

研究综述

doi: 10.13413/j.cnki.jdxblxb.2024517

纤维素材料在水溶液中吸附净化的研究进展

刘冠成, 张喆, 龙鑫, 杨柏

(吉林大学 超分子结构与材料国家重点实验室, 长春 130012)

摘要: 纤维素材料作为一种新型吸附剂, 具有优异的机械性能和化学稳定性, 通过化学改性可显著提升其吸附性能, 在去除水溶液中的污染物方面展现出对重金属离子、有机小分子和微塑料等污染物的良好吸附能力, 也可作为血液净化吸附剂用于治疗血液疾病. 综述纤维素材料在水溶液净化中的应用, 并总结纤维素材料作为吸附剂的研究进展.

关键词: 纤维素; 化学改性; 水净化; 血液净化

中图分类号: O63 **文献标志码:** A **文章编号:** 1671-5489(2025)01-0173-09

Research Progress of Adsorption Purification for Cellulose Materials in Aqueous Solutions

LIU Guancheng, ZHANG Zhe, LONG Xin, YANG Bai

(State Key Laboratory of Supramolecular Structure and Materials,
Jilin University, Changchun 130012, China)

Abstract: Cellulose materials as a novel class of adsorbents, it has excellent mechanical properties and chemical stability, their adsorption performance can be significantly enhanced through chemical modification. In the context of removing pollutants from aqueous solutions, cellulose materials show good adsorption capabilities for contaminants such as heavy metal ions, organic small molecules, and microplastics, they can also be used as blood purification adsorbent for the treatment of blood-related diseases. We review the application of cellulose materials in the purification of aqueous solutions, and summarize the research process of cellulose materials as adsorbents.

Keywords: cellulose; chemical modification; water purification; blood purification

近年来, 随着工业化的快速发展和环境污染的日益加剧, 探索如何有效去除水中有害污染物的方法已成为当务之急. 因此, 开发有效的吸附净化技术对维护良好的生态环境至关重要. 该技术要求使用低成本且环保的吸附剂, 这些吸附剂应具有可大规模生产和应用的潜力, 并且不会导致二次污染^[1]. 在可用于吸附的材料中, 纤维素材料具有生物降解性、经济性和可再生性, 是一种理想的天然高分子吸附剂^[2]. 由于其独特的结晶性和氢键特性, 纤维素不溶于大多数溶剂, 因此适合在多数溶剂尤其是水溶液中的净化. 此外, 纤维素材料表现出良好的血液相容性^[3-4], 使其能有效应用于体内水溶液的净化, 具有治疗血液疾病的潜力, 从而保障人类生活质量.

本文综述纤维素材料作为吸附剂在水溶液净化中的应用, 分析并讨论相关的关键挑战与未来发展前景, 为纤维素材料吸附剂的设计与应用策略提供有益参考.

收稿日期: 2024-12-19.

第一作者简介: 刘冠成(1997—), 男, 汉族, 博士研究生, 从事纤维素类新型吸附材料的研究, E-mail: liugc21@jlu.edu.cn. **通信作者简介:** 杨柏(1962—), 男, 汉族, 博士, 教授, 博士生导师, 从事聚合物光功能材料的研究, E-mail: byangchem@jlu.edu.cn.

基金项目: 吉林省自然科学基金(批准号: 202402011).

1 纤维素材料

纤维素是地球上含量最丰富的天然高分子,主要来源于木材和棉花,也可从其他植物的不同部位中提取.它具有绿色、良好的生物降解性、生物相容性、天然丰度和可持续性等特点,是吸附材料的优良载体,它本身也是一类有效的吸附材料.纤维素的分子式为多糖,是由 β -(1,4)-糖苷键连接的D-脱水吡喃葡萄糖单元整合的聚合物(图1)^[2].由于没有侧链或支链,纤维素链以有序结构存在.因此,纤维素是一种半结晶聚合物,它同时包含结晶相和非晶相.虽然它是一种线性聚合物,且包含的伯羟基和仲羟基均为亲水性,但由于纤维素链之间的强氢键,因此它不溶于水 and 普通有机溶剂.纤维素链之间的氢键和葡萄糖单元之间的范德华力导致纤维素中形成结晶区域^[5].

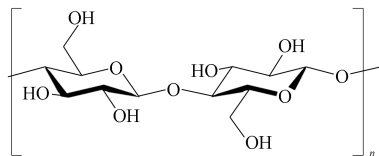


图1 纤维素的分子结构式

Fig.1 Molecular structural formula of cellulose

纤维素材料主要由纤维素及其衍生物组成.纤维素一般分为4种晶体类型:纤维素I型、II型、III型和IV型.其中,纤维素I型为天然纤维素,纤维素II型是具有反平行排列链的再生纤维素,由纤维素I型经碱液处理和重结晶制成.再生纤维素与天然纤维素的不同之处在于其相对分子质量较小、结晶度和聚合度较低,以及分子缠结较少.纤维素III型由纤维素I型或纤维素II型经液氨处理制成,纤维素IV型可通过纤维素III型通过热处理形成^[6].

纤维素衍生物主要通过纤维素上的羟基引入不同取代基制备.纤维素分子上的羟基可发生氧化、酯化、醚化和接枝共聚等反应^[6-8].通过调节纤维素分子的相对分子质量和取代官能团的分布可得到纤维素衍生物,主要产品有甲基纤维素(MC)、乙基纤维素(EC)、羟乙基纤维素(HEC)、羟丙基纤维素(HPC)、醋酸纤维素(CA)和羧甲基纤维素(CMC)等衍生物^[6].

