜分离性能和重复使用性(图 7)。此外,通过创新膜制备工艺,可进一步提升其 U(VI)分离性能^[68-69]。

但由于海水成分的复杂性,特别是共存碳酸根离子和钼离子的影响,仅通过修饰偕胺脲基团,MOF 膜在天然海水中的 U(VI)截留率很难突破 90%。通过修饰辅助官能团,有望进一步提升分离性能。第一种辅助基团是基于改变 U(VI)在海水中的存在形式,提升 MOF 膜分离能力。例如,Xiao 等^[70-71]通过羧基修饰,使 Anti-UiO-66-AO 和 LC-CA-AO 在含铀溶液中铀离子截留率提升 24.4%。这主要归因于羧基可将海水中 $\text{UO}_2(\text{CO}_3)_3^{4-}$ 解离为 UO_2^{2+} ,使其与偕胺脲基团充分配位结合,从而提升 Anti-UiO-66-AO 和 LC-CA-AO 对铀溶液中 UO_2^{2+} 的截留能力。另一种辅助基团是通过在膜表面引入配位点,

实现 MOF 膜分离能力的提升。例如,Ahmad 等^[72-74]在 MOF 表面引入胺配体,通过额外提供的配位点与偕胺脲基团进行协同整合,强化 N—OH 解离与 U(VI)结合,使 MOF 膜对铀溶液中 UO_2^{2+} 的截留率提高到 93% 以上。此外,亦可利用 U(VI)吸附的吸热反应特性,通过添加光热辅助基团提升 MOF 膜分离性能^[75-76]。

2.1.2 磷酸基团(PA)和羟基 基于磷酸基和羟基与 U(VI)间的强相互作用,有望通过两种基团中氧原子与 UO_2^{2+} 中 U(VI)进行配位整合,提升海水提铀效果^[77]。例如,Luo 等^[78]通过构建具有酚醛网络的微孔聚酰胺膜,实现对海水中 U(VI)的有效捕获,在天然海水中 U(VI)的截留率高达 84%[图 8(a)]。但是,由于磷酸基团在 MOF 中的修饰密度低、羟基对 U(VI)的结合能力弱^[79],通过在 MOF 膜表面单一修饰磷酸基或羟基无法使两种吸附基团充分吸附分离溶液中的 UO_2^{2+} ,因此需借助磷酸基和羟基间的耦合作用,辅以其他功能基团,以期达到最佳分离性能。Yu 等^[80]通过将羟基和磷酸基引入膜表面,辅以氨基构建铀离子阱,成功制备出 LAM 膜。基于膜表面丰富的活性基团($-\text{NH}_2$ 、 $-\text{PO}_4^{3-}$ 、 $-\text{OH}$),其在天然海水中 90 min 内截留率便达到 90% 以上,相较于单一官能团修饰,具有双基团修饰的 LAM 膜分离性能得到极大提升[图 8(b)]。Tyagi 等^[81]通过膦酰胺官能化,在 UiO-66- NH_2 (Ce)表面接枝磷酸基团,成功制备了 UiO-66- NH_2 (Ce)-PA 膜,其对天然海水中 U(VI)的截留率超过 95%。

