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# 聚酰胺膜耐氯改性及氯化修复研究进展

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**摘要**：介绍了间苯二胺-均苯三甲酰氯和哌嗪-均苯三甲酰氯两种典型的 PA 膜,深入剖析其最新的氯化破坏机理.在此基础上,进一步探讨了针对这两种膜的耐氯改性方法,包括改变单体结构、本体掺杂技术、物理涂覆方法以及化学接枝手段等.对 PA 膜氯化修复领域的最新研究进展进行了简要论述,包括初期氯化后的还原法修复和氯化降解后的修补剂修复.分析表明,耐氯 PA 膜的研制仍面临巨大挑战,PA 膜的耐氯改性研究应在不牺牲其分离性能的前提下,综合考虑膜的其他各项性能,灵活运用各种改性方法.

**关键词**：聚酰胺膜；反渗透；纳滤；氯化破坏机理；耐氯改性；氯化修复；分离；膜
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**Advances of chlorine-resistant modification and chlorination remediation of polyamide membrane.** ZHU Qin-yan, LI Xin-dong*, BAO Luo, JIA Jiang-hui, YU Si-Wei, ZHONG Zhao-huang, CAI Meng (Jiangxi Provincial Key Laboratory of Water Ecological Conservation at Headwater Regions; Innovation Center for Water Quality Security Technology at Ganjiang River Basin, Ganzhou 341000, China). *China Environmental Science*, 2025,45(1)：113~123

**Abstract**：Two typical PA membranes, m-phenylenediamine-trimesoyl chloride and piperazine-trimesoyl chloride, are introduced and their latest chlorine destruction mechanisms are analyzed in depth. On this basis, the chlorine-resistant modification methods for these two membranes are further discussed, including changing the monomer structure, intrinsic doping techniques, physical coating methods and chemical grafting methods. The latest research research advances in the field of chlorinated PA membrane remediation are briefly discussed, including the reduction method after initial chlorination and the remediation with repair agent after chlorination degradation. The analysis shows that the development of chlorine-resistant PA membranes is still facing great challenges, and the research on chlorine-resistant modification of PA membranes should be carried out without sacrificing its separation performance, taking into account all other properties of the membrane, and flexibly utilizing various modification methods.

**Key words**：polyamide membrane；reverse osmosis；nanofiltration；chlorination destruction mechanism；chlorine-resistant modification；chlorination remediation；separation; membrane

聚酰胺(PA)膜因其制备工艺简便、性能稳定、分离性能好等优势成为目前常用的纳滤膜和反渗透膜类型之一,广泛应用于海水淡化和工业废水处理等领域[1-2].PA 膜通常由起支撑作用的多孔基膜层和起分离作用的 PA 分离层(简称 PA 层)组成,其中 PA 层与原料液直接接触,在膜分离中起主要作用,常采用间苯二胺(MPD)或哌嗪(PIP)作为水相反应单体,均苯三甲酰氯(TMC)作为有机相反应单体在基膜表面经界面聚合反应制得[3-4],反应式如图 1 所示.

在实际运行中,为减少待处理过程中以及膜上易发生的生物污染,通常向水中投加活性氯(主要成分为 $Cl^-$、HClO、$ClO^-$)以杀灭微生物或抑制其生长繁殖[5-6].然而,PA 层的一些基团对活性氯具有较高反应活性,引发聚酰胺交联网络结构改变甚至断链,导致 PA 层与基膜层之间作用力减弱而产生脱落,缩短膜的使用寿命[7-9].因此,在膜组件的进水前端需进行脱氯处理使系统中的氯含量小于 $0.1\times10^{-6}$,膜过滤结束后,水作为饮用水供应时需再次氯化[10-11].此外,随着运行时间的增加,膜上逐渐形成泥垢层,膜性能恶化.为恢复膜的性能,需对其进行清洗,而膜的清洗过程中也常会用到高浓度的活性氯[4].脱氯预处理和再次氯化增加了运行成本和维护难度[12],膜清洗也要求 PA 膜具备一定的耐氯性,故开发具有优异

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耐氯性的 PA 膜是近年来膜分离领域的研究热点之一[13].

