



# 高性能疏松纳滤膜的制备研究进展

樊 华<sup>1</sup>, 王一雯<sup>1,2</sup>, 姜钦亮<sup>2</sup>, 范 敏<sup>2</sup>, 桂双林<sup>2</sup>, 韩 飞<sup>2</sup>

(1. 南昌大学资源环境与化工学院, 鄱阳湖环境与资源利用教育部重点实验室, 江西南昌 330031;

2. 江西省科学院能源研究所, 江西南昌 330096)

**[摘要]** 疏松纳滤(Loose nanofiltration, LNF)是近几年发展迅速并得到大量研究的一种纳滤分离技术。LNF膜是一种具有纳滤(NF)和超滤(UF)边界孔径的膜,可以在较低的压力下应用且具有较高的选择性,应用前景广阔,尤其在生物质和废水资源化方面表现出明显的优势,是目前的研究热点之一。介绍了近年来关于LNF膜在运行机理、制备方法和应用范围等方面的研究进展;重点介绍了目前LNF膜的制备方法,这些方法主要是通过提升膜表面的亲水性来提升膜的分离性能。主要包括最基本的制备方法(相转化法、界面聚合法),以及在此基础上发展起来的贻贝启发沉积法、有机无机杂化法等,并阐述了根据不同的应用环境,针对性地采用不同方法所制得膜的性能特点及其优势。由于不断提升的标准和越来越注重的资源循环需求,LNF膜在资源回收和废水处理领域都展现出了不俗的表现。最后结合LNF膜近年来的研究进展,对其未来的研究方向和应用前景进行了展望,为未来疏松纳滤膜的性能提升和应用提供参考。

**[关键词]** 疏松纳滤膜;相转化;界面聚合

**[中图分类号]** X703;TQ028.8 **[文献标识码]** A **[文章编号]** 1005-829X(2022)05-0001-10

## Research progress of preparation of high performance loose nanofiltration membranes

FAN Hua<sup>1</sup>, WANG Yiwen<sup>1,2</sup>, JIANG Qinliang<sup>2</sup>, FAN Min<sup>2</sup>, GUI Shuanglin<sup>2</sup>, HAN Fei<sup>2</sup>

(1. School of Resources, Environmental & Chemical Engineering, Nanchang University, Key Laboratory of Poyang Lake Environment and Resource Utilization, Ministry of Education, Nanchang 330031, China;

2. Energy Research Institute of Jiangxi Academy of Science, Nanchang 330096, China)

**Abstract:** Loose nanofiltration(LNF) is a nanofiltration separation technique that is developing rapidly and getting a lot of research in recent years. Due to its high selectivity in nanofiltration and strong ability to operate under lower pressure, LNF membrane, a membrane with nanofiltration(NF) and ultrafiltration(UF) boundary apertures, has become a research hot spot with broad application prospect. It exhibits distinct advantages in resource recovery from biomass and wastewater. The recent developments of LNF membranes in terms of operating mechanism, preparation methods, and application scope were reviewed. The current preparation methods of LNF films were mainly introduced, which was to improve the separation performance of membrane by improving the hydrophilicity of membrane surface. The most basic preparation methods of LNF membrane(phase transformation method, interface polymerization method), and the research progress of mussel inspired deposition method, organic-inorganic hybrid method etc developed on the basis of these methods were mainly introduced. Also, the performance characteristics and advantages of the films prepared by different methods according to different application environments were described. In terms of the application of LNF membranes, due to the increasing standards and focus on the demand for resource recycling, LNF membranes show excellent performance in the fields of resource recycling and wastewater treatment. In the end, combined with the recent research progress, the future research directions and application prospects of the LNF membranes were discussed. It provides reference for the performance improvement and future application

**[基金项目]** 国家自然科学基金项目(NSFC21567009);江西省科学院博士资助项目(2019-YYB-05);普惠制一类资助项目(2019-XTPH1-05)

of porous nanofiltration membrane.

**Key words:** loose nanofiltration membrane; phase inversion; interfacial polymerization

膜分离技术,如超滤、纳滤和反渗透,由于能耗小、效率高、操作条件简单、运行成本低、易于产业化且对环境友好,已被广泛应用于污水处理、海水淡化等领域。与超滤相比,纳滤对低分子质量(200~1 000 u)的有机物和多价离子均有更高的截留率;与反渗透相比,纳滤则具有更高的渗透率和更低的操作压力<sup>[1-4]</sup>。然而,传统意义中的纳滤膜并不能对大分子/盐混合物进行分离并回收,且由于普通纳滤膜对无机盐及大分子等的截留率非常高,往往导致运行过程中渗透压增高,进而导致高的运行能耗<sup>[5]</sup>。

为了对溶质和盐进行有效的分离,B.VAN DER

BRUGGEN等<sup>[6]</sup>在2004年提出了一个新的概念,疏松纳滤(LNF)膜。LNF膜是一类具有纳滤(NF)和超滤(UF)边界孔径的膜,它能够以高渗透通量对分子质量500~2 000 u范围的有机物/盐混合物进行充分分离<sup>[7]</sup>。因此,LNF膜可用于去除超滤无法截留的粒径较小的有机大分子,但允许盐离子通过膜。同时水通量明显高于紧密的纳滤膜,可以在较低的压力下更快地过滤。

目前商业LNF膜,如DK(GE Osmonics),NDX(GE Osmonics),TriSep SBNF(Microdyn Nadir),Sepro NF 2A(Ultura)和Sepro NF 6(Ultura)等已在工业中得到实际应用,膜的基本参数见表1。

表1 商业LNF膜主要信息

Table 1 Main information of commercial LNF membranes

| 生产供应商          | 膜名称         | 膜材料   | 截留分子质量(MWCO)/u | 水通量/(L·m <sup>-2</sup> ·h <sup>-1</sup> ·MPa <sup>-1</sup> ) | 盐截留率/%                   | 参考文献 |
|----------------|-------------|-------|----------------|--------------------------------------------------------------|--------------------------|------|
| GE Osmonics    | DK          | 聚酰胺   | ~150~300       | 100                                                          | 96.0(MgSO <sub>4</sub> ) | [8]  |
| GE Osmonics    | NDX         | 聚酰胺   | 500~700        | 79~101                                                       | 95.0(MgSO <sub>4</sub> ) | [9]  |
| Microdyn Nadir | TriSep SBNF | 醋酸纤维素 | ~150           | 120~177                                                      | 97.0(MgSO <sub>4</sub> ) | [10] |
| Ultura         | Sepro NF 2A | 聚酰胺   | 529            | 101                                                          | 21.2(NaCl)               | [11] |
| Ultura         | Sepro NF 6  | 聚酰胺   | 847            | 167                                                          | 7.3(NaCl)                | [11] |

由表1可知,尽管这些膜可对染料分子进行有效截留,也具有较高的纯水渗透通量<sup>[12]</sup>,但膜的盐截留/通过性能还需提高,且膜的水通量也仍有巨大的提高空间。同时,具有特殊应用环境的LNF膜也待开发。总体而言,寻找处理效率更高,针对性更强且更经济的LNF膜仍然是目前的研究重点。

