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磁性壳聚糖微球的改性研究进展及其在水处理中的应用

分享本文

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摘　要：磁性壳聚糖微球 (Magnetic chitosan microsphere，MCM) 是一种新型吸附材料，具有独特的磁响应特性和良好的吸附性能，以其突出的环保和可控性在生物医学、食品工程和污水处理等许多领域受到高度重视。传统方法制备的 MCM 存在纳米粒子易溶于酸性溶液、应用范围窄等问题，因此研究者们在其优化改性方面展开了大量工作。本文从磁性纳米粒子改性和壳聚糖改性两个方面详细综述了优化 MCM 的研究进展，包括磁性纳米粒子的修饰与替换，壳聚糖分子印迹改性、接枝改性、金属螯合改性、烷基化改性等方法。总结了改性后 MCM 对废水中重金属离子、印染废料中阴阳离子染料的吸附情况和去除效果。最后讨论了改性 MCM 面临的问题与挑战，展望了其未来发展趋势，提出了进一步提高改性 MCM 应用效率的方法和设想。

关键词：壳聚糖微球；磁性纳米粒子；重金属；吸附剂；改性方法；废水

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Research progress on modification of magnetic chitosan microspheres and its application in water treatment

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Abstract：Magnetic chitosan microsphere (MCM) is a new type of adsorption material, which has unique magnetic response characteristics and good adsorption performance. With its outstanding environmental protection and controllability, it has attracted high attention in many fields such as biomedicine, food engineering, sewage treatment and so on. MCM prepared by traditional methods has some problems, such as nanoparticles are easy to dissolve in acidic solution and narrow application range. Therefore, researchers have carried out a lot of work in its optimization and modification. In this paper, the research progress of optimizing MCM was reviewed in detail from two aspects: magnetic nanoparticles modification and chitosan modification, including modification and replacement of magnetic nanoparticles, chitosan molecular imprinting modification, grafting modification, metal chelation modification, alkylation modification and so on. The adsorption and removal effects of modified MCM on heavy metal ions in wastewater and ionic dyes in printing and dyeing waste were summarized. Finally, the problems and challenges faced by modified MCM were discussed. Its future development trend was prospected, and the methods and ideas to further improve the application efficiency of modified MCM were put forward.

Keywords：chitosan microspheres；magnetic nanoparticles；heavy metals；adsorbents；modification method；wastewater

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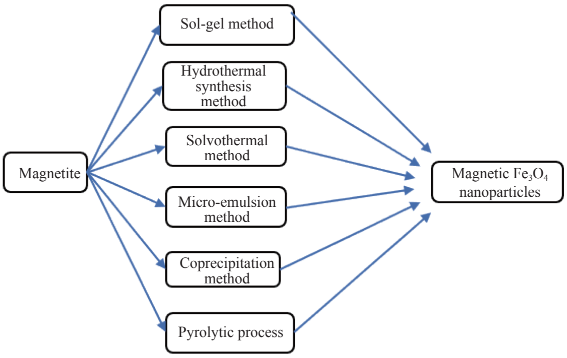
磁性壳聚糖微球 (Magnetic chitosan microsphere，MCM) 是指通过交联改性将磁性纳米粒子和壳聚糖结合，利用共聚、表面改性及外加磁场的方法，形成兼备壳聚糖的理化性质和磁响应特性的复合微球。目前 MCM 已经广泛应用在医学、食品和水处理等诸多领域。用于蛋白质的吸附与固定、酶的纯化、有机酸的提取、重金属离子和染料分子的去除等过程，应用后的 MCM 通过外磁力的作用能快速从溶液中分离，有效避免二次污染，解吸操作后可重复投入使用且效果几乎不受影响，对保护环境和节约成本有较大意义[1-3]。

传统方式制备的 MCM 存在酸碱适用度差、磁性纳粒子易团聚等问题，大量研究者通过对磁性纳米粒子和壳聚糖进行改进来解决这一问题。对磁性粒子常用的优化方法是对磁性 Fe_3O_4 进行修饰或是使用其他磁性粒子替换磁性 Fe_3O_4，提高其稳定性与分散性；对壳聚糖常用的改性方法有分子印迹法、接枝改性法、金属螯合法、烷基化改性法、磁化改性法等，对壳聚糖分子链上游离的氨基、羟基、乙酰氨基进行重组或嫁接使壳聚糖具有更好的吸附性和重复利用性[4-9]。

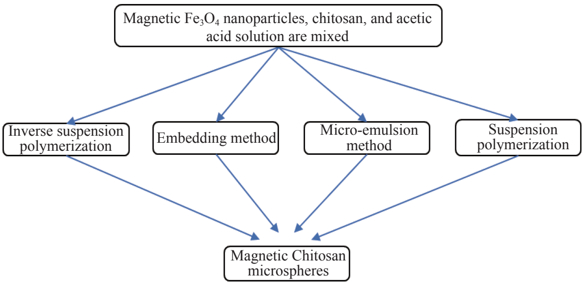
本文从磁性纳米粒子和壳聚糖两个角度综述常用的优化 MCM 的方法。总结了近几年改性 MCM 在去除废水中重金属离子、染料离子及去除其他有机杂质的研究及应用进展，深入探讨了 MCM 的未来发展趋势。