2 纤维素作为吸附材料的化学改性

近年来,纤维素材料被广泛应用于吸附净化领域,但纤维素的吸附性能较单一且其吸附能力有限,需通过化学改性方式提高纤维素的吸附性能,从而拓宽纤维素材料在吸附领域的应用.主要化学改性方法包括以下几方面.

2.1 酯化

纤维素的每个重复单元有3个羟基,能与羧基进行酯化反应.在酯化过程中引入羧基,增加纤维素材料的羧基含量,从而可增强其静电吸附作用或羧基螯合作用.如Geay等^[9]用丁二酸酐改性木浆,对水溶液中Cd(II)的吸附容量为168.0 mg/g,通过控制羧基含量实现了吸附性能的调控.

2.2 醚化

纤维素可通过在碱性条件下与有机卤化物以及环氧乙烷反应而醚化.与酯键相比,醚键的优势在于它们在水性体系中的稳定性,即使在低/高pH值下也能稳定存在.纤维素材料最常用的醚化改性方法是用氯乙酸进行羧甲基化,从而引入带有负电荷的羧基,可用于吸附阳离子^[10].纤维素也可与六甲基二硅氧烷反应生成硅烷醚,从而极大提高其表面的疏水性^[11].

2.3 氧化

纤维素材料常用的氧化方式有两种:1)用 NaIO_4 氧化,常用于活化纤维素材料,该氧化反应导致纤维素重复单元中无水葡萄糖环的C2—C3键选择性裂解,产生2个醛基^[12-14];2)纤维素的伯羟基可通过哌啶氧铵盐(TEMPO)介导的氧化选择性转化为6-脱氧-6-羧基纤维素^[15-18],所得纤维素材料吸附剂富含羧基,可用于吸附金属离子(图2).

2.4 接枝共聚

在接枝共聚改性方法中,可在纤维素材料上先接枝单体再实现共聚,也可通过各种引发方式使纤维素骨架产生自由基与单体直接反应^[19-23].在纤维素材料上实现接枝共聚改性的优势在于改性能提高

纤维素材料活性位点的密度, 从而提高纤维素材料的吸附性能, 但缺点是该方法对设备要求较高, 并对共聚反应的控制精确度要求较高。

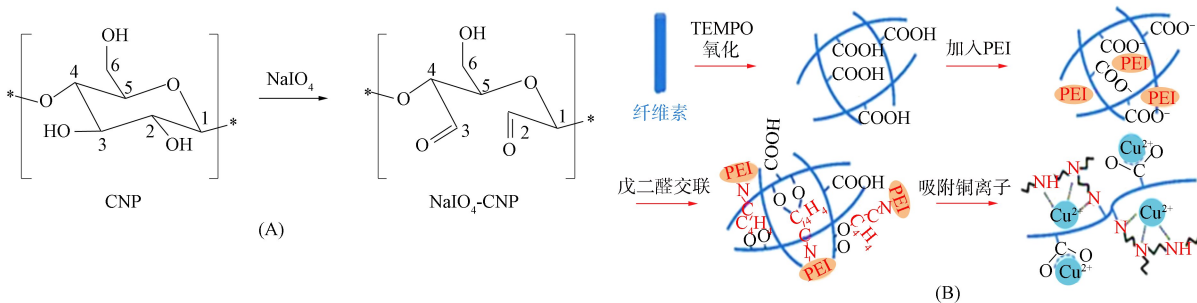


图 2 纤维素被 NaIO_4 氧化(A)和纤维素被 TEMPO 催化氧化(B)

Fig. 2 Cellulose is oxidized by NaIO_4 (A) and cellulose is catalytically oxidized by TEMPO (B)

3 纤维素材料在吸附净化领域的应用

3.1 吸附重金属离子

一些工业生产过程产生的废水中含有大量重金属离子, 这些有毒的重金属离子对人类健康和生态环境均有危害. 许多纤维素材料可作为重金属离子的吸附剂: 约含质量分数为 40% 纤维素的甘蔗渣可吸附制革废水中的 $\text{Cr}(\text{III})$ 和 $\text{Cr}(\text{VI})$ 离子^[24]; Khoramzadeh 等^[25] 用它进行生物吸附水溶液中的汞; 还可使用聚乙烯亚胺和 EDTA 对甘蔗渣进行化学改性, 引入螯合剂以吸附重金属离子^[26-28]. Low 等^[29] 将柠檬酸转化为柠檬酸酐, 然后与木浆中纤维素的一OH 基团反应, 形成酯键. 酯化过程提高了木纤维中羧酸的含量, 一COOH 基团被引入木浆中, 最终提高了天然木材对 $\text{Cu}(\text{II})$ 和 $\text{Pb}(\text{II})$ 离子的吸附能力. 也可将纤维素材料与有机卤化物(环氧氯丙烷)反应, 得到具有反应性的环氧基团. 再通过接枝聚乙烯亚胺(PEI)实现功能化, 所得吸附剂 Cell-PEI 可吸附 Hg, 其吸附容量为 288 mg/g ^[30].