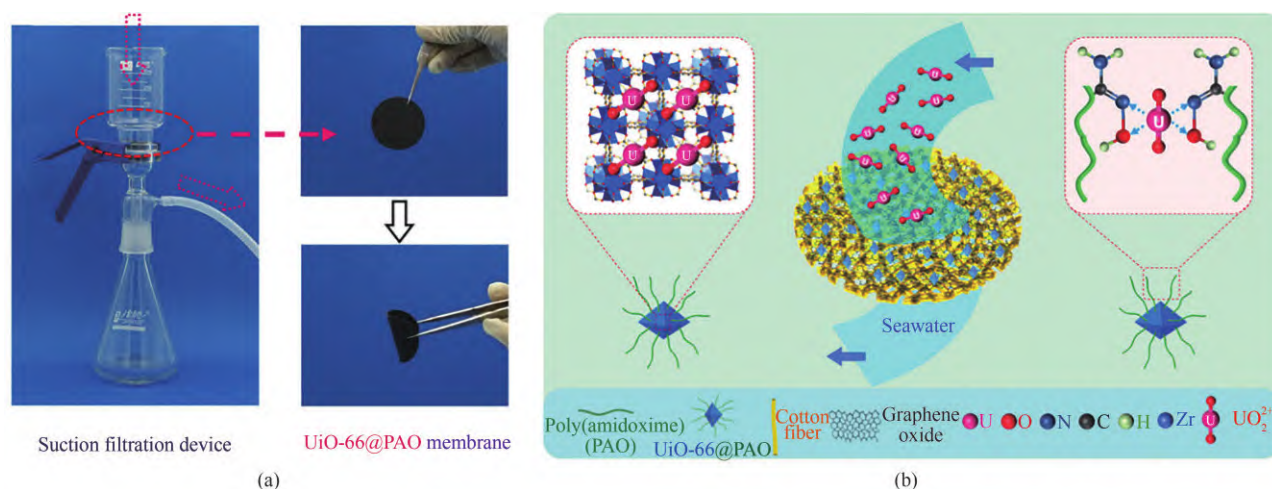


图 7 (a)UiO-66@PAO 膜制备流程示意图;(b)UiO-66@PAO 化学结构以及 UiO-66@PAO MOF 基膜选择性吸附铀的过程示意图^[67]

Fig.7 (a) Schematic diagram of the preparation process for UiO-66@PAO membrane; (b) Schematic diagram of the chemical structure for UiO-66@PAO and the process of selective adsorption of uranium by UiO-66@PAO MOF-based membrane^[67]

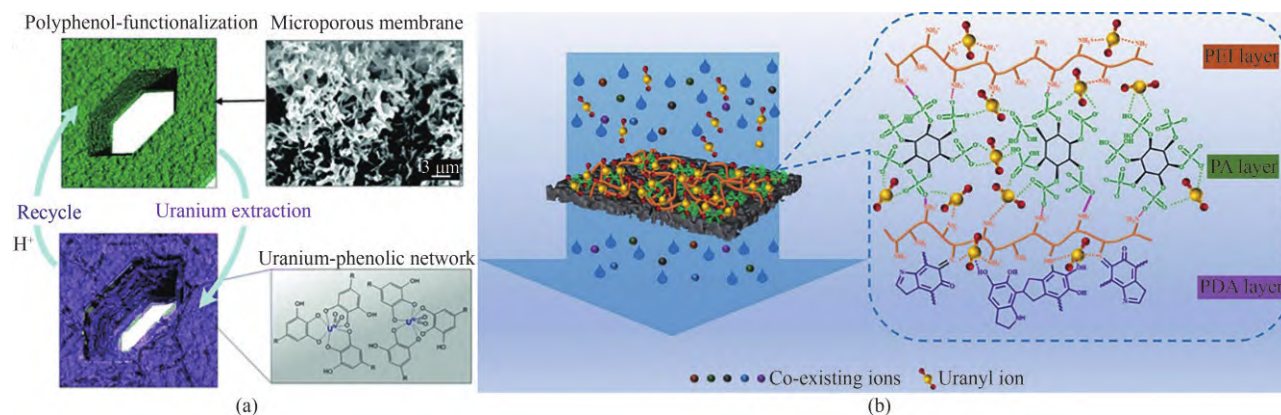


图8 (a)微孔聚酰胺膜的SEM和U(VI)捕获和释放示意图^[78]; (b) LAM膜在天然海水中U(VI)捕获示意图^[80]

Fig.8 (a) Schematic of SEM and U(VI) capture and release by microporous polyamide membranes^[78]; (b) Schematic of U(VI) capture by LAM membranes in natural seawater^[80]