1 磁性壳聚糖微球 (MCM) 改性的研究进展

壳聚糖与磁性 Fe_3O_4 纳米粒子交联后形成复合吸附材料，和传统吸附剂相比，MCM 能够同时进行单层或多层吸附，且吸附后易分离，有效提高吸附剂的使用性能，MCM 的制备方法如图 1 所示。在交联反应中交联剂在壳聚糖线性分子之间产生化学键，使分子相互连接，形成网状结构[10-13]。常用戊二醛、三聚磷酸钠、乙二醛和环氧氯丙烷等作交联剂，其结构及特点如表 1 所示。可知，采用戊二醛或乙二醛作交联剂，制备 MCM 时，产物易出现大小不均匀的现象，可通过严格控制分子比例及交联环境改善这一情况；采用环氧氯丙烷作交联剂时，应控制吸附液的酸碱度，及时调节溶液 pH，防止负电性过高，影响产物吸附效果；选用三聚磷酸钠作交联剂时，要求碱性交联环境，在交联前期配制溶液及交联后调整混合溶液 pH 时，都应详尽考虑酸或碱对壳聚糖的影响，防止交联过程破坏壳聚糖结构。



(a) Preparation process of magnetic nanoparticles



(b) Composite of nanoparticles and chitosan

图 1　磁性壳聚糖微球 (MCM) 的制备过程

Fig. 1　Preparation of magnetic chitosan microspheres (MCM)

1.1 改变磁性 Fe_3O_4 纳米粒子

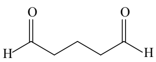
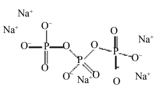
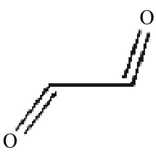
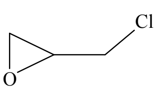
Fe_3O_4 磁性纳米粒子表面活性基团多、易于磁性分离、生物相容性好，但在酸性溶液中易发生团聚和溶解，降低有效使用面积。长期在废水中使用，纳米材料表面容易滋生微生物进而成膜，阻碍孔径、表面官能团与溶液接触，降低磁性 Fe_3O_4 壳聚糖微球的吸附效率。目前有两种常用的解决方法：(1) 对 Fe_3O_4 进行表面修饰，在不改变晶体结构的情况下，降低表面能、改善分散性，例如在 Fe_3O_4 表面包裹 SiO_2 或用油酸修饰；(2) 直接更换微球内包裹的磁性粒子，选用更加适合环境的材料制备复合材料。

1.1.1 修饰磁性 Fe_3O_4 纳米粒子

表面添加合适配体或利用分子的官能化对磁性 Fe_3O_4 纳米粒子进行修饰，改变其表面性质，优化粒子在酸性溶液的稳定性、减少聚集现象、提高分离效率是改良传统磁性微球的常用方式，修饰磁性粒子的常用物质如表 2 所示。

表 1 常用交联剂的结构及特点

Table 1 Structures and characteristics of common crosslinking agents

Crosslinker	Structure	Advantage	Shortcoming	Ref.
Glutaraldehyde		Aldehyde group combines with the amino group to form a new nitrogen-carbon double bond by Schiff base reaction and cross-linking, resulting in a stable structure and increased hydrophobic strength	Two carbonyl groups are far away from each other, the crosslinking site is bound and the spatial site resistance is large, and the product is not highly crystalline	[14-16]
Sodium tripolyphosphate		Non-toxic, amino protonation cross-linked with phosphate ions to improve the chemical stability of the substance while introducing phosphate	At higher pH, the product surface is negatively charged and the phosphate dissociates, reducing the adsorption capacity	[17-19]
Glyoxal		Amino group at the C2 position reacts with the carbonyl group in the Schiff reaction, and the hydroxyl group at the C6 position reacts with the carbonyl group in the acetal reaction, which is conducive to improving the fiber strength of the product	—NH^2 generates —NH_3^+, which is not suitable for strong acid environment because it is not conducive to Schiff reaction.	[20-21]
Epichlorohydrin		Carbon and chlorine bonds are broken and the hydroxyl group becomes ether after epoxy ring opening, so the cross-linking efficiency is high and the product is more stable; and the amino group is not occupied, so more sites are combined with pollutants	Suitable for alkaline environment, the preparation process should be cross-linked before neutralizing with acid	[22-23]

结合表 2 分析，针对应用环境选择不同物质修饰的磁性纳米粒子能有效提高其实用性。选用油酸对磁性粒子进行修饰，油酸的羧基和 Fe_3O_4 纳米颗粒上的铁原子结合，成功包裹纳米粒子，在不改变晶体结构的情况下，改善 MCM 纳米粒子的分散性，减少聚集情况，有效地降低产品制备难度；在磁性纳米粒子外部修饰 SiO_2，意在防止磁性粒子外露，有效提高产物对环境酸碱度的适应性，降低其表面能，使产物能够应用在 pH 值更低的环境。但是目前可选择的修饰物种类较少且选择修饰物的过程较为繁琐，选用不合适的修饰物可能会破坏磁性粒子的特定结构，降低其磁性。在今后的研究中可以通过 Zeta 电位和 FTIR 分析来研究油酸、SiO_2 等修饰物的特定化学键及特征结构，着力寻找与之相似的物质对磁性粒子进行修饰，拓宽修饰磁性粒子的研究领域。