Saliba 等^[31] 用酰胺脲基团通过丙烯腈和木屑的醚化反应对锯末进行化学改性, 从而在纤维素的结构中添加氨基. 氨基的氨基酰化是通过将其与羟胺反应实现的^[31]. 酰胺酰亚胺化锯末对 $\text{Cr}(\text{III})$ 和 $\text{Cu}(\text{II})$ 的吸附能力分别为 $202.8, 240.6 \text{ mg/g}$. Godiya 等^[32] 用自由基聚合酰胺(AM)改性 CMC 制备了 CMC/PAM 复合水凝胶(图 3), 其对 $\text{Cu}(\text{II})$, $\text{Pb}(\text{II})$ 和 $\text{Cd}(\text{II})$ 的吸附容量大幅度提升.

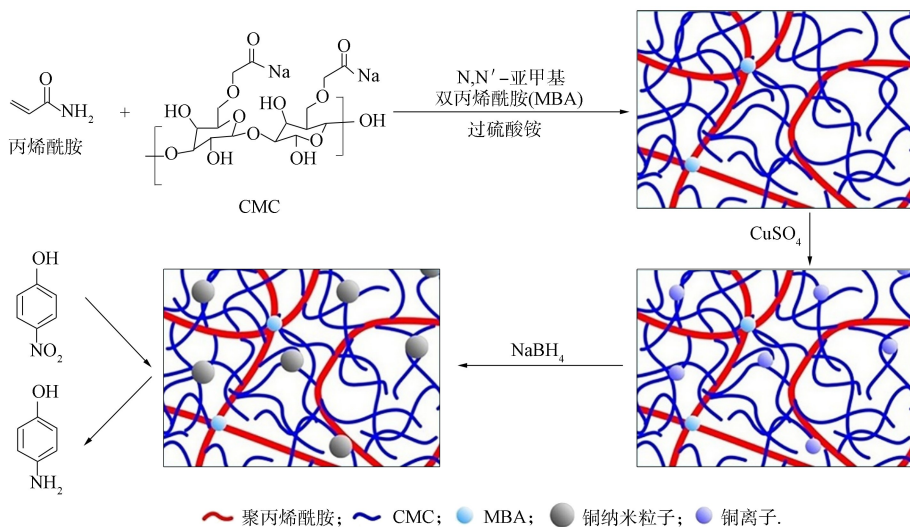


图 3 CMC/PAM 复合水凝胶吸附 $\text{Cu}(\text{II})$

Fig. 3 Adsorption of $\text{Cu}(\text{II})$ by CMC/PAM composite hydrogel

3.2 吸附有机小分子

除重金属离子污染外, 在工业制造和农业生产过程中也会产生有机小分子类污染物, 如染料和农

药等. 纤维素材料作为吸附剂, 对这些有机小分子的吸附清除已有较多研究成果^[33-35]. Tasri 等^[36]通过纤维素的酸性水解合成了纳米纤维素, 并将其与聚吡咯偶联(NCPPY), 表面改性使羧基和羟基等活性功能团与染料和金属离子相互作用, 可有效去除刚果红染料(CR), 最大去除效率为 85%(图 4).

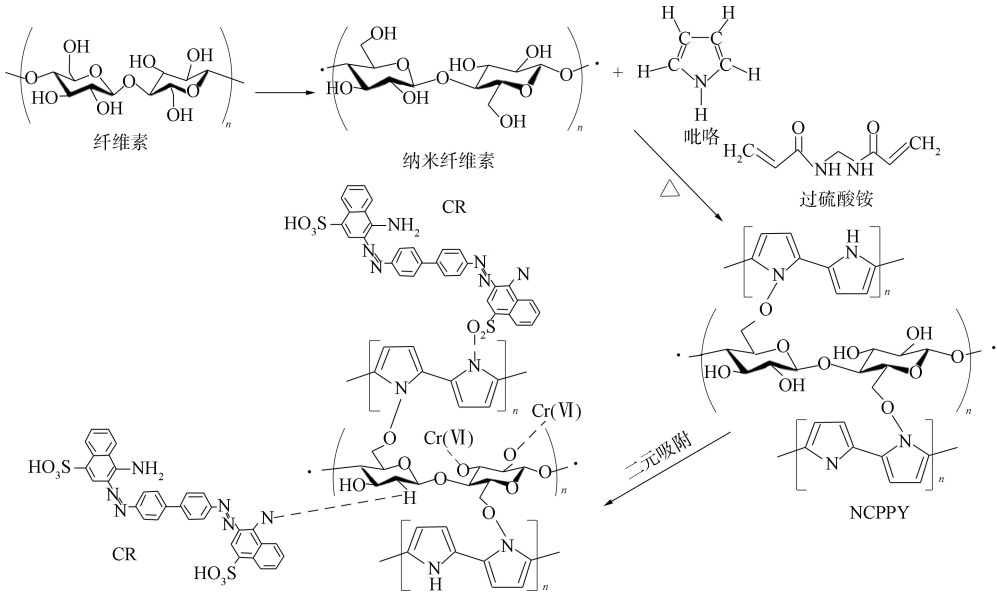


图 4 纤维素与聚吡咯偶联及其对 CR 和 Cr(VI) 的吸附

Fig. 4 Coupling of cellulose with polypyrrole and its adsorption of CR and Cr(VI)

Zhang 等^[37]将 CMC 和羧基化纤维素纳米纤维(CNF-C)复合, 增加了羧基含量, 提高了对亚甲基蓝(MB)染料的吸附(图 5). Zhao 等^[38]用聚乙烯亚胺(PEI)通过 Schiff 碱反应将戊二醛与膜上的酰胺键交联, 增强了纤维素复合膜的性能, 通过静电相互作用有效捕获染料分子(刚果红、亚甲基蓝和孔雀石绿). Liu 等^[39]通过在纤维素上接枝丙烯酸和丙烯酰胺, 可有效增加其吸附位点, 成功去除阴离子染料酸性蓝 93(AB93)和阳离子染料亚甲基蓝(MB).