现阶段关于LNF膜的相关研究很多,但大多数综述类文章是针对染料废水处理的膜工艺改进和应用现状或纳滤膜本身的制作发展,很少直接关注“疏松纳滤膜”本身。笔者将以近3年的文献为基础,对疏松纳滤膜的制备进行综述,最后,对疏松纳滤膜在应用中存在的问题及发展前景进行展望。

## 1 机理分析

纳滤膜分离污染物主要依据尺寸筛分效应及荷电效应<sup>[13]</sup>,但是LNF膜的有机物/盐二元混合物分离原理和膜污染机制可能与纳滤有所不同。在LNF膜的过滤过程中,尺寸筛分效应占主导,大分子在膜表面被截留<sup>[14]</sup>。但是通过对不同的单一染料大分子截留率和过滤通量的测量发现,与理论计算值相

比,分子质量较低的染料如中性红(NR)和亚甲基蓝(MB)等阳离子染料截留率更低<sup>[12]</sup>。因为除了尺寸筛分效应,静电斥力也会影响分离过程。阳离子染料会和膜表面负电荷相吸引,促进染料通过膜孔。同时活性染料如活性蓝2(RB 2)、活性橙16(RO 16)以及一些直接染料如刚果红(CR)<sup>[11]</sup>等阴离子染料的截留率高于理论值。这是由于一方面染料分子聚集,尺寸增大;另一方面带负电的染料分子聚集,增强了静电斥力,导致截留增加。此外LNF膜对一些有机物、腐殖酸的去除,也会产生同样的现象<sup>[15-16]</sup>。

对于分子/盐二元溶液的分离,道南效应起主导作用<sup>[17-18]</sup>。随着盐溶液浓度增大,渗透压差增加,较大的渗透压差破坏了渗透驱动力,使得通量减小。同时由于带电分子的聚集和团聚,膜表面形成污垢层,造成浓度极化,导致实际通量的下降值比理论下降值大得多。E. M. V. HOEK等<sup>[19]</sup>也提出了“滤饼增强的浓差极化”现象,即膜表面形成的未固结滤饼层会促进多孔滤饼层中的浓度极化,并加剧滤饼形成,导致通量下降和膜污染。另外高盐会使膜结构膨

胀,孔径变大,导致粒径较小的染料分子透过膜孔,而膜本身电解质的存在可以有效地屏蔽静电双层作用并增加染料的疏水性,减小膜的介电效应,降低大分子的排斥<sup>[12-13,16,19]</sup>。同时操作条件对于LNF膜的应用至关重要,良好的水利条件和压力能够有力地改善过滤效果,减少膜污染<sup>[16,20]</sup>。

## 2 LNF膜的制备

膜制备方法和膜材料是决定膜结构特性和分离性能的关键。一般而言通过增强LNF膜表面亲水性来提高膜分离性能是LNF膜改性的最常用方法之一,因为相对于疏松纳滤膜来说,浓差极化(cp)现象对其分离性能影响很小。在相同的膜面积和通量条件下,采用亲水性更强的LNF膜将显著降低所需的操作压力,降低运行成本,同时由于膜的强亲水性,也能减缓膜表面污染<sup>[21-22]</sup>。目前,LNF膜常用的制备方法主要有相转化法、界面聚合法、贻贝启发沉积法、有机无机杂化制备技术法以及其他方法。

### 2.1 相转化法

相转化法是大规模制备商业超滤膜最常用的方法之一,但由于该方法很难使膜获得高二价离子截留率和渗透性,无法被广泛应用于纳滤膜的制备。但对于LNF膜的制备来说,采用相转化法似乎更合适。膜的本体聚合物对膜的性能起着至关重要的作用,因此在相转化法制膜时使用新聚合物可以改善LNF膜性能<sup>[23]</sup>。Dongqing LIU等<sup>[24]</sup>通过使用5-磺基邻氨基苯甲酸(SPAA6)和 $\epsilon$ -己内酰胺的共聚物制备了LNF膜,研究结果表明,SPAA6在相转化过程中能够将球形晶体转化为膜结构中条状单元的网络,这种单元网络的出现提升了膜的稳定性及对染料的截留性能。而在相转化过程中添加纳米粒子也可以有效地改善膜的结构和表面性能<sup>[25-27]</sup>。Yatao ZHANG等<sup>[28]</sup>使用硅烷偶联剂(SBMA),采用反原子转移自由基聚合(RATRP)法制备了带电纳米 $\text{SiO}_2$ -SBMA颗粒,在所制备纳米颗粒直径变小的同时改善了粒子分散性。之后将制得的纳米粒子混入铸膜液中,通过相转化法制备了具有高渗透通量并且能有效分离活性染料和无机盐(尤其是二价盐)的LNF膜。Junyong ZHU等<sup>[29]</sup>使用同样的方法将聚甲基丙烯酸磺基甜菜碱接枝到氧化石墨烯(GO)表面,赋予其表面更好的亲水性和抗生物污染性,通过相转化

法将改性后的氧化石墨烯复合材料与聚醚砜混合,构建了新型氧化石墨烯/聚醚砜LNF膜。

此外,通过相转化法还可以很容易地制得中空纤维膜<sup>[30-31]</sup>。如Dawei JI等<sup>[32]</sup>在无溶剂的情况下,使用空气作为芯液,采用相转化法制备了聚砜PSF/氧化石墨烯GO中空纤维膜,形成了独特的密-松结构。同时由于添加了GO粒子,膜表面荷负电,在渗透性增强的同时,也提高了NaCl的透过率,其制备工艺及机理见图1。

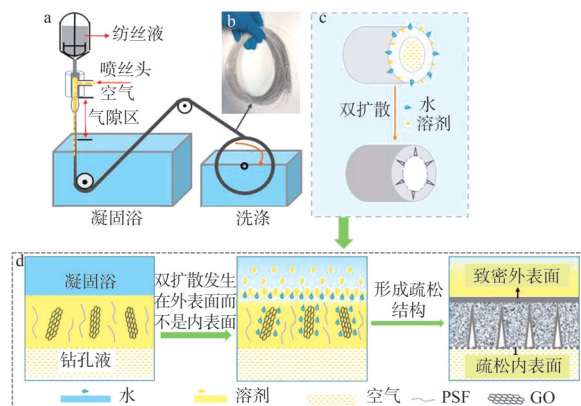


图1 中空纤维膜制备工艺示意图及穿透的指状孔隙和密松结构的形成机理

Fig. 1 Schematic diagram of hollow fiber membrane preparation process and formation mechanism of penetrating fingerlike pores and dense pine structure

### 2.2 界面聚合法

界面聚合(IP)也是LNF膜制备非常重要的方法之一。在界面聚合过程中,两种单体之间的缩聚反应在水相和有机相的边界进行,并最终在水/油界面上制成薄的、均匀的、完整的阻挡层<sup>[33]</sup>。

在界面聚合过程中,使用的单体很大程度上影响了膜的结构和分离性能,因此可以通过寻找新的单体来改善界面聚合所制得膜的性能<sup>[34]</sup>。聚醚胺(PEA)分子尺寸大且亲水,能够赋予膜疏松的结构和良好的亲水性,因此可被用于制作LNF膜,如使用PEA和三聚氯乙稀制备的聚酰胺纳滤膜,其水通量高,对盐截留率很低,对特定染料分子也有良好的截留性能<sup>[35]</sup>。此外,Jincheng DING等<sup>[36]</sup>以1,3-聚苯乙烯和磺化聚乙烯为原料,采用一步法合成了一种新型磺化聚乙烯(SPEI),由于SPEI磺酸基团对界面聚合的抑制作用,制备出的膜表面结构疏松,荷负电且更亲水,能有效分离分子/盐二元溶液。SPEI和三聚氯化苯交联见图2。