2.1.3 氨基 氨基和偕胺肟作用机理较为相似。氨基主要通过氮原子与U(VI)配位络合实现对U(VI)的高效吸附^[81-82],分离性能取决于氨基修饰数量与存在形式。Bai等^[83]分别合成了MIL-101-NH₂、MIL-101-ED(ED, 乙二胺)和MIL-101-DETA(DETA, 二乙烯三胺),研究表明其分离能力随氨基数量减少依次递减。其中,MIL-101-DETA的U(VI)截留率最高为99%,而MIL-101-NH₂仅为MIL-101-DETA截留率的约40%。此外,修饰氨基还可提高膜抗污染能力,使其在天然海水中保持优异分离能力。Yu等^[84]通过均相交联反应和季铵化,成功制备了QIEA-

PAN膜,其对天然海水中U(VI)的截留率高达88%,且相较过滤后的天然海水(不含有细菌和微生物),QIEA-PAN膜对U(VI)的截留率仅降低5.6%(图9)。但由于氨基修饰的MOF膜分离效果相较于前述偕胺肟基、羟基和磷酸基较弱,因此氨基仍主要作为偕胺肟基或磷酸基的辅助基团加以利用。

前已述及,偕胺肟基、磷酸基团、羟基以及氨基是基于吸附分离机理实现膜技术海水提铀的主要官能团。此外,天然植物提取物或者生物基材料也具有海水提铀的潜力。Cao等^[85]和Liang等^[57]分别尝试将大豆分离蛋白和DNA分子等天然生物基材料