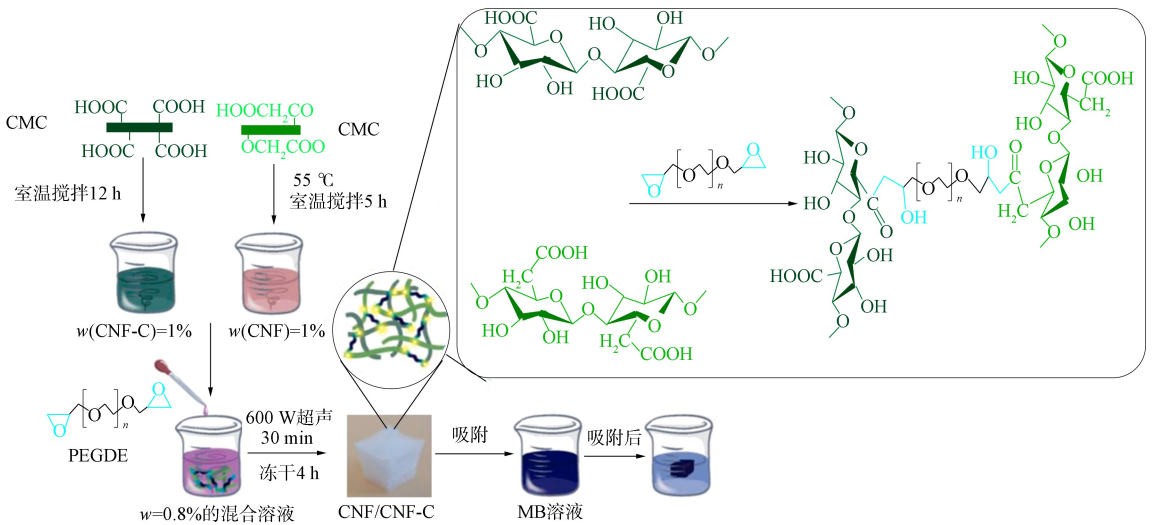


图 5 用于吸附亚甲基蓝染料的纤维素吸附剂制备

Fig. 5 Preparation of cellulose adsorbent for adsorbing methylene blue dye

3.3 吸附微塑料

微塑料(MPs)是指直径为 $0.1 \mu\text{m} \sim 1 \text{mm}$ 的塑料碎片和颗粒, 环境中已检出聚对苯二甲酸乙二醇酯(PET)等聚合物^[40]. 微塑料不易降解, 可通过水等多种途径进入生物体内并稳定存在, 是影响生物健康风险的重要因素.

Zhuang 等^[41]以纤维素纳米纤维(CNF)为基体材料,以 2,3-环氧丙基三甲基氯化铵(EPTMAC)为改性剂,以聚乙烯醇(PVA)为交联剂,采用液氮冷冻法制备具有定向结构的改性纤维素纳米纤维气凝胶,用于吸附中小尺寸微塑料. 改性后的气凝胶对小尺寸微塑料具有良好的吸附容量,达 146.38 mg/g. 此外,还可用聚乙烯亚胺(PEI)对纤维素纳米纤维(CNFs)进行改性,并通过简单的反应和冷冻干燥方法制备具有定向结构的改性气凝胶(图 6)^[42].

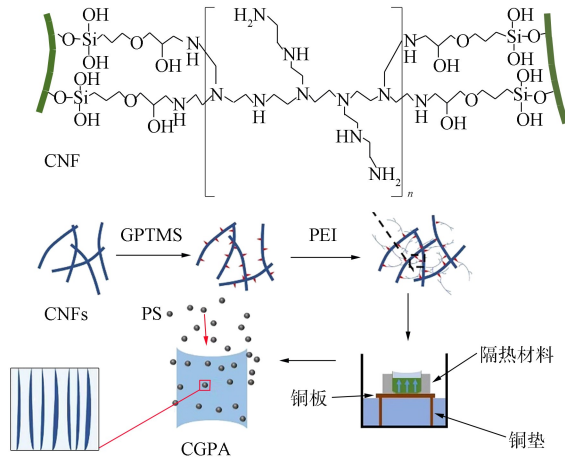


图 6 纤维素气凝胶的制备及反应机理

Fig. 6 Preparation and reaction mechanism of cellulose aerogel

3.4 血液净化

纤维素材料应用于生物大分子吸附,主要体现在血液净化领域. 血液净化技术是一种利用膜分离或吸附分离原理清除病人血液中内源性和外源性毒素的治疗技术,在肝衰、肾衰和脓毒血症等危重病的治疗中发挥关键作用^[43-44]. 相对于水溶性小分子毒素,对中大分子蛋白类血液毒素的有效清除是目前该领域的技术难点. 其中归属于血液净化技术中的血液灌流技术,主要是清除中大分子蛋白类血液毒素,即将患者的血液引出体外,与灌流器中的固态吸附材料接触,通过吸附清除血液毒素,然后将净化后的血液输回给患者,从而达到治疗疾病的目的(图 7)^[45-46]. 在血液灌流过程中,吸附材料会与人体血液直接接触,所以高效生物相容性好的吸附材料是灌流技术研究的核心.