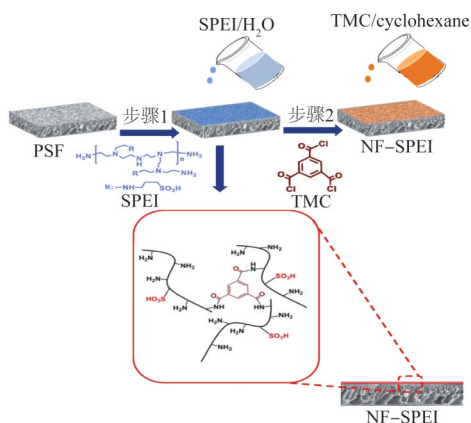


图2 SPEI和三聚氯化苯交联

Fig. 2 Cross-linked SPEI with tripolychlorobenzene

新合成材料也被广泛应用于膜的制备。S. LEE等<sup>[37]</sup>用掺杂胺官能化聚醚砜制备了具有丰富胺基的聚醚砜脲醛树脂亚层;通过三甲基氯化铵交联超滤膜上的胺基,形成富含活性酰氯基团的疏松层,用于接枝壳聚糖。通过调节胺官能化聚醚砜的掺杂量获得LNF膜(截留分子质量为690 u),该膜水通量很高(比NF270高1.3倍),对 $\text{MgSO}_4$ 的截留率达到了97.5%。P. H. H. DUONG等<sup>[38]</sup>将含磺基甜菜碱的两性离子共聚物加入水相中,在聚醚砜亚胺(PEI)不对称薄膜上进行界面聚合。所制备的膜变得更亲水,更光滑,更薄,同时水通量和抗污性能也有显著提高,对染料分子如亮蓝R(摩尔质量826 g/mol)有97%的截留率。同时也有研究表明,单胺分子可以通过降低交联度来调整聚酰胺层结构<sup>[39]</sup>。

改善界面聚合过程也是一种提升膜性能的办法。例如将单宁酸(TA)和哌嗪(PIP)共沉积在膜表面,通过改变TA和PIP的比例限制PIP的扩散,调节界面聚合过程,以此获得了具有截留分子质量为1 370 u的LNF膜<sup>[40]</sup>。由于喷涂技术独特的微分散和纳米分散效果,使用喷涂法,通过微相扩散控制界面聚合过程,使水溶液和有机溶液之间的整体界面有效地分成许多微相界面,能更好地控制界面聚合过程中的扩散行为和膜的形成<sup>[41]</sup>。

总的来说,界面聚合是非常重要的制膜方法,也是现阶段商用纳滤膜最常用的制造方法之一。由于界面聚合过程受温度湿度的限制,步骤较多,比较复杂,因此对界面聚合过程的改进是非常有必要的。实验室中对LNF膜的制备,很多改造方法

都是基于界面聚合的基础之上而来的,在下面的介绍中就不再对界面聚合进行一一说明。

### 2.3 贻贝启发沉积法

由于LNF膜有限的水渗透性和膜污染等问题,为了拓展LNF膜的使用方向,开发具有更宽孔径、高防污性能并带有抗菌效果的膜是非常必要的<sup>[42]</sup>。目前受生物启发的儿茶酚胺化学的贻贝沉积作为一种可有效解决问题的方法引起了广泛关注<sup>[43-44]</sup>。聚多巴胺(PDA)涉及的一步共沉积法可对各种基材牢固黏附,且其能在温和条件下自发聚集。Guangchao LI等<sup>[45]</sup>利用硫酸铜/过氧化氢产生的羟基自由基,通过引入两性离子聚合物(SBMA)可实现PDA快速沉积,且在PDA选择层中的两性离子可有效改善膜的防污和抗菌性能,铜离子可加速多巴胺的沉积和聚合,也赋予了改性膜更强的抗菌性能。同时,膜相对中性的表面可以有效地减少膜表面和污垢之间的相互作用。

然而PDA昂贵不易得,在产业化应用中极难实现。为了解决多巴胺的高成本问题,相似分子如植物多酚类没食子酸(约为多巴胺成本的5%)和单宁酸(TA)被用作PDA单体的替代品广泛应用于膜改性中<sup>[46]</sup>。植物多酚激发的涂层保留了PDA涂层的许多优点,同时多酚成本低、易得、环保,涂层颜色较浅<sup>[47]</sup>,更合适做膜的改性材料。Songbai LIU等<sup>[48]</sup>通过维生素C与 $\text{H}_2\text{O}_2$ 反应生成羟基自由基,将儿茶素接枝到壳聚糖上。同时,儿茶素与氨基的共价连接,将含氨基聚合物壳聚糖共沉积在HPAN超滤膜表面,制备了脱盐纳滤膜。也有研究人员将没食子酸(GA)加入PEI涂覆在HPAN基膜表面,得到对抗生素和染料分子截留很强的膜<sup>[44]</sup>。为了使二价盐能更好的通过膜,利用没食子儿茶素酸酯(EGCg)和聚乙烯亚胺共沉积可得到表面为电中性的膜,由于静电效应减小,该膜对二价盐 $\text{Na}_2\text{SO}_4$ 和 $\text{MgCl}_2$ 截留率分别为4.1%、5.5%,并且在强碱性环境下具有良好的耐有机溶剂性和结构稳定性<sup>[49]</sup>。同时试验显示,通过在膜上涂覆单宁酸,增强膜的亲水性,可促进膜上形成致密的选择层,有利于膜上盐的通过<sup>[50]</sup>。

尽管使用这种涂覆的方法可以制得具有高选择性的LNF膜,但在长期操作过程中形成的污垢以及频繁的清洗会改变膜的孔径和表面电荷性质<sup>[51]</sup>,因此,开发具有高防污和耐化学(极端酸碱度、活性氯化物)性能的LNF膜是非常重要的。例如通过将植物提取

多酚和多肽,如 $\epsilon$ -聚赖氨酸和天然物质焦性没食子酸(PG)共沉积在带负电荷的水解聚丙烯腈(HPAN)基底上,并在HPAN底物表面接枝四臂聚乙二醇甲氧基,可