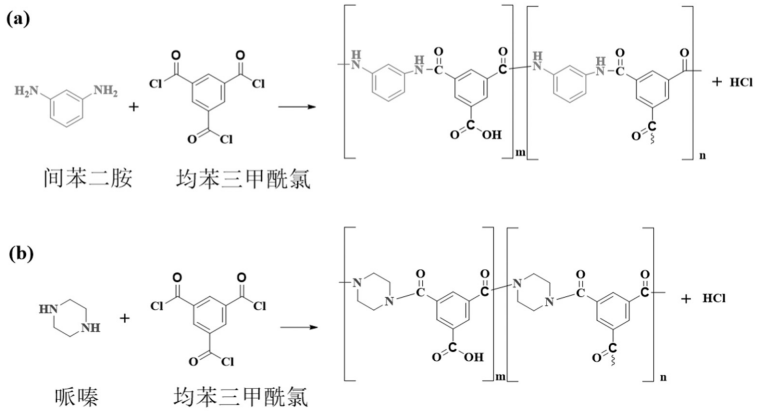


图 1 聚酰胺层制备反应式

Fig.1 Polyamide layer preparation equation

针对 PA 膜耐氯性差的问题,研究人员探索了 MPD−TMC 和 PIP−TMC 两种典型 PA 结构的氯化破坏机理,并从原理出发对 PA 膜进行耐氯改性.本文综述了两种典型 PA 膜的最新氯化机理,并从该角度对近年来 PA 膜耐氯改性方法归纳总结,包括改变单体、本体掺杂、物理涂覆和化学接枝法,简述氯化修复最新研究进展,最后对耐氯 PA 膜当前面临的主要问题和未来的研究方向进行了总结与展望,以期为 PA 膜未来的发展和应用提供有益的参考与指导.

## 1 氯化破坏机理

### 1.1 MPD−TMC 型

MPD−TMC 型 PA 膜常用于反渗透(RO)分离过程[14-15],为全芳香仲酰胺(酰胺键氨基侧与羰基侧均连接苯环结构),苯环与酰胺键是活性氯的反应位点[16],反应机理如图 2 所示.

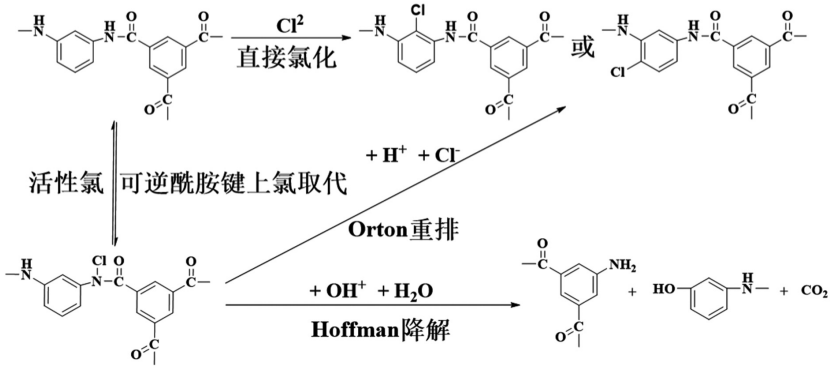


图 2 MPD−TMC 型 PA 膜氯化破坏机理

Fig.2 Chlorination destruction mechanisms of MPD−TMC type PA membrane

游离氯主要通过两种途径与 PA 膜发生反应,即直接环氯化和先可逆酰胺键上氯取代再不可逆 Orton 重排环氯化[17].当 pH<4 活性氯主体为 $Cl^+$,氯气分子与苯环直接发生取代反应,生成稳定的环氯化产物[18-19].可逆酰胺键上氯取代是活性氯与含仲酰胺结构的化合物之间广泛存在的反应[20],酰胺键上的 N 原子有一个孤电子对,易与缺电子的活性氯发生亲电取代[21-22],该反应为可逆反应,酰胺 N−Cl 在还原剂(如 $Na_2S_2O_3$)存在的条件下可以重新脱氯还原成酰胺 N−H 结构[23].被氯化后形成的 N−氯化物结构不稳定,溶液中 $H^+$与游离氯分别与氮和氯原子反应形成 N−H 键和 $Cl_2$,$Cl_2$ 快速与氨基侧苯环邻、对位上 H 发生不可逆取代反应,形成稳定的环氯化产物[24],不可逆 Orton 重排在酸性条件下更为明显[7].

也有研究者对 Orton 重排提出质疑[17,25−28],Huang 等[25]认为实际上并无 Orton 重排,只有可逆酰胺键上氯取代和苯环直接氯化两个独立的过程.

氯取代后的酰胺键易被亲核物质攻击,最终使酰胺键水解[29-31],包括酸性条件下的氧化降解和碱性条件下的 Hoffman 降解[22]两种途径.在极端的酸性氯化处理下发生氧化降解,实际膜在远低于该强度的氯化处理时就已被不可逆破坏[31].碱性环境下,$OH^-$作为亲核物质进攻氯取代后酰胺键上的碳原子,致使酰胺键断裂,但碱性条件下活性氯主要形式为 $ClO^-$,不利于酰胺键氯取代,这一矛盾使得 PA 膜的 Hoffman 降解速度往往很慢[30,32].