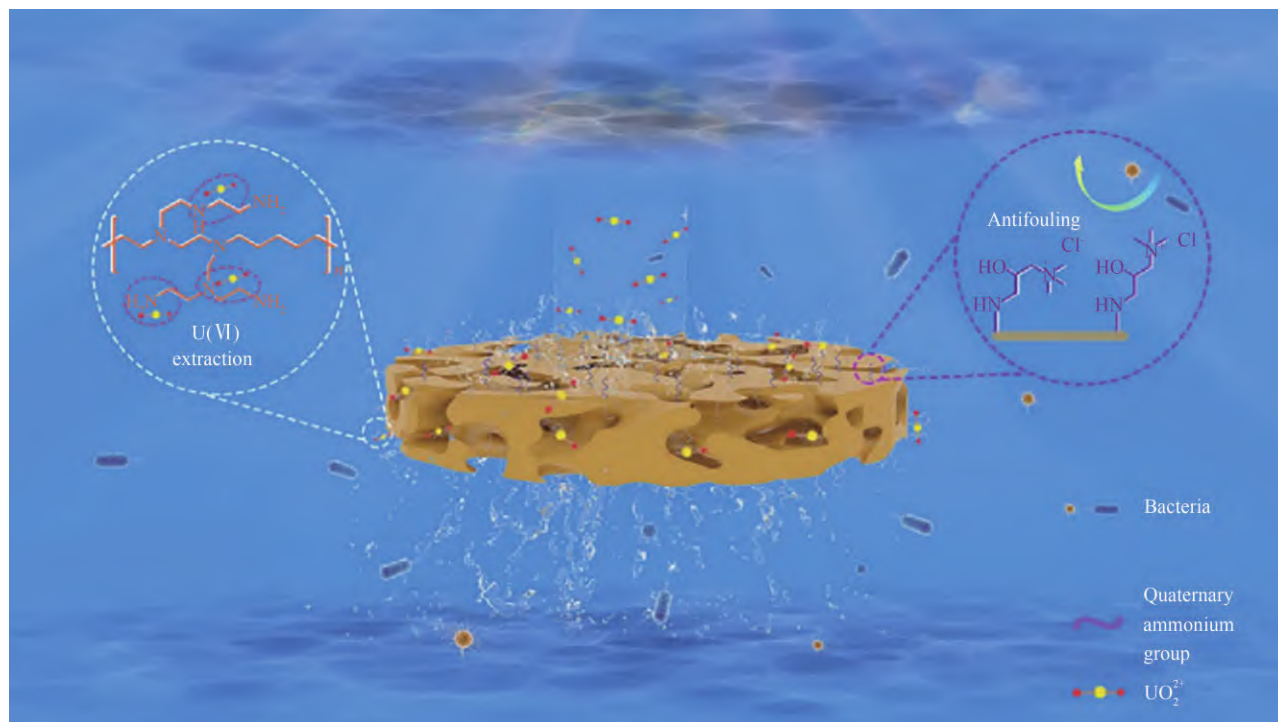


图9 氨基在天然海水中U(VI)萃取和防污工艺示意图^[84]

Fig.9 Schematic diagram of the U(VI) extraction and antifouling process for amines in natural seawater^[84]

用于海水提铀;Wang等^[20]则利用W-UiO-66仿生材料进行海水提铀。

目前,基于吸附机理的MOF膜海水提铀技术仍处于探索阶段。美国太平洋西北国家实验室(PNNL)和橡树岭国家实验室(ORNL)依据国际第四代核能论坛(GIF)的经济模型工作组(EMWG)的相关指南,通过全生命周期成本(WOC)核算发现,要使MOF膜在海水提铀领域具备商业和工业竞争力,其循环使用次数需大于10次,才能满足基本的经济要求。具体而言,在循环使用条件下,MOF膜的吸附容量需超过11 mg/g;在单次使用条件下,吸附容量需超过40 mg/g。此外,MOF膜的制备成本需控制在130 USD/kg(吸附材料)以下^[86-87]。然而,截至目前,尚未有MOF膜能够达到上述技术指标。

2.2 基于尺寸筛分机理的MOF膜海水提铀

虽然天然海水中离子成分复杂,但主要影响膜技术海水提铀效率的是 Fe^{3+} 、 Ca^{2+} 、 Mg^{2+} 、 Na^+ 、 K^+ 等含量较高的共存离子。因此亟须对上述较高含量共存离子进行分离,从而实现高效海水提铀。值得注意的是,上述高含量共存离子与 UO_2^{2+} 的水合尺寸存在较大差异,因此制备孔径位于10~11 Å(1 Å=0.1 nm)的MOF膜即可实现 UO_2^{2+} 与 Fe^{3+} 、 Ca^{2+} 、 Mg^{2+} 、 Na^+ 、 K^+ 间的高效分离,从而提升整体海水提铀效果(表1)。Chu等^[6]采用甘氨酸作为交联剂,成功制备了新型甘氨酸交联氧化石墨烯薄膜(GO-Gly)。上述膜材料具有约10 Å的均匀离子通道,可满足海水提铀要求,在模拟海水中对U(VI)的截留率接近100%(尺寸截留率:使用膜进行分离一定时间后,溶液中未透过膜的离子质量与原溶液中该离子质量之比),但对其他离子的截留率低于16%,从而证明了基于尺寸筛分机理实现高效海水提铀的可能性。

虽然上述GO-Gly膜可利用孔道实现对U(VI)近似100%截留,但其后续功能化潜力较弱,只适用于模拟海水提铀的理论研究。因此,寻求既可实现精密尺寸筛分又可进行功能修饰的膜材料就变得极为迫切。纯相MOF膜因具有高度均一的孔径和尺寸精确的孔道,有望实现亚埃级精准尺寸筛分^[47]。目前,原位生长法^[91]、二次生长法^[92]、反向扩散界面生长法^[93]以及快速热沉积法^[94](图10)等多种方法已成功用于致密、连生的纯相MOF膜制备。Yu等^[95]使用反向扩散界面生长法在PCTM基底上生长ZIF-8膜,依靠PCTM基底的优异力学性能,使ZIF-8膜不

表1 天然海水中 UO_2^{2+} 、 Fe^{3+} 、 Ca^{2+} 、 Mg^{2+} 、 Na^+ 、 K^+ 、 Cl^- 、 H_2O 的尺寸^[88-90]