纤维素材料具有良好的生物相容性和生物活性,适合作为血液灌流吸附剂载体(图 8),尤其以纤维素微球作为血液灌流吸附剂的载体(图 7(B)). 目前,纤维素及其衍生物已用于血液灌流清除毒素,而且也有商业化的产品用于治疗慢性肾脏病后期患者^[47-50].

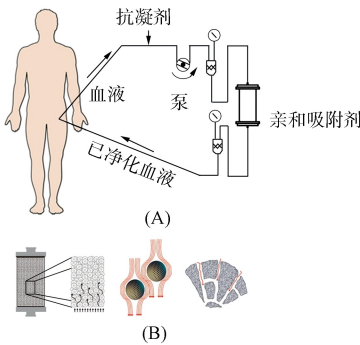


图 7 血液灌流(A)和通过填充微球的流动分布(B)示意图

Fig. 7 Schematic diagram of blood perfusion (A) and flow distribution through filling microspheres (B)

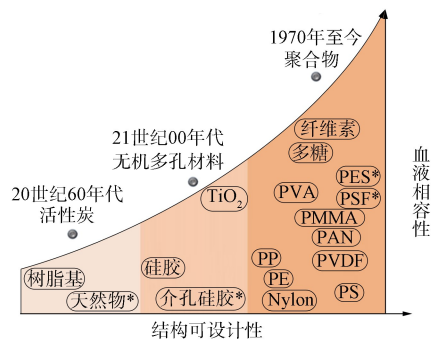


图 8 血液灌流材料的发展路线

Fig. 8 Development path of blood perfusion materials

Tang 等^[51]用疏水性烷基碳链(C18)修饰纤维素微球(图 9),可有效吸附胆红素,胆红素以单层形式吸附到纤维素微球的 C18 基团上,治疗黄疸疾病; Qiao 等^[4]用纤维素微球与碳纳米管复合吸附胆红素; Cao 等^[52]将多黏菌 B 交联接枝到纤维素微球上,可对体内毒素进行有效吸附;商业化应用于治疗

疾病的 Lixelle 血液灌流柱通过将十六烷基胺接枝到纤维素微球上即可有效吸附清除 β_2 -微球蛋白^[53-57].

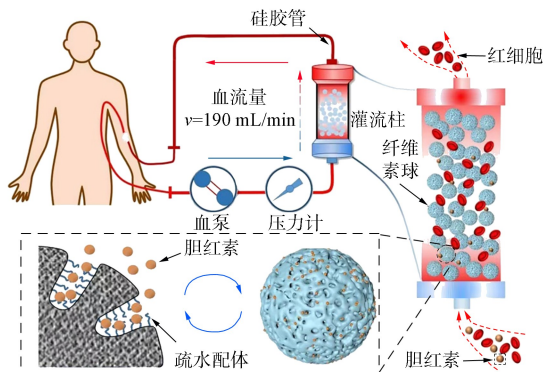


图 9 纤维素微球的血液灌流过程和胆红素吸附机制的示意图

Fig. 9 Schematic diagram of blood perfusion process and bilirubin adsorption mechanism of cellulose microspheres

Fang 等^[58]研究了一种以纤维素微球为载体, 环氧氯丙烷为偶联剂, 赖氨酸为配体的吸附剂, 通过带正电的赖氨酸配体与内毒素分子上带负电的磷酸基团相互作用实现对内毒素的吸附, 在兔子模型的体内研究中, 吸附剂在 2 h 的血液灌流处理后血液中的血浆内皮素(ET)水平从 (5.56 ± 0.54) EU/mL 降至 (0.41 ± 0.26) EU/mL ($1 \text{ EU} = 1 \text{ IU} = 1 \mu\text{mol}/\text{min}$); 多黏菌 B 是一种能与内毒素特异性结合的抗生素, 对内毒素有较好的清除能力, Cao 等^[52]以多黏菌 B 为配体, 纤维素微球为载体, 制备了一种在水溶液中吸附容量为 $3.605 \text{ EU}/\text{mg}$ 的内毒素吸附剂, 但以多黏菌 B 为配体的成本较高, 同时多黏菌 B 还会对肾脏和神经系统有损害, 存在潜在的健康风险; Zhou 等^[59]通过聚多巴胺和聚乙烯亚胺修饰制备了一种有抗菌性和较强内毒素吸附及去除能力的 CA 膜(PDCA 膜), 这种膜具有良好的血液相容性且无细胞毒性, 在动态实验条件下, PDCA 膜的内毒素吸附能力达 $(2\ 322.1 \pm 45.9)$ EU/g.

4 展 望

综上所述, 本文讨论了纤维素材料作为吸附剂在水溶液中净化的应用, 以及纤维素材料提高其吸附性能的化学改性途径. 通过化学改性可提高纤维素基吸附剂的吸附能力, 这是由于化学改性后纤维素材料上的活性结合位点增加所致. 尽管已有许多以纤维素材料为吸附剂进行水溶液吸附净化处理的研究报道, 但大多数吸附研究仅限于小批量规模, 仅有少数能在中试和工业规模上开发用于实际水溶液的吸附净化处理. 此外, 纤维素材料吸附剂的开发研究不应只局限在功能基团的选择上, 而应该在纤维素材料上设计特定结构的功能基元, 从而增强纤维素吸附剂的吸附选择性, 提高吸附剂的吸附效率. 纤维素材料也可作为吸附剂的基体材料, 在此基础上设计构造出特定的多孔材料, 通过调控多孔材料的孔径分布增强吸附剂对目标物质的清除效率.