### 1.2　PIP−TMC 型

PIP−TMC 型 PA 膜常用于纳滤(NF)分离过程[33-34],为半芳香聚酰胺类(仅酰胺键羰基侧连接苯环结构).由于 PA 膜的苯环氯化通常发生在氨基侧,而 PIP−TMC 型 PA 膜氨基侧没有苯环,且其酰胺键为叔酰胺键,并无酰胺键上的 N−H 氯取代,故与 MPD−TMC 型相比,PIP−TMC 型 PA 膜具有天然的更强耐氯性[35].然而,由于 PIP 与 TMC 酰胺化反应中的高空间位阻,来自未反应 PIP 的大量 N−H 键保留在 PA 层中,膜与活性氯接触后分离性能依然会下降,其氯化破坏机理研究较少,目前较为认可的机理为胺基氯取代和胺基转化为羟胺亚胺[35-37],如图 3 所示.与 MPD−TMC 型 PA 膜的可逆酰胺键上氯取代类似,PIP−TMC 型 PA 膜发生可逆胺基氯取代.胺基转化为羟胺亚胺破坏途径,游离氯先将未参与反应的胺基氧化为不稳定的羟胺,随后羟胺进一步脱去一个水分子形成亚胺.最新研究表明在相同氯化条件下,HClO 对 PIP−TMC 型 PA 膜性能的影响比 $ClO^-$更大,疏松的 PA 层更容易受到活性氯的攻击[38].

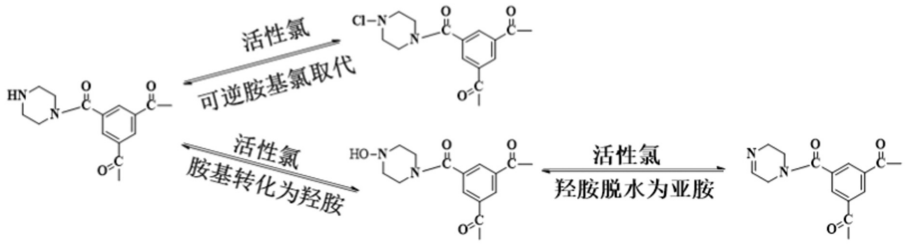


图 3　PIP−TMC 型 PA 膜氯化破坏机理

Fig.3　Chlorination destruction mechanisms of PIP−TMC type PA membrane

MPD−TMC 型 PA 膜的氯化主要是由于可逆酰胺键上氯取代和不可逆 Orton 重排引起的苯环氯化,PIP−TMC 型 PA 膜的氯化则以未反应的 PIP 上胺基发生的两种氧化反应为主.另外,在宽 pH 值范围内,当两种膜经受低浓度(如 $10\times10^{-6}$)的氯化处理时,在一定时间内其通量和截留率都会小幅度提升,这主要得益于分离层的结构优化[19,39-40].

## 2　耐氯改性方法

基于以上氯化破坏机理,近年来,研究者采取多种方法对 PA 膜进行耐氯改性,包括改变单体、本体掺杂、物理涂覆和化学接枝.由于 MPD−TMC 型和 PIP−TMC 型 PA 膜的氯化破坏机理不同,故下文将分别综述两种典型 PA 膜的耐氯改性方法,改性膜性能如表 1、表 2 所示.

### 2.1　MPD−TMC 型

#### 2.1.1　改变单体

改变单体法是选择新的两相反应单体,减少 PA 膜上的活性氯反应位点或延缓氯化反应.酰胺 N−H 是活性氯的首选攻击位点,研究表明 H 被取代后的叔酰胺键的耐氯性明显提高,因此叔酰胺膜的耐氯性比相似结构的仲酰胺膜耐氯性更好[41-42].刘立芬等[43]采用水相单体 N,N'−二甲基间苯二胺(DMMPD)和有机相单体多元酰氯 5−氯甲酰氧基−异肽酰氯(CFIC)聚合制备了叔酰胺 RO 膜,耐氯性较好但脱盐率低于 90%.然而,叔酰胺膜通过在单体中引入−NH 取代基团的方法在阻断氯化破坏途径的同时也破坏了聚酰胺链间的氢键,导致分子链之间交联度降低而影响膜的选择性,也会使膜的亲水性下降而影响其渗透性[44-45].许多研究选择保留酰胺 N−H 结构,由于 PA 膜的氯化取代主要发生多元胺一侧,故对酰胺键氨基侧苯环修饰以提高 PA 膜耐氯性,通过在与酰胺键相连的苯环的邻位或对位引

入大尺寸的官能团来增大空间位阻,阻碍氯原子从酰胺N上通过Orton重排转移到苯环上;或引入强吸电子基团降低苯环上电子云密度,以减弱活性氯与苯环的亲电取代反应;或使用不含苯环的水相反应单体[46].Yu 等[47]采用 4-甲基间苯二胺(MMPD)与1,3,5-三甲酰氯环己烷(HTC)制备 RO 膜,芳香环上邻位甲基的空间位阻效应降低了酰胺键上氯取代和 Orton 重排的概率,耐氯性能得以提升,改性膜的水通量上升但脱盐率降低.Konagaya 等[48]以带吸电子基团的3,39-氨苯砜/4,49-氨苯砜和PIP(含氮杂环化合物)的混合多元胺为水相单体,以间苯二甲酰氯/对苯二甲酰氯为有机相单体,制备得到的 PA-RO 膜的耐氯性较常规 PA-RO 膜有明显提高,但水通量均较低.然而,相比于 MPD-TMC 型 PA 膜,这些替代膜材料的合成过程往往更复杂,反应条件也更苛刻,所制备的膜的分离性能通常也更低[23,46].