Table 1 Size of UO_2^{2+} , Fe^{3+} , Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- , H_2O in the seawater^[88-90]

离子(分子)种类	水合离子(分子)直径/Å
UO_2^{2+}	11.6
Fe^{3+}	9.1
Mg^{2+}	8.6
Ca^{2+}	8.2
Na^+	7.2
K^+	6.6
Cl^-	6.6
H_2O	2.8

仅拥有很高的结构强度,而且在天然海水提铀测试中具有高渗透通量(0.12 L/h)和优异U(VI)截留率(约90%);Tan等^[96]通过使用层层自组装法,在单宁酸(TA)修饰的TAP基底上生长了ZIF-8,成功制备出TAPP-ZIF-60膜,使其在具备优异抗菌能力的基础上,还拥有超高水渗透通量[5459 L/(h·m²)]和优异U(VI)截留率(约95%),从而证明了MOF膜在海水提铀应用中的巨大潜力(图11)。

值得注意的是,目前基于尺寸筛分机理的MOF膜海水提铀研究仍然非常有限。一方面,基于MOF膜的海水提铀过程需要在一定操作压力以及实际海水环境中进行,对膜材料的机械强度和稳定性要求很高;另一方面,复杂的海洋生态环境中金属离子和微生物会在MOF膜表面沉积,使其需要具备一定的自清洁能力和抗沉积性能,以保持长期运行稳定性。此外,基于尺寸筛分机理应用于海水提铀的MOF膜需要孔径尺寸在10~11 Å,孔径尺寸过大或者过小都将影响MOF膜的截留率,从而限制了MOF膜类别。

3 MOF膜海水提铀性能总结

综上所述,当前MOF膜海水提铀研究仍主要基于优先吸附机理,即通过在基底材料中适度添加MOF材料,实现对海水中铀元素的高效吸附分离。Carboni等^[97]制备的MOF-2理论吸附容量为217 mg/g;Wu等^[98]制备的MOF-5理论吸附容量可达237.0 mg/g;Zhang等^[99]通过修饰磷酸基团,制备了Nu-1000-PO和MOF-808-PO两种MOF基膜,其理论吸附容量均超过100 mg/g。近期MOF膜的吸附容量进一步实现了新突破。Guo等^[100]制备的GZA吸附容量为