参 考 文 献

- [1] ASHORI A, CHIANI E, SHOKROLLAHZADEH S, et al. Cellulose-Based Aerogels for Sustainable Dye Removal: Advances and Prospects [J]. *Journal of Polymers and the Environment*, 2024, 32(12): 6149-6181.
- [2] KAUSAR A, ZOHRA S T, IJAZ S, et al. Cellulose-Based Materials and Their Adsorptive Removal Efficiency for Dyes: A Review [J]. *International Journal of Biological Macromolecules*, 2023, 224: 1337-1355.
- [3] XIE M, SUN J F, CHEN L. Procion Blue H-5R Functionalized Cellulose Membrane with Specific Removal of Bilirubin [J]. *Cellulose*, 2019, 26: 8073-8085.
- [4] QIAO L Z, LI Y L, LIU Y, et al. High-Strength, Blood-Compatible, and High-Capacity Bilirubin Adsorbent Based on Cellulose-Assisted High-Quality Dispersion of Carbon Nanotubes [J]. *Journal of Chromatography A*, 2020, 1634: 461659-1-461659-9.
- [5] MEDRONHO B, ROMANO A, MIGUEL M G, et al. Rationalizing Cellulose (in) Solubility: Reviewing Basic

- Physicochemical Aspects and Role of Hydrophobic Interactions [J]. *Cellulose*, 2012, 19: 581-587.
- [6] SEDDIQI H, OLIAEI E, HONARKAR H, et al. Cellulose and Its Derivatives: Towards Biomedical Applications [J]. *Cellulose*, 2021, 28(4): 1893-1931.
- [7] AZIZ T, FARID A, HAQ F, et al. A Review on the Modification of Cellulose and Its Applications [J]. *Polymers*, 2022, 14(15): 3206-1-3206-34.
- [8] YI T, ZHAO H Y, MO Q, et al. From Cellulose to Cellulose Nanofibrils: A Comprehensive Review of the Preparation and Modification of Cellulose Nanofibrils [J]. *Materials*, 2020, 13(22): 5062-1-5062-32.
- [9] GEAY M, MARCHETTI V, CLÉMENT A, et al. Decontamination of Synthetic Solutions Containing Heavy Metals Using Chemically Modified Sawdusts Bearing Polyacrylic Acid Chains [J]. *Journal of Wood Science*, 2000, 46: 331-333.
- [10] GERICKE M, TRYGG J, FARDIM P. Functional Cellulose Beads: Preparation, Characterization, and Applications [J]. *Chemical Reviews*, 2013, 113(7): 4812-4836.
- [11] CERNY P, BARTOS P, KRIZ P, et al. Highly Hydrophobic Organosilane-Functionalized Cellulose: A Promising Filler for Thermoplastic Composites [J]. *Materials*, 2021, 14(8): 2005-1-2005-14.
- [12] MELESE H, TSADE H. Cellulose Based Adsorbent for Cationic Methylene Blue Dye Removal [J]. *Discover Applied Sciences*, 2024, 6(2): 46-1-46-15.
- [13] KRAMAR A, IVANOVSKA A, KOSTIĆ M. Regenerated Cellulose Fiber Functionalization by Two-Step Oxidation Using Sodium Periodate and Sodium Chlorite: Impact on the Structure and Sorption Properties [J]. *Fibers and Polymers*, 2021, 22(8): 2177-2186.
- [14] LI Y, WANG F. Removal of Cu^{2+} from Aqueous Solution Using Three Alkyl-Amine-Modified Cellulose Absorbents Prepared via Schiff Base Grafting [J]. *Desalination and Water Treatment*, 2023, 282: 146-154.
- [15] LIU S S, LOW Z X, XIE Z L, et al. TEMPO-Oxidized Cellulose Nanofibers: A Renewable Nanomaterial for Environmental and Energy Applications [J]. *Advanced Materials Technologies*, 2021, 6(7): 2001180-1-2001180-23.
- [16] YU H J, ZHENG L C, ZHANG T, et al. Adsorption Behavior of $\text{Cd}(\text{II})$ on TEMPO-Oxidized Cellulose in Inorganic/Organic Complex Systems [J]. *Environmental Research*, 2021, 195: 110848-1-110848-12.
- [17] ABOU-ZEID R E, KAMAL K H, ABD EL-AZIZ M E, et al. Grafted TEMPO-Oxidized Cellulose Nanofiber Embedded with Modified Magnetite for Effective Adsorption of Lead Ions [J]. *International Journal of Biological Macromolecules*, 2021, 167: 1091-1101.
- [18] XING X Y, LI W Q, ZHANG J, et al. TEMPO-Oxidized Cellulose Hydrogel for Efficient Adsorption of Cu^{2+} and Pb^{2+} Modified by Polyethyleneimine [J]. *Cellulose*, 2021, 28(12): 7953-7968.
- [19] BHATTACHARYA A, MISRA B N. Grafting: A Versatile Means to Modify Polymers: Techniques, Factors and Applications [J]. *Progress in Polymer Science*, 2004, 29(8): 767-814.
- [20] GEORGIOUVELAS D, ABDELHAMID H N, LI J, et al. All-Cellulose Functional Membranes for Water Treatment: Adsorption of Metal Ions and Catalytic Decolorization of Dyes [J]. *Carbohydrate Polymers*, 2021, 264: 118044-1-118044-10.
- [21] BAYRAMOGLU G, ARICA M Y. Grafting of Regenerated Cellulose Films with Fibrous Polymer and Modified into Phosphate and Sulfate Groups: Application for Removal of a Model Azo-Dye [J]. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 2021, 614: 126173-1-126173-11.
- [22] LI M, ZHANG S Q, CUI S Y, et al. Pre-grafting Effect on Improving Adsorption Efficiency of Cellulose Based Biosorbent for $\text{Hg}(\text{II})$ Removal from Aqueous Solution [J]. *Separation and Purification Technology*, 2021, 277: 119493-1-119493-12.
- [23] LIU J T, CHEN Y C, JIANG S Y, et al. Rapid Removal of $\text{Cr}(\text{III})$ from High-Salinity Wastewater by Cellulose-g-poly-(acrylamide-co-sulfonic acid) Polymeric Bio-adsorbent [J]. *Carbohydrate Polymers*, 2021, 270: 118356-1-118356-10.
- [24] ULLAH I, NADEEM R, IQBAL M, et al. Biosorption of Chromium onto Native and Immobilized Sugarcane Bagasse Waste Biomass [J]. *Ecological Engineering*, 2013, 60: 99-107.
- [25] KHORAMZADEH E, NASERNEJAD B, HALLADJ R. Mercury Biosorption from Aqueous Solutions by Sugarcane Bagasse [J]. *Journal of the Taiwan Institute of Chemical Engineers*, 2013, 44(2): 266-269.