**表 1 MPD-TMC 型改性膜性能**

Table 1 Modified membrane properties of the MPD-TMC type

| 改性材料 | 改性方法 | 改性膜分离性能 | | | 耐氯能力 | 参考文献 |
|---|---|---|---|---|---|---|
| | | 测试条件 | 通量(L/(m$^2$·h)) | 截留率(%) | (NaClO 溶液浸泡) | |
| MMPD+HTC | 改变单体 | 1500mg/LNaCl 溶液 15bar | 53.0 | 97.5 | 3000×10$^{-6}$,1h pH=8 | [47] |
| GONPs | 本体掺杂 | 2000mg/LNaCl 溶液 16bar | 13.6±0.5 | 91.7±1.5 | 5000×10$^{-6}$,1h | [59] |
| MXene $Ti_3C_2Tx$ | 本体掺杂 | 2000mg/LNaCl 溶液 27.6bar | 36.8~40 | 97.9~98.5 | 2000×10$^{-6}$,1h | [60] |
| CDs+ $TiO_2$ | 本体掺杂 | / | 59.6 纯水 15bar | 99.2 2000mg/LNaCl 溶液 | 1000×10$^{-6}$,2h pH=4 | [54] |
| PEGDA | 物理涂覆 | 2000mg/LNaCl 溶液 15bar | >35.9 | >95.3 | 1200×10$^{-6}$,1h pH=4 | [69] |
| TA | 物理涂覆 | 2000mg/LNaCl 溶液 15.5bar | 60±8 | 98.82±0.18 | 500×10$^{-6}$,16h pH=4,7,8 | [70] |
| ADMH+MBA | 化学接枝 | 2000mg/LNaCl 溶液 15bar | 86.3±1.5 | 96.9±0.5 | 1000×10$^{-6}$,1h pH=4 | [71] |
| PVA | 化学接枝 | 500mg/LNaCl 溶液 5bar | >26.5 | >98 | 6240×10$^{-6}$,5h pH=9 | [72] |
| N-GOQD | 化学接枝 | 1000mg/LNaCl 溶液 15bar | 40.02 | 96.2 | 1000×10$^{-6}$,160h pH=7 | [74] |
| TA+银纳米颗粒 | 化学接枝 | 2000mg/LNaCl 溶液 15bar | 20.57 | 97.83 | 500×10$^{-6}$,4h pH=5,7,8 | [75] |

2.1.2 本体掺杂 本体掺杂法是在界面聚合过程中在PA层中加入功能添加剂,包括以物理方式掺入的纳米材料和以化学方式掺入的有机剂等改性方法.

自 2007 年 Jeong 等[49]提出将 NaA 沸石纳米颗粒分散在 PA 层中对 PA 膜进行改性以来,研究人员发现大部分纳米材料掺入 PA 层中都可以增加水传输通道和膜的有效过滤面积,从而增强了水的渗透性,有望打破 Trade-off 效应[50-53].将纳米材料(如二氧化钛($TiO_2$)[54]、氧化石墨烯(GO)[55]、金属有机框架(MOF)[56-57]等)经改性处理后掺入PA层,引入可与活性氯发生特定反应的基团来优先消耗掉渗透到膜内部的活性氯(或阻断活性氯进攻PA层的某步反应途径)或增强膜的静电排斥效应,是具有发展潜力的增强PA膜耐氯性的方法[58].Abbaszadeh等[59]将氧化石墨烯纳米片(GONPs)通过逐层组装的方式掺入RO膜PA层,改性后膜的水通量与原膜相似,截留率和耐氯性得到提升.Wang 等[60]在 RO 膜 PA 层中嵌入二维 MXene $Ti_3C_2Tx$ 材料提高膜的耐氯性,$Ti_3C_2Tx$ 纳米片表面官能团与活性氯的相互作用,有效地减缓了氯对PA层的攻击.但是,纳米材料不具有良好的分散性,易在单体溶液中发生团聚现象,导致孔隙堵塞或厚度增加,从而影响膜的渗透性能[61].此类纳米材料常需先进行改性处理,而后掺入膜中.Vatanpour 等[54]将碳点(CDs)与二氧化钛($TiO_2$)结合后掺入 MPD 溶液中与 TMC 反应制备 RO 膜,碳点上丰富的亲水基团不仅使 $TiO_2$ 分散更均匀,也为活

性氯的攻击提供了更多的活性位点,增强了膜表面的负电性,提升了膜的耐氯性.此外,纳米材料与 PA 膜两相本体之间相容性差,可能出现空穴缺陷而影响膜的选择性,在实际应用中逐渐脱离,降低膜的耐氯性能,甚至导致二次污染[61-63].Chen 等[64]将羧基淀粉纳米颗粒(CSNPs)引入 NF 膜的 PA 层,CSNPs 吸收水相单体改变反应界面,改性膜的分离性能大幅提升,同时由于 CSNPs 中的羟基与 TMC 中的酰氯基团反应生成聚芳酯,这增强了膜的耐氯性,也使 CSNPs 与 PA 层之间的联系更紧密.所以,改善纳米材料的团聚现象以及提高它与 PA 层之间的相容性是利用纳米材料提升 PA 膜总体性能的重要措施.