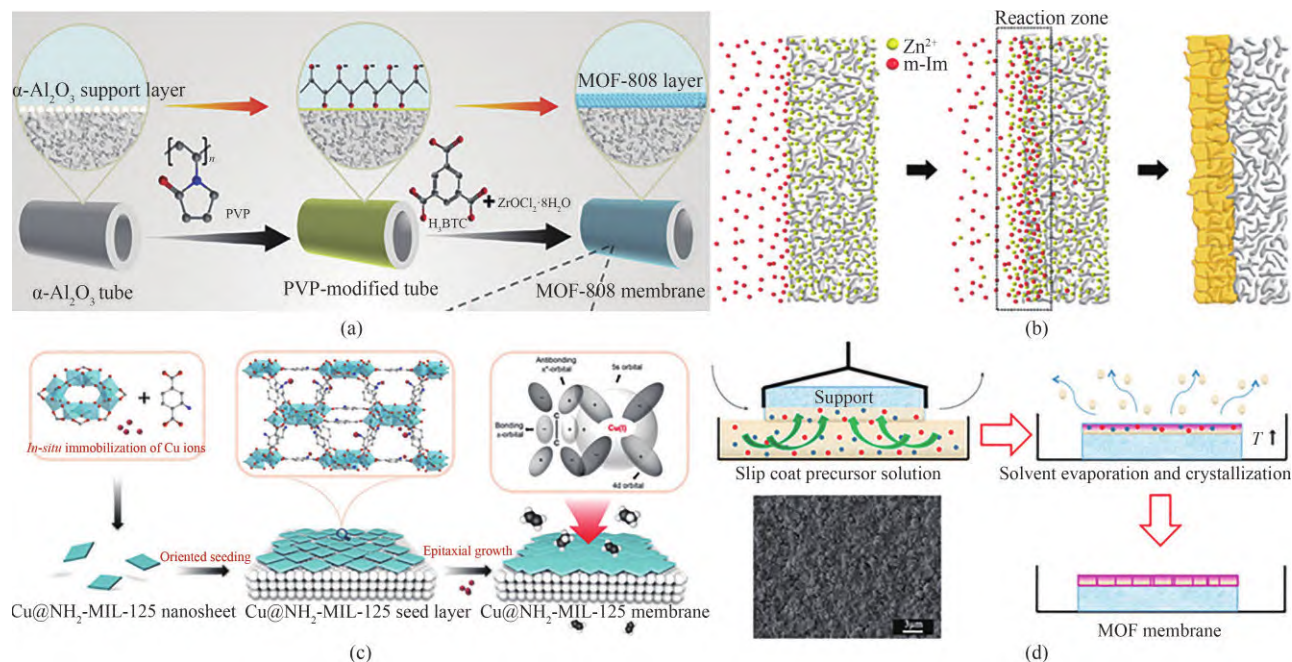


图10 (a)直接生长法制备MOF-808膜示意图^[91];(b)反向扩散界面生长法制备ZIF-8膜示意图^[93];(c)二次生长法制备MIL-125(Cu)膜示意图^[92];(d)快速热沉积法制备ZIF-8膜示意图^[94]

Fig.10 (a) Schematic diagram of MOF-808 membrane prepared by direct growth method^[91]; (b) Schematic diagram of ZIF-8 membrane prepared by reverse diffusion interfacial growth method^[93]; (c) Schematic diagram of MIL-125(Cu) membrane prepared by secondary growth method^[92]; (d) Schematic diagram of ZIF-8 membrane prepared by rapid thermal deposition method^[94]