- [26] ZHANG C Z, SU J J, ZHU H X, et al. The Removal of Heavy Metal Ions from Aqueous Solutions by Amine Functionalized Cellulose Pretreated with Microwave-H₂O₂ [J]. RSC Advances, 2017, 7(54): 34182-34191.
- [27] GE H, HUANG H L, XU M, et al. Cellulose/Poly(ethylene imine) Composites as Efficient and Reusable Adsorbents for Heavy Metal Ions [J]. Cellulose, 2016, 23: 2527-2537.
- [28] HU T, HU X L, TANG C, et al. Adsorbent Grafted on Cellulose by *in situ* Synthesis of EDTA-Like Groups and Its Properties of Metal Ion Adsorption from Aqueous Solution [J]. Cellulose, 2022, 29(2): 941-952.
- [29] LOW K S, LEE C K, MAK S M. Sorption of Copper and Lead by Citric Acid Modified Wood [J]. Wood Science and Technology, 2004, 38: 629-640.
- [30] NAVARRO R R, SUMI K, FUJII N, et al. Mercury Removal from Wastewater Using Porous Cellulose Carrier Modified with Polyethyleneimine [J]. Water Research, 1996, 30(10): 2488-2494.
- [31] SALIBA R, GAUTHIER H, GAUTHIER R, et al. Adsorption of Copper(II) and Chromium(III) Ions onto Amidoximated Cellulose [J]. Journal of Applied Polymer Science, 2000, 75(13): 1624-1631.
- [32] GODIYA C B, CHENG X, LI D W, et al. Carboxymethyl Cellulose/Polyacrylamide Composite Hydrogel for Cascaded Treatment/Reuse of Heavy Metal Ions in Wastewater [J]. Journal of Hazardous Materials, 2019, 364: 28-38.
- [33] VARGHESE A G, PAUL S A, LATHA M S. Remediation of Heavy Metals and Dyes from Wastewater Using Cellulose-Based Adsorbents [J]. Environmental Chemistry Letters, 2019, 17: 867-877.
- [34] HAMIDON T S, ADNAN R, HAAFIZ M K M, et al. Cellulose-Based Beads for the Adsorptive Removal of Wastewater Effluents: A Review [J]. Environmental Chemistry Letters, 2022, 20(3): 1965-2017.
- [35] GOEL N K, KUMAR V, MISRA N, et al. Cellulose Based Cationic Adsorbent Fabricated via Radiation Grafting Process for Treatment of Dyes Waste Water [J]. Carbohydrate Polymers, 2015, 132: 444-451.
- [36] TASRI S, MOHAMED M S, PADMANBAN V C, et al. Surface Modification of Nanocellulose Using Polypyrrole for the Adsorptive Removal of Congo Red Dye and Chromium in Binary Mixture [J]. International Journal of Biological Macromolecules, 2020, 151: 322-332.
- [37] ZHANG T J, XIAO S Y, FAN K H, et al. Preparation and Adsorption Properties of Green Cellulose-Based Composite Aerogel with Selective Adsorption of Methylene Blue [J]. Polymer, 2022, 258(14): 125320-1-125320-13.
- [38] ZHAO X Q, YANG M B, SHI Y C, et al. Multifunctional Bacterial Cellulose-Bentonite@Polyethyleneimine Composite Membranes for Enhanced Water Treatment: Sustainable Dyes and Metal Ions Adsorption and Antibacterial Properties [J]. Journal of Hazardous Materials, 2024, 477(15): 135267-1-135267-17.
- [39] LIU L, GAO Z Y, SU X P, et al. Adsorption Removal of Dyes from Single and Binary Solutions Using a Cellulose-Based Bioadsorbent [J]. ACS Sustainable Chemistry & Engineering, 2015, 3(3): 432-442.
- [40] WRIGHT S L, KELLY F J. Plastic and Human Health: A Micro Issue? [J]. Environmental Science & Technology, 2017, 51(12): 6634-6647.
- [41] ZHUANG J, RONG N N, WANG X R, et al. Adsorption of Small Size Microplastics Based on Cellulose Nanofiber Aerogel Modified by Quaternary Ammonium Salt in Water [J]. Separation and Purification Technology, 2022, 293: 121133-1-121133-11.
- [42] ZHUANG J, PAN M Z, ZHANG Y H, et al. Rapid Adsorption of Directional Cellulose Nanofibers/3-Glycidoxypropyltrimethoxysilane/Polyethyleneimine Aerogels on Microplastics in Water [J]. International Journal of Biological Macromolecules, 2023, 235: 123884-1-123884-10.
- [43] YAO G S, JI F L, CHEN J W, et al. Nanobody-Functionalized Conduit with Built-in Static Mixer for Specific Elimination of Cytokines in Hemoperfusion [J]. Acta Biomaterialia, 2023, 172: 260-271.
- [44] LI M J, CHEN M M, YANG F C, et al. Protein/Polysaccharide Composite towards Multi-in-one Toxin Removal in Blood with Self-anticoagulation and Biocompatibility [J]. Advanced Healthcare Materials, 2023, 12(26): 2300999-1-2300999-12.
- [45] JU J, LIANG F X, ZHANG X X, et al. Advancement in Separation Materials for Blood Purification Therapy [J]. Chinese Journal of Chemical Engineering, 2019, 27(6): 1383-1390.
- [46] DOU W Y, WANG J, YAO Z K, et al. A Critical Review of Hemoperfusion Adsorbents: Materials, Functionalization and Matrix Structure Selection [J]. Materials Advances, 2022, 3(2): 918-930.