**表 2　PIP−TMC 型改性膜性能**

Table 2　Modified membrane properties of the PIP−TMC type

| 改性材料 | 改性方法 | 改性膜分离性能 | | | 耐氯能力 (NaClO 溶液浸泡) | 参考文献 |
|---|---|---|---|---|---|---|
| | | 测试条件 | 通量(L/(m$^2$·h)) | 截留率(%) | | |
| 氨基功能化聚乙二醇(PEG) | 改变单体 | 50mg/L 妥布霉素溶液 8bar | 37 | 96 | $2000\times10^{-6}$,24h pH=5,7,8 | [76] |
| 季铵化螺环哌嗪(QSPIP) | 改变单体 | 1000mg/L$MgCl_2$ 溶液 6bar | 138 | 93 | $200\sim800\times10^{-6}$,400h pH=6 | [77] |
| 磺化共价有机框架纳米片(SCONs) | 本体掺杂 | 2000mg/L$MgCl_2$ 溶液 4bar | 35.36 | 98.97 | $500\times10^{-6}$,5h pH=7 | [78] |
| 2−氨基苯酚−4−磺酰胺(APSA) | 本体掺杂 | 1000mg/L$MgSO_4$ 和 $MgCl_2$ 溶液 4bar | 8.0~8.2 | 95.9~96.3 | $1000\times10^{-6}$,4h pH=5,10 | [79] |
| 聚多巴胺+氧化石墨烯 | 物理涂覆 | 1000mg/L NaCl 溶液 6bar | 61.68 | 93.05 | $6000\times10^{-6}$,3h pH=11 | [80] |
| GTA | 化学接枝 | 250mg/L NaCl 溶液 4.1bar | 62.1 | 98.2 | 约 0.5mg/L 低浓度余氯自来水中过滤运行 6h | [11] |
| TPEI | 化学接枝 | / | >27 纯水 6bar | >93 1000mg/L$MgSO_4$ 和 $MgCl_2$ 溶液 6bar | $2000\times10^{-6}$,8h pH=4,10 | [13] |
| TAP+季铵化 | 化学接枝 | 1000mg/L$MgSO_4$ 溶液 4bar | 37.8 | 98.3 | $2000\times10^{-6}$,24h pH=4,7.5,10 | [82] |

开发基于有机剂添加的高效分离膜是近年来的膜分离领域的研究热点之一.相似地,在界面聚合过程中引入可优先与活性氯反应的有机剂是提升膜耐氯性的新方法.柳圳等[65]将 N,N'−亚甲基双丙烯酰胺(MBA)作为水相添加剂,在紫外辅助下制备耐氯性能良好的 RO 膜,MBA 的掺入提高了改性膜的通量,又几乎不损失截留率,由于 MBA 的交联以及牺牲保护作用,改性膜的耐氯性也得到提升.Li 等[66]制备了一种含硫醚单元的新型三酰基氯化单体(T−TDC),将其混入 TMC 溶液与 MPD 反应制备 PA−RO 膜,还原硫醚单元引入薄膜分子链中与活性氯反应保护酰胺键,极性砜和亚砜基团可以形成氢键,减缓膜的降解.基于有机剂添加的耐氯改性策略操作简便,但有机剂新基团的引入,可能导致水油两相反应单体的反应活性降低,从而影响膜的结构与形态,最终影响膜的分离性能,故有机剂的种类选择与添加比例显得尤为重要.

2.1.3　物理涂覆　在 PA 膜表面涂覆物理保护层是提高膜耐氯性能较为经济、便捷的方法,利用耐氯材料与膜表面之间的氢键或范德华力,通过喷涂或浸涂等手段将其附着在 PA 层表面,作为能优先与活性氯反应的牺牲层或不与活性氯反应的阻隔层[67-68].Gholami 等[69]将聚乙二醇二丙烯酸酯(PEGDA)作为牺牲层涂覆在 PA−RO 膜表面,涂覆后膜的截留率上升,水通量下降.Yan 等[70]用单宁酸(TA)和乙醇简单处理界面聚合后、热处理前的 RO 膜,得到的 TA 表层作为牺牲层有效提升了膜的耐氯性能,同时膜表面亲水基团的引入提升了膜的渗透性,但乙醇的溶胀作用降低了膜的截留能力.然而,物理涂覆的保护层和 PA 层之间缺乏有力的连接,在长时间使用过程中易被冲刷掉,失去对膜的保护作用[13],且涂层通常会增加膜的渗透阻力,并牺牲

膜的选择性[46].