在改善膜亲水性和抗污性能的同时,使膜对大肠杆菌和金黄色葡萄球菌具有良好的抗菌性,甚至灭活细菌<sup>[52]</sup>,其膜制备过程见图3。

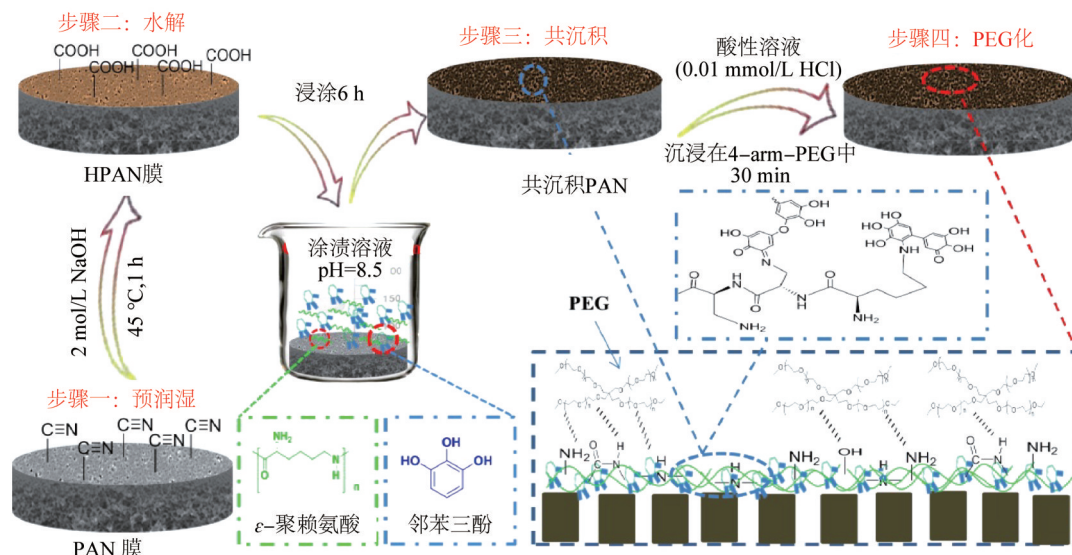


图3 纳滤复合膜的总体制备工艺示意

Fig. 3 Schematic illustration of the overall preparation process of the NF composite membrane

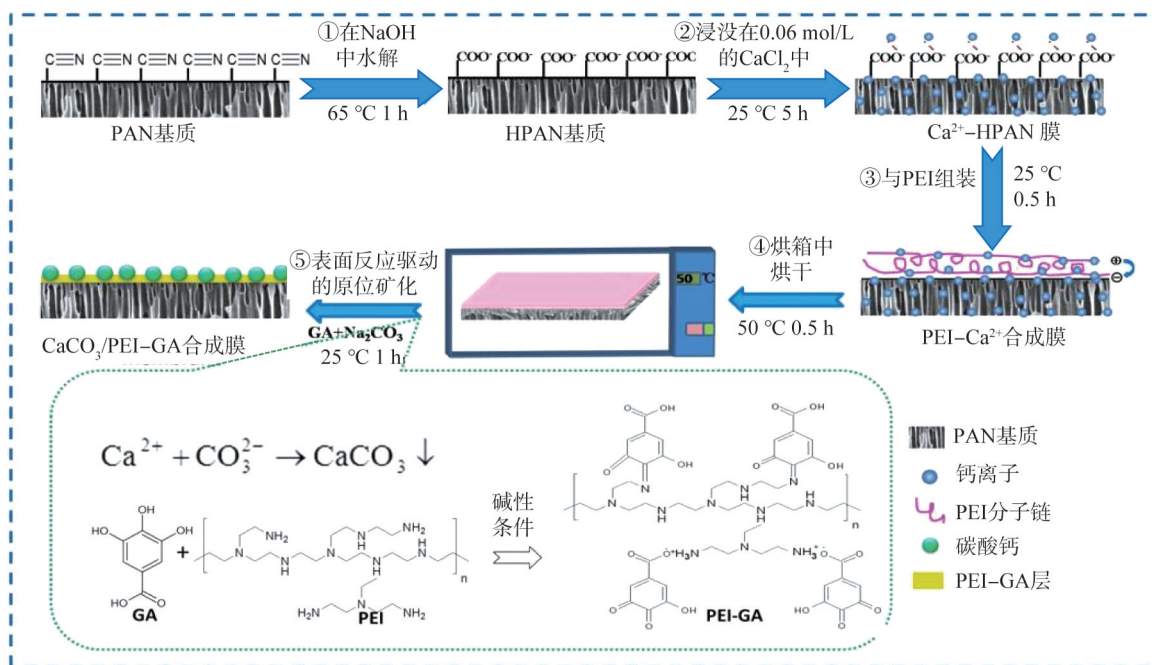
## 2.4 有机无机杂化法

纳滤膜通常是有机-无机杂化膜,即可以通过在有机膜中掺杂无机纳米材料来提升膜的性能。常见的纳米材料有纳米二氧化钛<sup>[53]</sup>、二氧化硅<sup>[54]</sup>、金属-有机骨架(MOF)<sup>[55]</sup>等。在相同的成膜条件下,纳米粒子可在膜的孔内表面形成大量聚集的球体,且存在于膜的基质骨架中,改善膜孔的连通性,增强膜的水通量,形成更疏松的膜<sup>[28]</sup>。同时纳米材料的加入也可以提高LNF膜的亲水性、粗糙度和相对表面积,在提高膜水通量的同时提高盐离子的通过率<sup>[56]</sup>。

为了解决纳米粒子的聚集问题,Qi ZHANG等<sup>[53]</sup>以钛酸四丁酯为前驱体,无水乙醇为溶剂,在膜表面原位生成二氧化钛网。与之前使用界面聚合将填料分散在水/有机相中的制膜方法相比,这种方法制得的膜表面二氧化钛纳米粒子分散均匀,没有可见的聚集,对各种染料的截留率很高,对二价盐 $\text{Na}_2\text{SO}_4$ 的截留率仅为17%,显著提高了膜分离性能。S. KAMARI等<sup>[54]</sup>使用从小麦秸秆中提取的 $\text{SiO}_2$ 涂覆 $\text{Fe}_3\text{O}_4$ 纳米粒子,并用壳聚糖对纳米粒子进行功能化改性,通过相转化法制作了低成本生物聚醚磺膜。该膜对重金属有非常好的截留作用,可用于处理含金属离子和有机染料的各种工业废水,为LNF膜的

应用拓宽了方向。MOF作为传统纳米粒子的替代品,也被用于膜的改性<sup>[55]</sup>。结果表明,MOF通过降低交联度,同时增加膜的厚度、表面负电荷和粗糙度,以此来改变膜特性,是非常有潜力的膜改性方法。另外还可以使用分层组装的方法在膜上组装纳米粒子,如在水解聚丙烯腈(HPAN)膜表面组装聚乙烯亚胺-没食子酸(PEI-GA)层,并在膜表面通过原位矿化的方法组装 $\text{CaCO}_3$ 纳米粒子,从而制备亲水防污的LNF膜<sup>[57]</sup>, $\text{Ca}^{2+}$ 在聚合物层中原位生长过程见图4。

除了一些常见的无机离子,纳米材料还包括氧化镓、COF、二硫化钼等二维材料,其原子厚度和独特的物理/化学性质使之成为了LNF膜改性的一大选择<sup>[58-60]</sup>。GO由于独特的2D纳米片结构、大比表面积、良好的机械性和强亲水性成为提高膜性能的极佳选择<sup>[60]</sup>。Zhongyong QIU等<sup>[61]</sup>使用热致相分离法(TIPS)制作了一种坚固的三维/二维聚丙烯腈/GO均相纳米多孔膜。通过溶剂交换的方法保证GO在高浓度PEG-400中分散良好。所得的膜具有优异的机械强度、防污性能和良好的亲水性,可以长期运行,并且均匀的结构解决了传统方法遇到的活性层剥离的问题。但是GO薄膜水通量低且遇水膨