1.1.2 替代磁性 Fe_3O_4 纳米粒子

随着合成技术的快速发展，生产出符合使用

表 2 不同材料对磁性 Fe_3O_4 纳米粒子的修饰效果

Table 2 Modification effects of different materials on magnetic Fe_3O_4 nanoparticles

Modifying substance	Modification effect	Experimental result	Advantage	Ref.
Oleic acid	It is spherical and becomes larger in size and evenly dispersed	When the reaction temperature was 31℃, 400 nm microspheres were prepared, showing high sensitivity	Reduce surface energy without changing crystal structure and improve magnetic nanoparticle dispersion	[24]
SiO_2	SiO_2uniformly coated magnetic nanoparticles	When pH=2.0, the maximum adsorption capacity of Cr(Ⅵ) is 236.4 $mg·g^{-1}$	Improve the acid resistance of adsorbent, reduce the content of magnetic particles, and still ensure the smooth separation	[25]
Attapulgite	Nanoparticles were successfully attached to the rod	When pH is adjusted to 0.97%, the maximum adsorption rate of Pd^{4+} and Pd^{2+} is 0.98%	High density adsorption of iron ions on the rocks, while retaining a large number of adsorption sites for polyelectrolytes	[26]
Phase change material	Phase change material and magnetic iron oxide were encapsulated in chitosan microspheres at the same time	Enthalpy of crystallization at 30 and 32°C and the enthalpy of melting at 43℃ dropped to 75.0 and 73.0 $J·g^{-1}$, respectively	Combination of the two substances as a core effectively enriches the functionality and applicability of chitosan, while increasing the magnetic	[27]

要求的、形状可控的、稳定性良好的其他磁性纳米粒子更易实现。加之粒子的修饰与功能化十分复杂，选用合适材料修饰磁性 Fe_3O_4 难度较大。大量研究者倾向于应用其他磁性粒子替换磁性 Fe_3O_4 纳米粒子，改善磁性微球的吸附性能和去除效果。部分可替换的磁性纳米粒子如表 3 所示。可知，分析不同的应用环境，制备具有不同磁性内核的吸附剂有利于增强吸附剂的环境适应能力，能够最大化发挥作用，且吸附容量与解吸效率较高，是一种有效制备、应用 MCM 的方式，为多功能聚合物的制备开辟了新途径；为需要满足热能储存、吸附等多种工程要求的环境，提供有发展前进的应用可能。但是部分磁性微球的分散性有待提高，在今后的工作中，应致力于研究如何确保磁性微球能够更均匀地分散，实现制备的材料具有最高活性。

表 3　部分新型粒子替换 Fe_3O_4 粒子的实例

Table 3　Examples of some new particles replacing Fe_3O_4

Magnetic particle	Product characteristic	Experimental result	Ref.
$CoFe_2O_4$	Uniform dispersion of magnetic particles, excellent magnetic response, good adsorption characteristics	At the end of adsorption, the solution was nearly colorless and the maximum desorption efficiency was about 92.85%	[28]
$MnFe_2O_4$	Does not damage the structure of the position itself, and at the same time has a synergistic effect on the adsorption performance of chitosan and $MnFe_2O_4$	Maximum removal efficiency of MB at pH=6.0 and initial concentration of 671.4 mol·L^{-1} was 96.4%, and the maximum adsorption capacity was about 85.3 mg·g^{-1}	[29]
$Co_{0.5}NiFe_2O_4$	Excellent core-shell structure and magnetic response performance	Maximum decolorization rate of cationic dyes reached over 95.0% at a dose of 20 mg·g^{-1}	[30]
Magnetic graphene oxide	Preparation of composite products of graphene oxide and iron oxide for solid-liquid separation by external magnetic field and high adsorption of pollutants	Average adsorption capacity of the product was 80.8 mg·g^{-1}; the maximum desorption efficiency was 86.3 mg·g^{-1} at 40℃ and pH=6.8	[31]

1.2　改性壳聚糖

1.2.1　分子印迹改性

用模板分子与壳聚糖制备配合物，聚合后洗脱模板分子，高聚物内形成含有特定功能基团的立体空穴，有选择性吸附模板分子，生成新物质，有效地解决壳聚糖作为吸附剂的选择性识别能力弱的问题。壳聚糖分子印迹聚合物的制备过程如图 2 所示。

用分子印迹技术对 MCM 进行改性，能增加特异识别性、提高吸附性能，结构更加稳定。Kong 等[32] 设想从溶液中选择性的吸附铜离子，

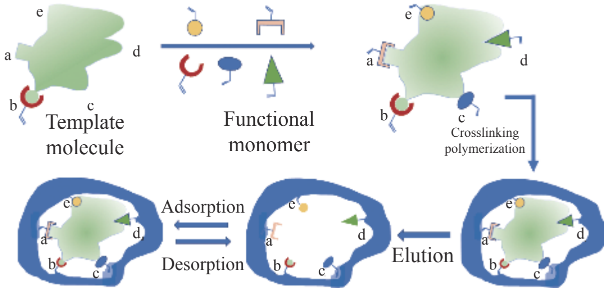


图 2　分子印迹聚合物制备过程 (a, b, c, d, e 代表模板分子上与功能单体的作用点)