2.1.4 化学接枝 化学接枝将改性材料与 PA 膜表面的基团以稳定共价键的形式结合,减小 PA 膜被氯化的可能性,接枝位点为酰胺键上的 N−H 和界面聚合后膜上残留的高活性酰氯基团或其水解后的稳定产物羧基.酰胺键上的 N−H 是活性氯取代的首选位点,也是 Orton 重排的限速步骤[20,25],故研究者们常接枝含亲水基团的材料取代 H,消耗氯化位点,根据选择材料的性质,也可能同时增大空间位阻效应.Zhang 等[71]将二甲基乙内酰脲(ADMH)接枝到 PA−RO 膜表面,后用 MBA 交联,增加了膜中氮原子含量,提高膜的亲水性,实现抗污和耐氯性能的提升,但修饰膜的通量较原膜略有下降.Liu 等[72]通过接枝中性亲水性聚合物聚乙烯醇(PVA)到商业 PA−RO 膜表面取代 N−H 上的 H,提升膜的耐污能力和耐氯性,接枝后膜表面变得更光滑,亲水性更强,膜面电荷减少,同样伴随着通量的小幅度下降.Kown 等[73]利用残余的酰氯基团与 N,N'−二甲基丙胺(DMAP)发生反应,随后通过叔胺基诱导山梨糖醇缩水甘油醚(SPGE)内的环氧基团开环聚合,并将 SPGE 固定在膜表面,生成了一层多醚类高分子以防止活性氯对膜的攻击,改性膜在氯化处理后氯取代量只有原膜的一半.但是,酰氯极易水解,利用残余酰氯基团的方法需要在界面聚合制备 PA 膜后立刻对膜进行修饰,造成了实际应用的不便[58].Yi 等[74]利用膜表面残留的酰氯基团水解后产生的更稳定的羧基,将氮掺杂氧化石墨烯量子点(N−GOQD)接枝到 PA−RO 膜上,提升了膜的耐氯性,同时 N−GOQD 丰富的氨基和极性基团抵消了接枝层的阻力,从而增加了水通量.Suresh 等[75]接枝 TA 和银纳米颗粒形成的独特络合物到 PA−RO 膜表面,TA 的接枝提升了 PA−RO 膜的亲水性,水通量大幅提升,NaCl 截留率稍有上升,耐氯性提高.然而,化学接枝虽然相对物理涂覆更稳定,但其难以保证覆盖整个膜面,定点接枝常会存在缺陷,也同样面临膜分离性能易下降的问题.

### 2.2 PIP−TMC 型

PIP−TMC 型 PA 膜的改变单体[76-77]、本体掺杂法[78-79]和物理涂覆[80]与 MPD−TMC 型类似.化学接枝的目的是消耗或保护膜表面未反应 PIP 上的−NH 基团,接枝位点为未反应 PIP 上的−NH、TMC 上的酰氯基团或其水解后产生的羧基.侯琴等[11]采用 2,3−环氧丙基三甲基氯化铵(GTA)对膜分离层中 PIP 上的 N−H 进行后处理修饰,使用三乙醇胺作为催化剂提升接枝反应速率,并利用其溶剂活化作用提高膜的渗透性,改性后的膜兼具高通量和耐氯性.Zhu 等[81]将三聚氰胺接枝到 PA−NF 膜未反应的酰氯基团上,接枝膜具有更粗糙的形态、更小的孔径、更高的亲水性和正电荷,水通量略有下降,对盐类(NaCl、$MgCl_2$、$MgSO_4$ 和 $Na_2SO_4$)截留率较高,耐氯性能优越.Chen 等[13]设计了噻吩功能化的聚乙烯亚胺(TPEI)材料,并将其接枝到传统的 PA 膜酰氯上,制备了新型纳滤膜,亲水性氨基和富电子噻吩基团覆盖的双功能化选择表面赋予膜优异的分离性能和耐氯性.Li 等[82]通过在分离层上原位接枝 2,4,6−三氨基嘧啶(TAP)和随后的季铵化反应生成两性离子,制备了耐氯、防污双功能 NF 膜,两性离子带来的空间位阻和丰富的氨基基团延缓氯化饱和,提高了膜的耐氯性.

现有对 PA 膜的耐氯改性研究主要是通过调整聚酰胺分子链化学结构和引入牺牲基团来强化其耐氯性,改性后膜的耐氯效果的提升往往是多种机制共同作用下的结果.在选用耐氯改性方法时,常会将耐氯与打破 Trade−off 效应、改善膜污染、提升耐酸性等目的相结合,全面提升膜的性能.此外,改性方法之间可相互组合[83-84],一种改性材料也可使用不同方法对膜进行多次改性[85],以期获得更优性能的改性膜.