图4  $\text{Ca}^{2+}$ 在聚合物层中原位生长过程Fig. 4  $\text{Ca}^{2+}$  grows in situ in the polymer layer

胀<sup>[30]</sup>,因此找到更合适的GO替代品是近年来关注的重点。过渡金属二元化合物(TMDs)纳米片由于具有更光滑的表面,没有任何含氧亲水官能团伸出平面成为近期的热门研究对象<sup>[58]</sup>。二硫化钼与GO结构相似,原子厚度的二硫化钼片膜透水性比氧化石墨烯膜高3~5倍,同时表现出良好的非膨胀性<sup>[62]</sup>,成为代替GO的一大选择。W. HU等<sup>[63]</sup>在膜中加入少量TA改性二硫化钼,制得了更亲水、负电性更强的膜。由于二硫化钼的存在,膜显示了超高的水通量并且对多种不同的染料分子截留率达到了 $(99.87 \pm 0.1)\%$ ,在水中展现出了优越的非膨胀性。层状双氢氧化物LDHs也是一种比较好的二维材料,Shuang ZHAO等<sup>[64]</sup>通过螯合辅助原位生长(CAIG)的方法,利用PEI对金属离子的好螯合能力,同时加入Ni/Co,制备了松散杂化纳滤膜,解决了LDHs纳米颗粒在有机膜表面生长困难且需要高温才能进行反应的问题,同时螯合剂的引入增强了纳米粒子与膜表面的相互作用,使膜上的纳米粒子短期无聚集,长期稳定性好。

总之,加入纳米粒子可以使膜获得优异的松散纳米纤维性能,但是其仍然存在一些缺点,例如特定单体的复杂预合成过程、纳米颗粒的团聚以及填料

和基体之间缺乏相互作用。除此之外,目前附加纳米材料的LNF膜只应用于实验室规模的试验,大规模生产商用LNF膜还需要进一步讨论和研究,同时这种膜除了染料去除领域外,在其他领域的应用也需要探索。

## 2.5 其他方法

除了常见的一些平板膜之外,还有一些特殊的LNF膜制造方法。由于操作压力高,在纳滤膜或反渗透膜组件中很难应用中空纤维结构<sup>[65]</sup>,但LNF膜可以在相对较低的压力下操作,且中空纤维膜耐久性更好,可用盐酸冲洗而不变形,因此制作疏松的中空纤维膜也是非常好的选择<sup>[30, 66-67]</sup>。Zhiyong CHU等<sup>[66]</sup>通过干湿法纺丝工艺制作了新型的增强聚醚砜中空纤维膜,通过提高膜的抗侧压力,保证了膜的渗透稳定性。也有一些研究是关于工艺的改良,如在处理二元废水时加入电渗析,如图5所示,利用离子交换膜和LNF膜的优点,可实现叠层结构“松散纳滤膜基离子交换膜”,解决商业纳滤膜严重的膜污染问题<sup>[68]</sup>。还有Shiwei GUO等<sup>[69]</sup>研究了后处理对LNF膜的影响,结果表明,经过后处理获得的膜具有更高的MWCO、更大的孔径和更宽的孔径分布,但经过后处理的膜可能会产生更严重的膜污染。

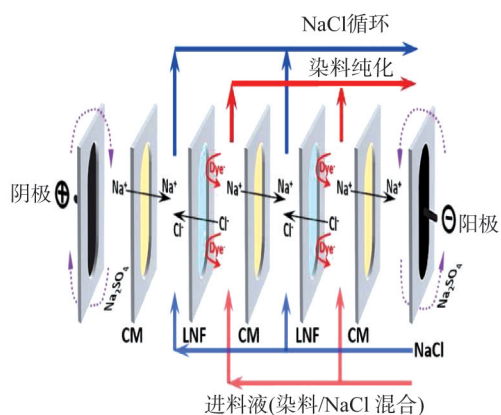


图5 电渗析与LNF膜

Fig. 5 Electrodialysis and LNF membrane

### 3 LNF膜的应用

目前,几乎所有的纳滤膜都是由聚酰胺(分离层)制成的,这种膜易受强酸和游离氯的影响,对高温和酸碱度也很敏感<sup>[69]</sup>。而LNF膜有更多的材料选择,这使得它们在极端条件下具有更好的耐用性和稳定性。因此,LNF膜扩展了纳滤膜技术的应用领域,特别是在资源回收方面。例如回收农副产物中的多酚<sup>[70]</sup>,在生物制品加工中回收天然色素<sup>[71]</sup>等。为了提高糖回收率和牛乳低聚糖的纯度,J. M. L. N. DE MOURA BELL等<sup>[72]</sup>开发了一种新技术,即在酵母完全水解乳糖和发酵单糖后,通过LNF膜过滤分离初乳中的发酵乳清,使95%的高纯度低聚糖得以回收。在制糖工艺中,利用LNF膜去除和回收蔗糖中的天然色素也是非常重要的实践方向之一。Jianquan LUO等<sup>[73]</sup>采用管状松散超滤(UF)、螺旋缠绕LNF和螺旋缠绕纳滤(NF)组成的一体化膜工艺对甘蔗原汁进行中试提纯,在高通量运行情况下,脱色率保持在95%以上,并且蔗糖回收率高达98%。

在废水处理领域,LNF膜也具有优异的表现。纺织废水中除了含有大量染料分子,通常还伴有高浓度的盐(如NaCl或Na<sub>2</sub>SO<sub>4</sub>)<sup>[7,47-49,51]</sup>。然而,商业纳滤膜的高盐截留率导致大量的水和能量消耗,且无法对有价值资源进行有效回收<sup>[74]</sup>。相比之下,LNF膜以高盐透过率,充分保留了染料分子,并高效分离了盐,也因此降低了浓差极化和操作压力,有利于减少膜污染,提高通量。除此之外,F. OULAD等<sup>[75]</sup>通过测试LNF膜对于藻类染料的高去除率,试验了LNF膜对于处理真正的藻类废水的效果也很好,在保证

了膜对藻类高效截留的同时,通量也比较稳定。LNF膜还可以用来去除农业用水中的农药残留<sup>[21]</sup>,回收垃圾渗滤液中的腐殖质用于植物生长的有效肥料<sup>[15]</sup>以及去除天然水中的天然有机物(NOM)<sup>[40]</sup>等。例如M. PEYDAYESH等<sup>[76]</sup>开发了一种顶层自组装乙二醇接枝的多壁碳纳米管(ED-g-mwcnt)的不对称聚醚砜LNF膜,膜表面带正电荷,可用于净化重金属废水。与纯聚醚砜膜相比,其对Zn(96.7%)、Cd(92.4%)、Cu(91.9%)、Ni(90.7%)、Pb(90.5%)等的重金属截留率较好。