Fig. 2　Preparation process of molecularly imprinted polymer (a, b, c, d and d represent the interaction point between the template molecule and the functional monomer)

研究了一种新型的离子印迹 MCM，实验验证该产物具有单层和多层混合吸附的特点，能有效地选择性去除溶液中的铜离子，且在解吸过程中空穴结构和化学性质未受影响，产物的稳定性较高可以重复使用。更多关于分子印迹技术在 MCM 中的研究如表 4 所示。

分子印迹改性后的微球壳体因其表面带有大量特异识别功能的立体空穴，能更准确、高效地从吸附质中识别与吸附待处理杂质。例如表 4 中的铀酰离子，长存在于高盐放射性流出物中，传统方法提取铀酰离子面临速度慢、选择性差等困难，通过制备铀酰离子印迹磁性微球使其表面产生特定的识别位点，能够在废水中高效识别、吸附铀酰离子，同时利于洗脱收集和二次利用。这一思路对环境保护和核能可持续发展都具有重大意义。这些改性 MCM 应用于废水处理，对杂质更有针对性的吸附且吸附效率提高的同时磁响应特性不受影响。然而分子印迹改性 MCM 还需要进一步的发展以应对复杂吸附质，因此研究、制备能够同时对多种目标分子进行选择和吸附的多模板印迹聚合物是未来的一大挑战。

1.2.2　接枝改性

较强的氢键作用和良好的结构规整性，导致

表 4　磁性壳聚糖微球 (MCM) 分子印迹改性

Table 4　Molecular imprinting modification of magnetic chitosan microspheres (MCM)

Template molecule	Crosslinking agent	Advantage	Results of control experiments	Results of control experiments	Ref.
Cu^{2+}	Epichlorohydrin	Cu^{2+} cross-linked with I-CM, breaking the coordination of —NH_2 and —OH, decreasing crystallization ability and acid solubility	Surface leveling of the blank control was completely soluble in acetic acid, and the adsorption rate was about 36.7%	At 80℃ and pH=5.0, the initial mass concentration of Cu^{2+} was 338.7 $mg\cdot L^{-1}$ and the product adsorption amount was 72.8 $mg\cdot g^{-1}$	[33]
2,4,6 Trichlorophenol	Ethylene glycol dimethacrylate	A large number of binding sites to improve product stability and recognition	Maximum adsorption of the product was about 58.0 $mg\cdot g^{-1}$ at 25℃ and pH=2.0-6.0	Maximum adsorption of the product was about 75.0 $mg\cdot g^{-1}$ at 25℃ and pH=2.0-6.0	[34]
Uranyl ion	N. N- Methylene bisacrylamide	C=C bond interacts with uranyl ion and the binding energy increases, electrostatic attraction between phosphoric acid and lanthanum, effective adsorption of uranium by phosphoric acid and N-isopropylacrylamide	Maximum adsorption capacity was 105.0 $mg\cdot g^{-1}$ at 25℃ and pH=6.0	At 25℃ and pH=6.0, the maximum adsorption amount was 232.0 mg·g-1 and U(VI) was reduced to U(IV)	[35]
Piroxicam (PIX)	Ethylene glycol dimethyl acetamide	Cavity fits to the target template, PIX has high affinity to the active site and forms stable hydrogen bonds with the acrylic group	pH=4.0, magnetization saturation value of 20.0 $emu\cdot g^{-1}$, low adsorption efficiency	pH=4.0, maximum adsorption efficiency of 42.3 $mg\cdot g^{-1}$, and magnetization saturation value of 38.0 $emu\cdot g^{-1}$	[36]
Deep eutectic solvent	Glutaraldehyde	Increased specific surface area for efficient selective identification and binding to cavities	20-60℃, the average adsorption capacity is about 15.0 $mg\cdot g^{-1}$, which is about 1.9 times that of MgO	20-60℃, the average adsorption capacity is 80.8 $mg\cdot g^{-1}$, which is about 11.0 times that of MgO	[31]

壳聚糖的溶解性较差，严重限制其应用范围。通过接枝共聚反应在壳聚糖的分子链上引入功能性侧基，将两种性质完全不同的分子链结合在一起，形成接枝共聚物改善壳聚糖的性能，拓宽其应用范围[37]。接枝改性的两种途径：(1) 以壳聚糖的分子链为骨架，骨架上产生大分子自由基后引发另一种单体与之聚合；(2) 通过分子链上的反应性官能团与其它的聚合物链偶合[38-39]，具体过程如图 3 所示。