## 3 氯化修复

PA 膜在长时间使用中总会逐步氯化降解及性能衰减[7,17,86],初期的氯化会导致膜结构的改变,影响其分离性能,当氯化严重时,膜发生裂解.对于初期氯化的膜,可用还原法对其进行脱氯处理而再生其耐氯性,对于已降解的膜,可使用修补剂对其修复.

### 3.1 还原法

氯化本质上是氧化反应,故可通过在膜表面接枝具有氧化还原性质的基团,氯化后用还原剂适当恢复膜的耐氯性能,即赋予膜再生耐氯性.Wang 等[87]合成一种新型的胺官能团海因衍生物聚(3−烯丙基−5,5−二甲基海因共乙烯胺)(P(ADMH−co−VAm)),将其接枝到 PA−RO 膜表面,P(ADMH−co−VAm)作为牺牲层为膜提供较高的耐氯性,氯化后生成的 N−卤胺

使膜具有较强的抗菌性能,N-卤胺通过与膜表面细菌的生化反应再生回海因衍生聚合物,实验室和中试规模的研究均表明该膜具有可再生的高耐氯性和抗菌性能.Lu 等[88]将氧化还原活性材料对氨基二苯胺(p-ADA)接枝到 PA-RO 膜表面,p-ADA 先于酰胺键与活性氯反应,提升了膜的耐氯性,随后以硫代硫酸钠对氯化后的膜进行还原,通过 p-ADA 醌结构与苯环结构的相互转换实现膜的再生耐氯性(图 4).经“氯化-还原”循环实验后,修饰膜的归一化通量保持在 0.522,而对比膜为 0.278,归一化 NaCl 截留率为 0.998,显著高于对比膜(0.963).Zhang 等[85]使用聚乙烯亚胺和柠檬酸制备胺功能化碳点,经本体掺杂与表面接枝两次改性 PA-NF 膜,改性后的膜通量与截留率均较原膜有所上升,氯化后胺基转变为硝基,还原剂 AA(抗坏血酸)可还原部分硝基,该膜具有一定的再生耐氯性.但是,一旦这些牺牲部分被氯饱和,而没有及时进行还原操作,PA 层仍会受到活性氯的攻击.因此,需要对氯化反应进行监测来维持牺牲基团的耐氯性.Huang 等[23]将甘氨酸(Gly)接枝到 PA-RO 膜表面,Gly 的 N-H 部分作为氯化的第一活性位点保护 PA 层,Gly 分子上的胺基(-NH)和羧基(-COOH)的质子化会被 N-H 基团上的氯取代所抑制,使膜表面负电荷增加,脱氯后恢复,故该研究通过膜的 Zeta 电位的变化来监测 Gly 牺牲基团的氯化程度,并在氯饱和前通过简单的碱性还原将 N-Cl 还原为 N-H (pH=10).

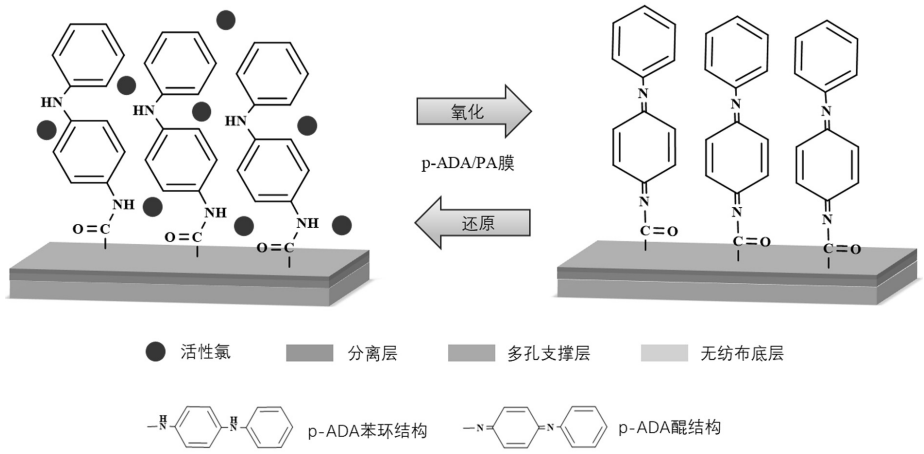


图 4　p-ADA/PA 膜氧化还原机理[88]

Fig.4　Oxidation and reduction mechanisms of p-ADA/PA membrane[88]