### 4 总结和展望

与纳滤膜相比,LNF膜拥有更高的渗透性,对盐更低的截留率和更高的分离选择性,在从废水中回收资源方面显示出了巨大的优势。其中,高分离选择性是LNF膜应用的关键特性,尤其是从复杂的工业废水中回收有价值资源<sup>[65,77-78]</sup>。目前可以采用多种不同的方法如相转化,界面聚合,贻贝启发沉积,有机无机杂化等多种方法来制备及增强LNF膜的选择性。未来,随着资源的缺乏以及可持续发展战略的推进,LNF膜以其优越的分离性质和低能耗,势必会在更多的领域得到广泛的应用。然而,在不同严苛环境条件(如强酸、强碱、细菌污染等)下存在的膜污染和膜清洁方面的问题还有待解决。未来,研究并开发化学性质稳定、耐酸碱且有一定抗菌效果的LNF膜是非常必要的。此外,LNF膜的应用还在实验室试验阶段,大规模的产业化应用也有待实践。

#### 参考文献

- [1] 高晓琪,俞开昌,王小毛.疏松型纳滤膜对饮用水中无机阳离子的截留特性及分离选择性[J].环境科学学报,2020,40(8):2700-2707.  
GAO Xiaoqi, YU Kaichang, WANG Xiaomao. Rejection behaviors and separation selectivity of loose nanofiltration membranes for mineral ions in drinking water[J]. Acta Scientiae Circumstantiae, 2020, 40(8):2700-2707.
- [2] WEI Yuxuan, LÜ Yanlong, GUO Beidou, et al. Hierarchical molybdenum disulfide nanosheet arrays stemmed from nickel-cobalt layered double hydroxide/carbon cloth for highly-efficient hydrogen evolution reaction[J]. Journal of Energy Chemistry, 2021, 57:587-592.
- [3] MA Jingwen, CAI An, GUAN Xinglong, et al. Preparation of ultrathin molybdenum disulfide dispersed on graphene via cobalt doping: A bifunctional catalyst for hydrogen and oxygen evolution reaction[J]. International Journal of Hydrogen Energy, 2020, 45(16):9583-9591.

- [4] ABDEL-FATAH M A. Nanofiltration systems and applications in wastewater treatment: Review article [J]. Ain Shams Engineering Journal, 2018, 9(4): 3077-3092.
- [5] NATH K, DAVE H K, PATEL T M. Revisiting the recent applications of nanofiltration in food processing industries: Progress and prognosis [J]. Trends in Food Science & Technology, 2018, 73: 12-24.
- [6] VANDER BRUGGEN B, CURCIO E, DRIOLI E. Process intensification in the textile industry: The role of membrane technology [J]. Journal of Environmental Management, 2004, 73(3): 267-274.
- [7] GUO Shiwei, WAN Yinhua, CHEN Xiangrong, et al. Loose nanofiltration membrane custom-tailored for resource recovery [J]. Chemical Engineering Journal, 2021, 409: 127376.
- [8] CISSÉ M, VAILLANT F, PALLET D, et al. Selecting ultrafiltration and nanofiltration membranes to concentrate anthocyanins from Roselle extract (*Hibiscus sabdariffa* L.) [J]. Food Research International, 2011, 44(9): 2607-2614.
- [9] HERMANS S, BERNSTEIN R, VOLODIN A, et al. Study of synthesis parameters and active layer morphology of interfacially polymerized polyamide-polysulfone membranes [J]. Reactive and Functional Polymers, 2015, 86: 199-208.
- [10] MARUF S H, GREENBERG A R, DING Yifu. Influence of substrate processing and interfacial polymerization conditions on the surface topography and permselective properties of surface-patterned thin-film composite membranes [J]. Journal of Membrane Science, 2016, 512: 50-60.
- [11] LIN Jiuyang, TANG C Y, YE Wenyuan, et al. Unraveling flux behavior of superhydrophilic loose nanofiltration membranes during textile wastewater treatment [J]. Journal of Membrane Science, 2015, 493: 690-702.
- [12] YE Wenyuan, LIN Jiuyang, BORREGO R, et al. Advanced desalination of dye/NaCl mixtures by a loose nanofiltration membrane for digital ink-jet printing [J]. Separation and Purification Technology, 2018, 197: 27-35.
- [13] TANG C Y, CHONG T H, FANE A G. Colloidal interactions and fouling of NF and RO membranes: A review [J]. Advances in Colloid and Interface Science, 2011, 164(1/2): 126-143.
- [14] DER BRUGGEN B V, DAEMS B, WILMS D, et al. Mechanisms of retention and flux decline for the nanofiltration of dye baths from the textile industry [J]. Separation and Purification Technology, 2001, 22/23: 519-528.
- [15] YE Wenyuan, LIU Hongwei, JIANG Mei, et al. Sustainable management of landfill leachate concentrate through recovering humic substance as liquid fertilizer by loose nanofiltration [J]. Water Research, 2019, 157: 555-563.
- [16] YE Wenyuan, BERNSTEIN N J, LIN Jiuyang, et al. Theoretical and experimental study of organic fouling of loose nanofiltration membrane [J]. Journal of the Taiwan Institute of Chemical Engineers, 2018, 93: 509-518.
- [17] 石紫, 王志, 王宠, 等. 染料分离有机纳滤膜制备技术研究进展 [J]. 膜科学与技术, 2020, 40(1): 340-351.
- SHI Zi, WANG Zhi, WANG Chong, et al. Research progress in the preparation of organic nanofiltration membranes for dye separation [J]. Membrane Science and Technology, 2020, 40(1): 340-351.
- [18] LIN Jiuyang, YE Wenyuan, BALTARU M C, et al. Tight ultrafiltration membranes for enhanced separation of dyes and  $\text{Na}_2\text{SO}_4$  during textile wastewater treatment [J]. Journal of Membrane Science, 2016, 514: 217-228.
- [19] HOEK E M V, ELIMELECH M. Cake-enhanced concentration polarization: A new fouling mechanism for salt-rejecting membranes [J]. Environmental Science & Technology, 2003, 37(24): 5581-5588.
- [20] ARSUGA J M, LÓPEZ-MUÑOZ M J, AGUADO J, et al. Temperature, pH and concentration effects on retention and transport of organic pollutants across thin-film composite nanofiltration membranes [J]. Desalination, 2008, 221(1/2/3): 253-258.
- [21] SHAN Linglong, LIANG Yuanzhe, PROZOROVSKA L, et al. Multifold enhancement of loose nanofiltration membrane performance by intercalation of surfactant assemblies [J]. Environmental Science & Technology Letters, 2018, 5(11): 668-674.
- [22] HILAL N, AL-ZOUBI H, MOHAMMAD A W, et al. Nanofiltration of highly concentrated salt solutions up to seawater salinity [J]. Desalination, 2005, 184(1/2/3): 315-326.
- [23] AGARWAL P, HEFNER R E Jr, GE Shouren, et al. Nanofiltration membranes from crosslinked Troger's base Polymers of Intrinsic Microporosity (PIMs) [J]. Journal of Membrane Science, 2020, 595: 117501.
- [24] LIU Dongqing, ZHU Zexian, ZHAO Yiping, et al. Low pressure modified polyamide 6 membrane for effective fractionation of dyes and NaCl [J]. Science of the Total Environment, 2019, 695: 133908.
- [25] TAVANGAR T, KARIMI M, REZAKAZEMI M, et al. Textile waste, dyes/inorganic salts separation of cerium oxide-loaded loose nanofiltration polyethersulfone membranes [J]. Chemical Engineering Journal, 2020, 385: 123787.
- [26] JIN Jinbo, DU Xilan, YU Jie, et al. High performance nanofiltration membrane based on SMA-PEI cross-linked coating for dye/salt separation [J]. Journal of Membrane Science, 2020, 611: 118307.
- [27] ZHANG Luhong, GUAN Hongfang, ZHANG Na, et al. A loose NF membrane by grafting  $\text{TiO}_2$ -HMDI nanoparticles on PES/ $\beta$ -CD substrate for dye/salt separation [J]. Separation and Purification Technology, 2019, 218: 8-19.
- [28] ZHANG Yatao, SONG Qiangqiang, LIANG Xu, et al. High-flux, high-selectivity loose nanofiltration membrane mixed with zwitterionic functionalized silica for dye/salt separation [J]. Applied Surface Science, 2020, 515: 146005.
- [29] ZHU Junyong, TIAN Miaomiao, HOU Jingwei, et al. Surface zwitterionic functionalized graphene oxide for a novel loose nanofiltration membrane [J]. Journal of Materials Chemistry A, 2016, 4(5):