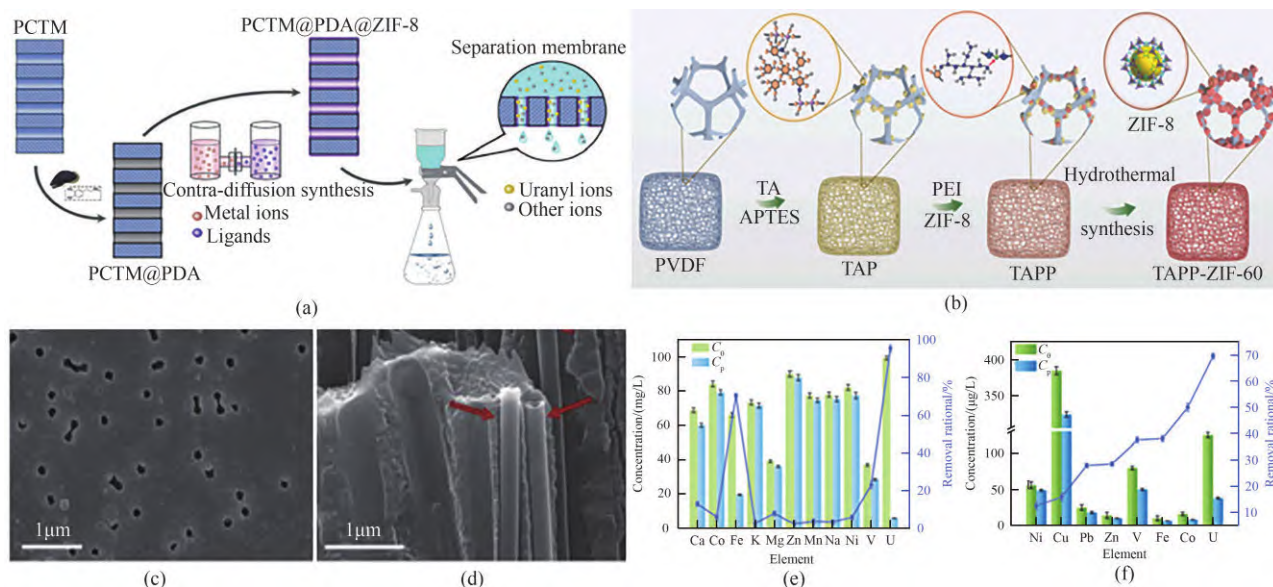


图11 (a)ZIF-8-PCTM膜制备及分离示意图;(b)TAPP-ZIF-60膜制备流程示意图;(c) ZIF-8-PCTM膜表面SEM图像;(d) ZIF-8-PCTM膜界面SEM图像^[95];(e)模拟海水中高浓度共存离子对TAPP-ZIF-60铀截留率的影响;(f)天然海水中高浓度共存离子对TAPP-ZIF-60铀截留率的影响^[96]

Fig.11 (a) Schematic diagram of ZIF-8-PCTM membrane preparation and separation; (b) Schematic diagram of the preparation process of TAPP-ZIF-60 membrane; (c) SEM image of the surface of ZIF-8-PCTM membrane; (d) SEM image of the interface of ZIF-8-PCTM membrane^[95]; (e) Effect of high concentration of coexisting ions in simulated seawater on the uranium rejection rate of TAPP-ZIF-60; (f) Effect of high concentration of co-existing ions in natural seawater on the uranium rejection rate of TAPP-ZIF-60^[96]

602.41 mg/g; Feng 等^[101]制备的 HKUST-1 MOF 基膜吸附容量为 840.3 mg/g; Su 等^[60]合成的 ZIF-67 MOF

基膜的理想吸附容量更高,达 1683.8 mg/g(表 2)。但值得注意的是,受天然海水复杂离子和海洋

表 2 MOF 膜在模拟海水中对 U(VI) 的分离性能
Table 2 Separation performance of MOF membranes for U(VI) in simulated seawater

序号	材料	吸附容量/(mg/g)	时间/h	方法	文献
1	MOF-808-PO	100	0.33	adsorption	[99]
2	MOF-3	109	2.50	adsorption	[97]
3	NU-1000-PO	110	0.33	adsorption	[99]
4	Zn(HBTC)(L)(H ₂ O) ₂	115	0.08	adsorption	[102]
5	Co-SLUG-35	118	4.00	adsorption	[103]
6	MOF-2	217	1.00	adsorption	[97]
7	MOF-5	237.0	0.08	adsorption	[98]
8	PCN-222-PA	401.6	0.50	adsorption	[79]
9	MUU	475	4.00	adsorption	[104]
10	GZA	602.41	2.00	adsorption	[100]
11	HKUST-1	840.3	2.00	adsorption	[101]
12	ZIF-67	1683.8	2.50	adsorption	[60]

生态系统影响, MOF 膜在天然海水(指从海洋中直接获取, 不进行任何处理的海水)中的吸附容量通常将降低为理想吸附量的 1%~5%。Yu 等^[71]制备的 Anti-UiO-66 MOF 膜在模拟海水(指根据天然海水中各种离子含量配制的与天然海水离子浓度一致的混合离子溶液; 模拟海水中仅含有各种离子, 而不含天然海水中的各种微生物等其他物质)中的理想吸附量为 295.95 mg/g, 而在天然海水中的真实吸附量为 2.68 mg/g, 仅为理想吸附量的 1%。已报道的 MOF 膜的天然海水中吸附量均不高于 10 mg/g, 循环使用次数低于 10 次(表 3), 尚未达到工业化的标准, 综合分离性能仍需进一步提升。

表 3 MOF 膜在天然海水中对 U(VI) 的分离性能及循环次数
Table 3 Separation performance and cycle times of MOF membranes for U(VI) in natural seawater