### 3.2　修补剂

对氯化降解后的 PA 膜进行修复,能恢复一部分性能,延长膜使用寿命,降低更换成本.PA 膜降解的主要原因是酰胺结构的过度断裂[22],采用表面处理的手段,如涂覆或沉积,通过氢键与膜表面结合,让修补剂附着在膜上[65],填补氯化膜 PA 层的缺陷或重新生成交联结构[89],修补剂多采用含羟基或氨基等亲水性基团且易成膜的物质.俞萍萍[90]采用 TA 为修复试剂(图 5(a)),通过物理涂覆、物理涂覆+氯化铁($FeCl_3$)螯合交联和物理涂覆+戊二醛(GA)化学交联三种方法修复氯化降解的 PA 膜,三种方法均可有效恢复降解膜的反渗透性能,修复膜的脱盐率接近或高于原始膜,而通量则高于原始膜,物理涂覆法和螯合交联法可轻松实现原位修复,而化学交联法则有一定的温度要求.Xie 等[91]利用海藻酸钠和壳聚糖表面的氨基和羧基连接 PA-RO 膜上的断裂部分(图 5(b)),恢复其交联和密度,减轻 PA 氯化导致的 NaCl 截留率的降低.郭中尉[89]采用两种不同特性的修复试剂 TA 与 PEI 在劣化 PA-RO 膜面进行连续化学沉积(图 5(c)),构建出连续交联层以恢复其截留率,经 $1500\times10^{-6}$ 次氯酸钠溶液(pH=9)处理 9h 后,NaCl 截留率下降至 96.07%,降幅仅为 2.2%.

虽然可采取一定的方法对氯化后的 PA 膜进行修复,但氯化伴随着膜微观结构的变化,原样逆回几乎不可能,还会面临反应复杂、膜性质改变、分离性能不稳定和二次污染等各种问题.所以,目前对于 PA 膜的耐氯研究热点仍是如何延缓活性氯与膜的反应进程,而不是被动地修复已被破坏的膜结构.

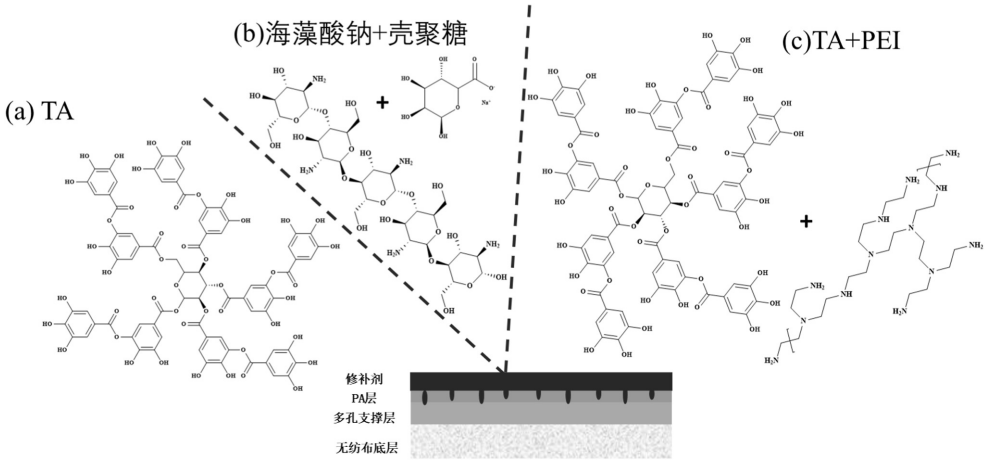


图 5 用于修复降解 PA 膜的材料

Fig.5 Materials used to remediate degraded PA membrane

## 4 展望

PA 膜的氯敏感性制约了其在水处理领域的进一步推广应用,增强 PA 膜的耐氯性对降低运行成本、提升水处理效率具有重要意义.目前关于 MPD-TMC 型 PA 膜的氯化机理仍有争议,PIP-TMC 型 PA 膜的氯化机理研究较少,还需继续深入探索,对 PA 膜进行耐氯改性和氯化修复的方法仍存在一定局限性:1)改性膜在耐氯性能提高的同时常会面临膜分离性能下降的问题;2)大部分改性膜的耐氯性不可逆,即氯化位点被游离氯饱和后无法再生,改性膜性能下降;3)有些改性材料的制备过程繁琐,成本过高,不利于实际应用.

综上所述,开发分离性能好、具备再生耐氯性、制备过程简单、成本低的多优势耐氯膜将会是未来 PA 膜重要的研究方向.在分子水平上进行单体的设计开发是个不错的选择,通过微观上基团的选择与构象的调整,定制膜的性质与结构,可利用机器学习从大量化合物中寻找尚未探索的单体组合或优化反应参数,进一步提升科研效率.此外,在耐氯膜的研制过程中,可与工程实际相结合,选择采用实际水样进行研究或根据处理水质的特性制备适应特殊环境的耐氯膜,对于在实验室条件下各方面表现优越的耐氯膜,考虑进行中试实验进一步考察膜性能及工业化可能性.最后,仍需加快对具有全新化学结构的 PA 膜以及非聚酰胺类膜材料的开发,从根本上解决膜的不耐氯问题.

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