- 1980-1990.
- [30] HAN Gang, FENG Yingnan, CHUNG T S, et al. Phase inversion directly induced tight ultrafiltration (UF) hollow fiber membranes for effective removal of textile dyes [J]. *Environmental Science & Technology*, 2017, 51(24): 14254-14261.
  - [31] HAN Gang, CHUNG T S, WEBER M, et al. Low-pressure nanofiltration hollow fiber membranes for effective fractionation of dyes and inorganic salts in textile wastewater [J]. *Environmental Science & Technology*, 2018, 52(6): 3676-3684.
  - [32] JI Dawei, XIAO Changfa, AN Shulin, et al. Preparation of high-flux PSF/GO loose nanofiltration hollow fiber membranes with dense-loose structure for treating textile wastewater [J]. *Chemical Engineering Journal*, 2019, 363: 33-42.
  - [33] PAUL M, JONS S D. Chemistry and fabrication of polymeric nanofiltration membranes: A review [J]. *Polymer*, 2016, 103: 417-456.
  - [34] ZHANG Xiaotai, HUANG Hai, LI Qiang, et al. Facile dual-functionalization of polyamide reverse osmosis membrane by a natural polypeptide to improve the antifouling and chlorine-resistant properties [J]. *Journal of Membrane Science*, 2020, 604: 118044.
  - [35] MI Yifang, WANG Na, QI Qi, et al. A loose polyamide nanofiltration membrane prepared by polyether amine interfacial polymerization for dye desalination [J]. *Separation and Purification Technology*, 2020, 248: 117079.
  - [36] DING Jincheng, WU Huiqing, WU Peiyi. Preparation of highly permeable loose nanofiltration membranes using sulfonated polyethyleneimine for effective dye/salt fractionation [J]. *Chemical Engineering Journal*, 2020, 396: 125199.
  - [37] LEE S, CHOI E Y, KIM C K. Fabrication and properties of nanofiltration membranes assembled with chitosan on poly(ether sulfone) membranes surface-functionalized with acyl chloride groups [J]. *Industrial & Engineering Chemistry Research*, 2019, 58(16): 6679-6686.
  - [38] DUONG P H H, DAUMANN K, HONG Peiying, et al. Interfacial polymerization of zwitterionic building blocks for high-flux nanofiltration membranes [J]. *Langmuir: the ACS Journal of Surfaces and Colloids*, 2019, 35(5): 1284-1293.
  - [39] SHINTANI T, AKAMATSU K, HAMADA S, et al. Preparation of monoamine-incorporated polyamide nanofiltration membranes by interfacial polymerization for efficient separation of divalent anions from divalent cations [J]. *Separation and Purification Technology*, 2020, 239: 116530.
  - [40] LI Qin, LIAO Zhipeng, FANG Xiaofeng, et al. Tannic acid assisted interfacial polymerization based loose thin-film composite NF membrane for dye/salt separation [J]. *Desalination*, 2020, 479: 114343.
  - [41] SHAN Linglong, GU Jiahui, FAN Hongwei, et al. Microphase diffusion-controlled interfacial polymerization for an ultrahigh permeability nanofiltration membrane [J]. *ACS Applied Materials & Interfaces*, 2017, 9(51): 44820-44827.
  - [42] LI Yukun, LUO Jianquan, WAN Yinhua. Biofouling in sugarcane juice refining by nanofiltration membrane: Fouling mechanism and cleaning [J]. *Journal of Membrane Science*, 2020, 612: 118432.
  - [43] ZHU Junyong, TSEHAYE M T, WANG Jing, et al. A rapid deposition of polydopamine coatings induced by iron(III) chloride/hydrogen peroxide for loose nanofiltration [J]. *Journal of Colloid and Interface Science*, 2018, 523: 86-97.
  - [44] CHENG Xiquan, WANG Zhenxing, ZHANG Yanqiu, et al. Bio-inspired loose nanofiltration membranes with optimized separation performance for antibiotics removals [J]. *Journal of Membrane Science*, 2018, 554: 385-394.
  - [45] LI Guangchao, LIU Bin, BAI Langming, et al. Improving the performance of loose nanofiltration membranes by poly-dopamine/zwitterionic polymer coating with hydroxyl radical activation [J]. *Separation and Purification Technology*, 2020, 238: 116412.
  - [46] CHENG Xiquan, WANG Zhenxing, GUO Jing, et al. Designing multifunctional coatings for cost-effectively sustainable water remediation [J]. *ACS Sustainable Chemistry & Engineering*, 2018, 6(2): 1881-1890.
  - [47] ZHANG Xi, REN Pengfei, YANG Haocheng, et al. Co-deposition of tannic acid and diethylenetriamine for surface hydrophilization of hydrophobic polymer membranes [J]. *Applied Surface Science*, 2016, 360: 291-297.
  - [48] LIU Songbai, WANG Zhan, SONG Peng. Free radical graft copolymerization strategy to prepare catechin-modified chitosan loose nanofiltration (NF) membrane for dye desalination [J]. *ACS Sustainable Chemistry & Engineering*, 2018, 6(3): 4253-4263.
  - [49] ZHANG Na, JIANG Bin, ZHANG Luhong, et al. Low-pressure electroneutral loose nanofiltration membranes with polyphenol-inspired coatings for effective dye/divalent salt separation [J]. *Chemical Engineering Journal*, 2019, 359: 1442-1452.
  - [50] LI Qin, LIAO Zhipeng, FANG Xiaofeng, et al. Tannic acid-polyethyleneimine crosslinked loose nanofiltration membrane for dye/salt mixture separation [J]. *Journal of Membrane Science*, 2019, 584: 324-332.
  - [51] HUANG Jiachen, LUO Jianquan, CHEN Xiangrong, et al. How do chemical cleaning agents act on polyamide nanofiltration membrane and fouling layer? [J]. *Industrial & Engineering Chemistry Research*, 2020, 59(40): 17653-17670.
  - [52] ZHAO Shuang, SONG Peng, WANG Zhan, et al. The PEGylation of plant polyphenols/polypeptide-mediated loose nanofiltration membrane for textile wastewater treatment and antibacterial application [J]. *Journal of the Taiwan Institute of Chemical Engineers*, 2018, 82: 42-55.
  - [53] ZHANG Qi, FAN Lin, YANG Zhen, et al. Loose nanofiltration membrane for dye/salt separation through interfacial polymerization with in situ generated TiO<sub>2</sub> nanoparticles [J]. *Applied Surface Science*, 2017, 410: 494-504.
  - [54] KAMARI S, SHAHBAZI A. High-performance nanofiltration mem-