序号	材料	吸附容量	循环次数	方法	文献
1	ZIF-8	62.30 mg/g	7	adsorption	[95]
2	SSUP	12.33 mg/g	6	adsorption	[105]
3	W-UiO-66	6.20 mg/g	5	adsorption	[20]
3	UiO-66-NH ₂ @CS-PDA	5.52 mg/g	5	adsorption	[82]
4	UiO-66-NH ₂	5.52 mg/g	10	adsorption	[82]
5	UiO-66-AO	5.20 mg/g	4	adsorption	[73]
6	ZIF-90-ABOA	2.80 mg/g	5	adsorption	[106]
7	HF-PEI-GDAC	3.34 μg/L	5	adsorption	[107]
8	MIL-101-AO	3.30 μg/L	5	adsorption	[108]

相较而言, 基于尺寸筛分机理的 MOF 膜海提铀研究起步较晚, 但分离性能大都非常优异。Chu 等^[6]使用 GO-Gly 膜在天然海水中对 U(VI) 可以达到

100% 的截留, 分离性能相较基于吸附机理的海水提铀效果更为出色; Liu 等^[91, 109]报道的 UiO-66 膜、MOF-808 膜均具有优异的 U(VI) 截留性能, 在海水提铀应用方面的潜力巨大。

4 结语与展望

综上所述, 鉴于 MOF 膜海水提铀技术操作简单、能耗低、分离性能优异以及无二次污染等优点, 历经多年发展, 科研人员已经成功制备了修饰有偕胺肟基团、磷酸基团、羟基和氨基等吸附基团的多种类型 MOF 膜材料, 基于优先吸附或尺寸筛分机理实现了高效海水提铀。然而, 文中所涉及各类 MOF 膜在海水提铀方面的测试仅限于实验室规模, 尚未开展相关的中试实验。因此, 未来在这一领域仍有大量的研究和探索工作需要开展。

对于基于优先吸附海水提铀的 MOF 膜, 尽管其在模拟海水中展现出优异吸附量和重复使用性, 但是受复杂离子和生态环境的影响, 目前仍未有 MOF 膜达到海水提铀工业化应用指标的相关文献报道。为此, 需要克服天然海水对 MOF 膜 U(VI) 吸附量的影响, 同时提高膜的抗污染性, 进而推动其在海水提铀方面的工业应用。

对于基于尺寸筛分海水提铀的 MOF 膜, 虽然其在天然海水中对 U(VI) 表现出约 100% 的分离性能和优异操作稳定性, 但是仍需克服以下方面的难题: 首先, 利用尺寸筛分进行海水提铀对孔径(10~11 Å)有较高的要求; 其次, MOF 膜需要在高压等苛刻条件下长时间运行, 这对膜稳定性和机械强度具有较高要求; 最后, 复杂的海水生态环境和高盐环境易导致严重膜污染, 从而劣化其分离性能。对于基于尺寸筛分海水提铀的 MOF 膜, 今后将致力于构建连续致密、稳定性高、机械强度大、抗污能力强的新型 MOF 膜, 从而便于其工业化应用。

未来 MOF 膜在海水提铀中应用的研究建议可从以下三方面开展: (1) 目前用于海水提铀的 MOF 材料以锆基 MOF 为主。近期研究证实, 铝基 MOF 对铀酰离子存在强吸附作用, 未来针对海水提铀, 可重点开展针对铝基 MOF 材料的研发。(2) 基于尺寸筛分机理对 MOF 材料的孔径要求严格, 符合要求的 MOF 材料种类有限。为此, 未来可将优先吸附和尺寸筛分机理相结合, 旨在通过在更大孔径 MOF 膜上修饰特定官能基团, 结合优先吸附与尺寸筛分机

理,协同提升MOF膜的截留能力。(3)目前尚缺乏传质理论模型指导MOF膜的设计与构筑。未来可通过结合先进表征技术与分子模拟理论计算,从分子水平揭示MOF膜埃米级传质通道内离子的传质与分离机理,建立面向海水提铀的精准传质理论模型。

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