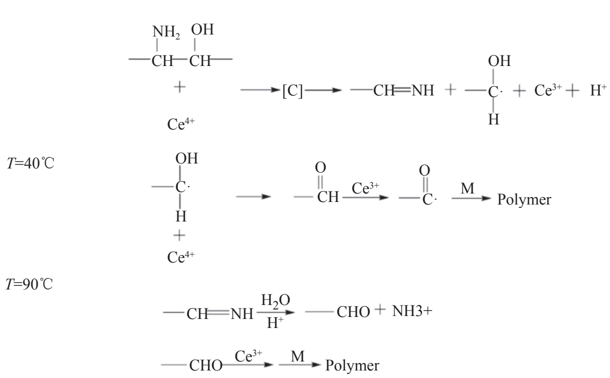


图 3　不同接枝方式

Fig. 3　Different grafting methods

Xu 等[40] 通过将 2-丙烯酰胺基-2-甲基丙烷磺酸和丙烯酸接枝聚合到 MCM 表面，制备新型的接枝共聚物，将其与未改性的 MCM 做对照试验，吸附印染废水中的阳离子染料，研究表明改性后成功引入磺酸基和羧基，两种基团去质子化后增强与带负电离子的相互作用，吸附能力明显增强，此外在模拟循环系统中能高效再生和重复使用，这表明其在实际应用中是一种很有前景的吸附剂，在未来的发展中为转基因生物材料的回收提供一种新的可能。Li 等[41] 合成了一种基于聚丙烯酰胺接枝壳聚糖的磁性复合微球，可用于吸附水溶液中的铜离子、铅离子及汞离子。通过对比试验分析，和未改性的 MCM 相比，新型材料对各种金属离子的吸附能力均有所提高，且对汞有较高的选择吸附性，并系统研究了在二元、三元金属的复杂体系中壳聚糖基吸附剂对汞的选择行吸附效果，对未来深入研究选择性吸附具有重要意义。其他磁性接枝改性壳聚糖微球的研究如表 5 所示。可知，接枝改性后的 MCM 的吸附容量明显提高，由于接枝改性使磁性壳聚糖分子链引入丰富基团，主链与支链上游离的基团与吸附质之间产生静电

表 5　MCM 的接枝改性

Table 5　Graft modification of MCM

Grafting material	Product preparation	Removal of ions	Control experiment	Experimental result	Ref.
Glutamine	Glutamine-modified magnetic chitosan microspheres	Acid green 25 (AG25), Mercury ions	Maximum adsorption of G25 at pH=2.0 was 460.0 $mg \cdot g^{-1}$ and the maximum adsorption of Hg^{2+} at pH=6.0 was 80.0 $mg \cdot g^{-1}$	Maximum adsorption of G25 was 900.0 $mg \cdot g^{-1}$ at pH=2.0 and 140.0 $mg \cdot g^{-1}$ for Hg^{2+} at pH=6.0	[42]
Ammonium persulfate (NH4)	Aminated magnetic chitosan microspheres	Methylene blue (MB), Brilliant red (RBR)	Adsorption amount for MB was 105.0 $mg \cdot g^{-1}$ at pH=12.0 and 450.0 $mg \cdot g^{-1}$ for RBR at pH=10.0	Maximum adsorption amounts for MB and RBR were 210.9 and 638.7 $mg \cdot g^{-1}$ at pH=12.0, respectively	[43]
1,6-hexanediamine	1, 1,6-hexanediamine-functionalized magnetic chitosan microspheres (AF-MCTS)	Cr(Ⅵ)	Maximum adsorption capacity was 110.0 $mg \cdot g^{-1}$	Maximum adsorption capacity was 208.3 $mg \cdot g^{-1}$	[44]

相互作用，有效提高其吸附容量与经济效益。表 5 中，谷氨酰胺、1,6-己二胺等物质的引入使微球表面成功接枝氨基基团，对照实验证明氨基基团活性高，在吸附过程中起重要作用，有助于离子的富集。之后的研究中，若能够有效解决选择性接枝在不同位置时如何有效保护不参与反应的基团和部分物质接枝率低这两个问题，新型 MCM 有望在废水处理、酶的固定与释放、生物载体等领域有更好的发展前景。

1.2.3　金属螯合改性

通过氨基、羟基与金属离子作用形成螯合环，金属离子被螯合在壳聚糖上形成螯合物，使吸附剂热稳定性强且吸附容量高，在处理印染废水时表现出更好的吸附效果[45]；或者是直接使用壳聚糖作为配合物，调节溶液 pH 后，直接用于去除废水中的重金属离子。Peng 等[46] 将纤维素和壳聚糖混合制备新型纳米多孔磁性复合微球 (NMCMs)，克服壳聚糖机械强度弱、耐化学性差的同时丰富的氨基和羟基可以螯合大量的铜离子，在溶液中金属离子的初始浓度为 150.0 mg/L，pH=5.0 时的吸附效果最好，吸附量为 65.8 mg/g，较高的机械强度和化学稳定性利于回收再利用且最大限度地减少了二次废物的产生。Shi 等[47] 将罗丹明衍生探针和 MCM 结合形成对汞极度敏感的磁性复合微球。在高初始浓度下，对汞的最大吸附量为 337.0 mg/g，最大去除效率为 97%，即使在复杂环境中汞的去除量也可达到 90%，相同条件下传统吸附剂只能去除约 46%，新型复合材料对溶液中汞表现出优异的检测性和吸附性，可以广泛应用于检测和修复工业废水。Wang 等[48] 将 Ti^{4+}固定到磁性纳米复合微球上，形成具有超顺磁性且含大量螯合 Ti^{4+}的 MPCS-Ti^{4+}亲和粒子，粒径分布在 126~280 mm 之间，通过实验验证，MPCS-Ti^{4+}在水溶液中分散性提高、对磷酸肽具有高亲和力和选择性且能在短时间内完成磁分离进行重复使用。