- brane blended by  $\text{Fe}_3\text{O}_4/\text{SiO}_2$ -CS bionanocomposite for efficient simultaneous rejection of salts/heavy metals ions/dyes with high permeability, retention increase and fouling decline[J]. Chemical Engineering Journal, 2021, 417: 127930.
- [55] ZHAO Yangying, LIU Yanling, WANG Xiaomao, et al. Impacts of metal-organic frameworks on structure and performance of polyamide thin-film nanocomposite membranes[J]. ACS Applied Materials & Interfaces, 2019, 11(14): 13724-13734.
- [56] YANG Shishi, JIANG Qinliang, ZHANG Kaisong. Few-layers 2D  $\text{O}-\text{MoS}_2$  TFN nanofiltration membranes for future desalination[J]. Journal of Membrane Science, 2020, 604: 118052.
- [57] ZHANG Jinglong, YANG Libin, WANG Zhan, et al. A highly permeable loose nanofiltration membrane prepared via layer assembled in situ mineralization[J]. Journal of Membrane Science, 2019, 587: 117159.
- [58] HAN Jiaojiao, ZHANG Qiuyue, HUANG Minyue, et al. Two-dimensional  $\text{WS}_2$  membranes constructed on different substrates for efficient dye desalination[J]. Desalination, 2020, 480: 114380.
- [59] YANG Shishi, ZHANG Kaisong. Few-layers  $\text{MoS}_2$  nanosheets modified thin film composite nanofiltration membranes with improved separation performance[J]. Journal of Membrane Science, 2020, 595: 117526.
- [60] XU Guorong, XU Jianmei, SU Huichao, et al. Two-dimensional (2D) nanoporous membranes with sub-nanopores in reverse osmosis desalination: Latest developments and future directions[J]. Desalination, 2019, 451: 18-34.
- [61] QIU Zhongyong, JI Xiaofei, HE Chunju. Fabrication of a loose nanofiltration candidate from Polyacrylonitrile/Graphene oxide hybrid membrane via thermally induced phase separation[J]. Journal of Hazardous Materials, 2018, 360: 122-131.
- [62] SUN Luwei, HUANG Hubiao, PENG Xinsheng. Laminar  $\text{MoS}_2$  membranes for molecule separation[J]. Chemical Communications (Cambridge, England), 2013, 49(91): 10718-10720.
- [63] HU W, CUI Xinwei, XIANG Li, et al. Tannic acid modified  $\text{MoS}_2$  nanosheet membranes with superior water flux and ion/dye rejection[J]. Journal of Colloid and Interface Science, 2020, 560: 177-185.
- [64] ZHAO Shuang, ZHU Hongtai, WANG Zhan, et al. A loose hybrid nanofiltration membrane fabricated via chelating-assisted in situ growth of Co/Ni LDHs for dye wastewater treatment[J]. Chemical Engineering Journal, 2018, 353: 460-471.
- [65] SINGTO S, SAJOMSANG W, RATANATAWANATE C, et al. Flexible and hydrophilic copolyamide thin-film composites on hollow fiber membranes for enhanced nanofiltration performance[J]. ACS Applied Materials & Interfaces, 2020, 12(25): 28624-28634.
- [66] CHU Zhiyong, CHEN Kaikai, XIAO Changfa, et al. Improving pressure durability and fractionation property via reinforced PES loose nanofiltration hollow fiber membranes for textile wastewater treatment[J]. Journal of the Taiwan Institute of Chemical Engineers, 2020, 108: 71-81.
- [67] LAAKSO T, PIHLAJAMÄKI A, MÄNTTÄRI M. Effect of polycation structure on the fabrication of polyelectrolyte multilayer hollow fiber membranes for loose nanofiltration applications[J]. Separation and Purification Technology, 2018, 194: 141-148.
- [68] YE Wenyuan, LIU Riri, CHEN Xiangyu, et al. Loose nanofiltration-based electrodialysis for highly efficient textile wastewater treatment[J]. Journal of Membrane Science, 2020, 608: 118182.
- [69] GUO Shiwei, LUO Jianquan, YANG Qiangjian, et al. Decoloration of molasses by ultrafiltration and nanofiltration: Unraveling the mechanisms of high sucrose retention[J]. Food and Bioprocess Technology, 2019, 12(1): 39-53.
- [70] CASSANO A, CONIDI C, RUBY-FIGUEROA R, et al. Nanofiltration and tight ultrafiltration membranes for the recovery of polyphenols from agro-food by-products[J]. International Journal of Molecular Sciences, 2018, 19(2): 351.
- [71] SALEEM H, TRABZON L, KILIC A, et al. Recent advances in nanofibrous membranes: Production and applications in water treatment and desalination[J]. Desalination, 2020, 478: 114178.
- [72] DE MOURA BELL J M L N, COHEN J L, DE AQUINO L F M C, et al. An integrated bioprocess to recover bovine milk oligosaccharides from colostrum whey permeate[J]. Journal of Food Engineering, 2018, 216: 27-35.
- [73] LUO Jianquan, HANG Xiaofeng, ZHAI Wei, et al. Refining sugarcane juice by an integrated membrane process: Filtration behavior of polymeric membrane at high temperature[J]. Journal of Membrane Science, 2016, 509: 105-115.
- [74] CHEN Pengli, MA Xiao, ZHONG Zhaoxiang, et al. Performance of ceramic nanofiltration membrane for desalination of dye solutions containing NaCl and  $\text{Na}_2\text{SO}_4$ [J]. Desalination, 2017, 404: 102-111.
- [75] OULAD F, ZINADINI S, ZINATIZADEH A A, et al. Preparation and characterization of loose antifouling nanofiltration membrane using branched aniline oligomers grafted onto polyether sulfone and application for real algal dye removal[J]. Chemical Engineering Journal, 2020, 401: 125861.
- [76] PEYDAYESH M, MOHAMMADI T, NIKOUZAD S K A. A positively charged composite loose nanofiltration membrane for water purification from heavy metals[J]. Journal of Membrane Science, 2020, 611: 118205.
- [77] ZHANG Huiru, HE Qiming, LUO Jianquan, et al. Sharpening nanofiltration: Strategies for enhanced membrane selectivity[J]. ACS Applied Materials & Interfaces, 2020, 12(36): 39948-39966.
- [78] IBRAHIM G P S, ISLOOR A M, MOSLEHYANI A, et al. Bio-inspired, fouling resistant, tannic acid functionalized halloysite nanotube reinforced polysulfone loose nanofiltration hollow fiber membranes for efficient dye and salt separation[J]. Journal of Water Process Engineering, 2017, 20: 138-148.

[作者简介] 樊华(1963—), 副教授。E-mail: 859833571@qq.com。

通讯作者: 姜钦亮, 博士。E-mail: qljiang6@163.com。

[收稿日期] 2022-03-02(修改稿)