- [47] WEBER V, ETTENAUER M, LINSBERGER I, et al. Functionalization and Application of Cellulose Microparticles as Adsorbents in Extracorporeal Blood Purification [J]. *Macromolecular Symposia*, 2010, 294(2): 90-95.
- [48] KOBAYASHI A, NAKATANI M, FURUYOSHI S, et al. *In vitro* Evaluation of Dextran Sulfate Cellulose Beads for Whole Blood Infusion Low-Density Lipoprotein-Hemoperfusion [J]. *Therapeutic Apheresis*, 2002, 6(5): 365-371.
- [49] WANG Y J, YU Y T. *In vitro* and *in vivo* Evaluation of Amino Acid-Functionalized Cellulose Beads for Whole Blood Hemoperfusion [J]. *Key Engineering Materials*, 2005, 288: 393-396.
- [50] YAMAMOTO S, SATO M, SATO Y, et al. Adsorption of Protein-Bound Uremic Toxins through Direct Hemoperfusion with Hexadecyl-Immobilized Cellulose Beads in Patients Undergoing Hemodialysis [J]. *Artificial Organs*, 2018, 42(1): 88-93.
- [51] TANG W, YUAN Z T, SUN B, et al. Facile and Scalable Fabrication of Regenerated Cellulose Microspheres with High Strength and Porosity as a Potential Matrix for Hemoperfusion [J]. *Journal of Macromolecular Science*, 2024, 63(7): 588-603.
- [52] CAO X D, ZHU B Y, ZHANG X F, et al. Polymyxin B Immobilized on Cross-Linked Cellulose Microspheres for Endotoxin Adsorption [J]. *Carbohydrate Polymers*, 2016, 136: 12-18.
- [53] DHANDE O S, TEICHERT A, BROUMAND V, et al. Effects of Extracorporeal Blood Flow Rates on Patient Tolerance for LIXELLE[®] Treatment during Outpatient Hemodialysis [J]. *Blood Purification*, 2024, 53(4): 306-315.
- [54] OHASHI A, NAKAI S, HORI H, et al. Suppression of Inflammation during Cell-Free Concentrated Ascites Reinfusion Therapy Using a Blood Purification Device [J]. *Therapeutic Apheresis and Dialysis*, 2020, 54(5): 511-515.
- [55] TSUCHIDA K, YOSHIMURA R, NAKATANI T, et al. Blood Purification for Critical Illness: Cytokines Adsorption Therapy [J]. *Therapeutic Apheresis and Dialysis*, 2006, 10(1): 25-31.
- [56] ODA Y, ISHIOKA K, OHTAKE T, et al. Dialysis-Related Amyloidosis Presenting as a Fever of Unknown Origin: Symptoms and Management [J]. *Internal Medicine*, 2023, 62(24): 3669-3677.
- [57] ZHANG M J, LIU X J, ZHOU W, et al. Ordered Porous Materials for Blood Purification [J]. *Separation and Purification Technology*, 2023, 327(15): 124844-1-124844-16.
- [58] FANG H, WEI J, YU Y T. *In vivo* Studies of Endotoxin Removal by Lysine-Cellulose Adsorbents [J]. *Biomaterials*, 2004, 25(23): 5433-5440.
- [59] ZHOU Y, ZHANG Q, XIA Z X, et al. Mixed-Charge Cellulose Nanocrystal Modified Cellulose Acetate Membrane with Endotoxin Scavenging Ability and Antibacterial Properties [J]. *Journal of Applied Polymer Science*, 2024, 141(33): e55834-1-e55834-15.

(责任编辑: 单 凝)