1.2.4　MCM 的烷基化改性

壳聚糖分子与环氧衍生物发生加成反应，适当引入烷基，同时破坏氨基葡萄糖残基上的 C3 羟基与另一条壳聚糖分子链的糖苷基形成的氢键、与另一条壳聚糖分子链的一个糖残基呋喃环上的氧原子形成的氢键 (两种分子间氢键如图 4 所示)。明显的削弱分子间氢键，改善其溶解性，改性后的壳聚糖能溶于水，和溶于大多的醇。

壳聚糖的分子链上重复单元的第三位和第六

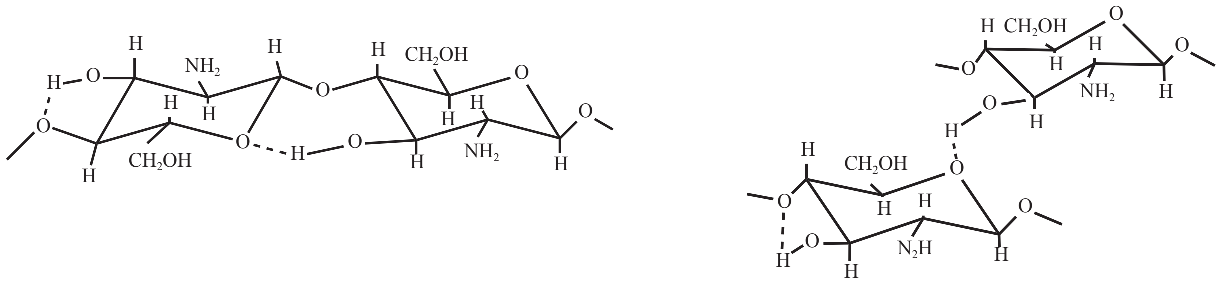


图 4　壳聚糖分子间氢键

Fig. 4　Intermolecular hydrogen bond of chitosan

位碳原子上的羟基和第二位碳原子上引入烷基，发生壳聚糖羟基上的—O位烷基化、氨基上的—N位烷基化、羟基和氨基同时反应的—N、O位烷基化这三种不同位置的改性。由于氨基活性较高，此类改性常为N—烷基化改性，如果需要单独改性O—烷基化，改性前通常先用希夫碱法或邻苯二甲酰化法对氨基进行保护[49-50]。三种改性位置的特点如表6所示。

表 6　壳聚糖烷基化改性的不同位置优缺点

Table 6　Advantages and disadvantages of different positions of chitosan alkylation modification

Route	Modification position	Advantage	Disadvantage
O-site alkylation	Hydroxyl groups at C3 and C6 positions	Amino group has a polycationic character, decreases crystallinity, weakens intermolecular hydrogen bonds, and interacts with negative charges to inhibit bacteria and sterilization	Amino group is more active than the hydroxyl group, and the reaction starts with the amino group at the C2 position, which is not easy to prepare
N-position alkylation	Amino in the C2 position	Intermolecular hydrogen bonds are broken, regularity is reduced, crystallinity of the molecule is decreased, new functional groups are introduced, and the complex has new properties	Special nature of arsenate, solution alkaline good, the removal of metal ions when the solution pH plays an important role, the two need to coordinate
O, N-position alkylation	Amino group at C2 position, hydroxyl group at C3 and C6 positions	Adding substances with different biocompatibility differences, hydrophobicity changes, and simpler preparation process	Introduction of large substituents reduces intermolecular hydrogen bonds and changes hydrolysis ability

Li 等[24]利用乳液聚合法制备含有N-异丙基丙烯酰胺(NIPAm)的磁性纳米复合微球，通过对复合微球的结构、热敏性和酸碱敏感性的研究，证明其具有多重响应特性，在生物科技和医学药物运输中使用效果提高。辛梅华等[51]制备了新型N—烷基化改性壳聚糖微球，并通过实验分析得出酸碱度、NaCl含量对产物吸附性能影响较大，在pH=3.6时MCM在1 h内达到吸附平衡，最大吸附量为400 mg/g；NaCl的存在，使溶液中Na^+和Cl^-的浓度提高，导致溶液的静电排斥增大，同时由于Cl^-的竞争吸附作用使吸附量明显降低。

2　MCM在废水处理上的应用

MCM相较于传统吸附剂，网状壳体结构在有效增加接触面积的同时也增加了高聚物的稳定性，能更好的通过离子交换、静电吸附、范德华力及氢键等达到吸附水中的有机杂质、无机杂质的目的。目前主要将其应用于处理废水中的阴阳离子染料、重金属离子及常见有机杂质的去除。

2.1　印染废水中染料的去除

染料的利用率较低，使用后的印染废水中含有染料离子，整体规模大、色度高、有毒性，未经处理直接排放将严重影响水环境的安全和人体健康。壳聚糖分子链上存在游离的氨基，具有阳离子型聚电解质特性，可以作为离子型染料的吸附剂。但实际应用中发现其易流失、耐酸性差、机械强度低，作为无用染料吸附剂的吸附效果差[52]。进行壳聚糖改性研究后发现用壳聚糖包裹磁性粒子，既能保留有机物高分子链上基团的活性，又可以在外界磁场的作用下定向流动，实现快速分离。许家辉等[53]以磁性强、易分散的$SrFe_{12}O_{19}$为内核制备新型纳米复合微球，用于吸附废水中的亚甲基蓝染料离子，实验验证在25~50℃、染料初始浓度为30 mg/g时，对亚甲基蓝的最大吸附率为97.4%，与传统吸附剂相比新型吸附剂的机械强度和吸附效率都显著提高，为染料废水的合理处理提供有效的科学方法。更多相关研究见表7。分析可知，壳聚糖及其衍生物包裹磁性纳米粒子，交联反应大幅提高其在酸碱介质中的稳定性，同时利用溶液的酸碱度不同，使氨基与羟基发生不同程度的质子化，易于与阴/阳离子染料之间结合，发生静电吸附作用，有效、快速地分离印染废水中的无用染料，为处理印染废料提供了更简单、更有效的方法，避免二次污染。在之后的研究中可尝试将两种或多种简单易得、无毒无害的物质与壳聚糖结合制备复合微球，提高整体适应性，去除复杂体系、含量微小的有毒有害染料，不断提高吸附剂去除无用染料的效果。

2.2　废水中重金属离子的去除

重金属污染是生产和生活废水污染中较难解决的问题，传统的吸附材料(活性炭、沸石等)在吸附完成之后难与水体发生分离，易造成二次污

表 7　MCM 做吸附剂处理印染废水

Table 7　Treatment of printing and dyeing wastewater with MCM as adsorbent

Adsorbent	Dye	Principle of action	Experimental result	Repeat regeneration experiment	Ref.
β-cyclodextrin modified magnetic chitosan microspheres	Methylene blue dye	Electrostatic adsorption between -OH and methylene blue	Maximum adsorption capacity was 123.7 $mg \cdot g^{-1}$ and the maximum adsorption capacity was positively correlated with pH and negatively correlated with temperature	Adsorption amounts of the first and third experiments were 123.7 $mg \cdot g^{-1}$ and 115.9 $mg \cdot g^{-1}$, and the decolorization rates were 93.7% and 92.7%, respectively	[54]
Silver particle-modified magnetic chitosan microspheres	Composite dye system	The —NH_2 and —OH of the shell layer are protonated and deprotonated significantly at different acid and alkaline levels, and are easily bound to anionic and cationic dyes	At 35℃ and pH=4.0, the maximum dye adsorption was 271.2 $mg \cdot g^{-1}$; the maximum removal rate of dye was 99.5%.	Adsorption rates of dyes were 99.0%, 95.0% and 91.0% for the three repeated regeneration experiments, respectively	[55]
Polyacryloyloxyethyl trimethyl ammonium chloride grafted magnetic chitosan microspheres	Sunset yellow dye	Quaternary ammonium group has increased hydrophilicity, and the quaternary ammonium group can be electrostatically attracted to sunset yellow with or without -NH2 protonation	Maximum adsorption capacity at 25℃ and pH=2.0 was 787.1 $mg \cdot g^{-1}$	Adsorption rate was 96.2% after five adsorption elution cycles	[56]
$Sr_{3.8}Fe_{25.7}O_{70.4}$ Chitosan magnetic particles	Crystalline Violet (CV) Alkaline Red (BR9)	Initial concentration difference provides resistance to two-phase mass transfer and promotes dye adsorption through hydrogen bonding, electrostatic adsorption	Maximum removal rates of CV and BR9 at 30-40℃ and pH>7 are 94.5% and 97.5%, respectively, and are highly efficient and environmentally friendly.	Dye removal rate remains above 90.0% after five cycles	[57]

染[58-60]。通常使用壳聚糖作吸附剂对其进行处理，但在强酸或强碱环境下壳聚糖易发生变性使吸附剂失效。研究者想到将其与磁性粒子结合生成 MCM，在增大吸附容量、加强吸附效果的同时保证吸附剂能在外加磁场的作用下定向移动，回收利用避免二次污染。蒲生彦等[61]基于交联共同作用制备了 CS-EGDE/Fe_3O_4 凝胶微球，将其作为新型吸附剂，考察在不同实验条件下对体系中 Pb(Ⅱ)、Cu(Ⅱ)、Zn(Ⅱ) 的吸附效果，研究了共价指数的差异对吸附剂出现选择性吸附现象的影响。和现存的吸附剂相比，CS-EGDE/Fe_3O_4 凝胶微球具有吸附率高、利于回收、不易造成二次污染等优势，为处理废水中的重金属离子提供了一种环保、经济的新思路。表 8 列举了更多重金属的去除研究。

由表 8 可知，MCM 吸附重金属，具有良好的稳定性，微球中改性壳聚糖的三维有序晶体结构发生变化，对于废水中少量 (微量) 重金属离子的情况，也能够实现有效吸附、快速定向分离。经过多次洗脱后，MCM 仍有较高的吸附效率，可以重复使用，提高吸附材料的经济效益的同时有效避免二次污染。吸附过程主要是通过原子或离子间的相互作用力，在今后的研究中，若能同时提高化学吸附和离子交换吸附能力，MCM 的经济效益将提高，更加适应工业处理需要。

2.3　其他有机杂质的去除

社会快速发展推动着食品、生物、医学等向更深领域探索。MCM 因其能高效吸附、快速从吸附质中分离等特点，开始应用于食品、生物、医学等领域，用作吸附剂提取果蔬中的有益成分，研发多品类的果蔬深加工产品；分子印迹改性后，用作印迹聚合物识别、吸附蛋白质与酶；用作载

表 8　MCM 作吸附剂处理重金属离子

Table 8　Treatment of heavy metal ions with MCM as adsorbent

Adsorbent	Heavy Metal	Principle of action	Experimental result	Repeat Regeneration Experiment	Ref.
Magnetic chitosan microspheres	P	Adsorption of porous carbon films depends mainly on electrostatic effect	Maximum adsorption amount was 4.8 mg·g^{-1} at pH=7.0	After treatment and reuse, the adsorption effect is almost unaffected	[62]
Quaternary ammonium magnetic chitosan microspheres	Cr, P	Adsorption mechanism of chromium and phosphorus is mainly electrostatic interactions	At 25°C and pH=6.0, the saturation adsorption amounts of P and Cr were 416.0 and 419.0 mg·g^{-1}, respectively	After performing four adsorption-desorption cycles, the adsorption effect was not affected by	[63]
Novel cross-linked chitosan magnetic beads modified with cysteinyl urea Schiff base	Cu、Cr	Acidic environment -NH_2 and -C=N- have high nitrogen content to facilitate chelation, and both protonate and electrostatically adsorb with CRO_4^{2-} and $HCrO_4^-$	The maximum adsorption amounts of most Cr at pH=2.0 and pH=5.0 were 156.5 and 138.5 mg·g^{-1}, respectively	After three adsorption-desorption cycles, the adsorption efficiency of metal ions was still higher than 91.0%	[64]
Magnetic carboxymethyl chitosan composite microspheres	Mn^{2+}	pH=6.5-7.5 to prevent the generation of manganese hydroxide precipitation; electrostatic adsorption of surface adsorption sites with Mn^{2+}	At 25°C and pH=7.0, the adsorption capacity of Mn^{2+} was 75.7 mg·g^{-1} and the adsorption rate was higher than 90.0%	After five elution tests, the adsorption efficiency for Mn^{2+} was still 77.9%	[65]
Nanoporous magnetic cellulose-chitosan composite microspheres	Cu	Hydrogen bonding and miscibility between the two effectively suppress the crystal structure; copper and nitrogen atoms are chemically bonded	Adsorption amount was 65.8 mg·g^{-1} at pH=5.0	Five cycles of experiments, the adsorption capacity of Cu, no significant decline	[47]
Magnetic Fe_3O_4 chitosan microspheres	Ag	Electrostatic interaction causes surface cations to form complexes with electron-rich organic ligands	Extraction efficiency of lakes and wastewater ranged from about 84.9% to 98.8%	Average extraction efficiency was still 77.2% after multiple repetitions of the experiment	[66]

体成为各种药物的运载工具等。MCM 在不同领域中更多的应用实例如表 9 所示。可知，MCM 在食品、生物和医学等领域仍能发挥良好作用，能有效吸附、提取物质，在提高效率的同时降低成本，但食品及医药与人们的健康息息相关，因此在制备吸附剂时应确保使用的交联剂无毒。在未来的研究中应致力于开发出更多的价格低廉、绿色环保的交联剂用于制备 MCM。

表 9　在不同领域作吸附剂的应用实例

Table 9　Application examples of adsorbent in different fields

Adsorbent	Adsorbed material	Mechanism of action	Experimental result	Ref.
PEI-modified magnetic chitosan microspheres	Ibuprofen	Regular spherical shape, narrow particle size distribution, successful introduction of a large number of amino	Maximum adsorption capacities of the three composites with different ratios were 89.3, 100.0 and 138.6 mg·g^{-1}, respectively	[67]
Magnetic chitosan microspheres	Apple juice organic acid	Acid ions form ionic bonds with protonated amino groups	At 25℃, the average adsorption capacity was 112.4 mg·g^{-1} and the saturation capacity was 188.7 mg·g^{-1}	[68]
Molecularly imprinted polymer modified magnetic group microspheres	Chloramphenicol	Hydrogen bonds, ionic bonds make strong interactions between molecules	30-40℃, the maximum adsorption capacity is 32.5 mg·g^{-1}	[69]
Quaternary ammonium-functionalized magnetic chitosan microspheres	Beet juice coloring agent	Electrostatic adsorption of quaternary ammonium groups and impurities, ion exchange reaction between Cl^- and quaternary ammonium cations	Maximum adsorption efficiency was 99.4% and the maximum adsorption capacity was 127.2 mg·g^{-1}	[70]
Novel magnetic chitosan microspheres	Lysozyme	Cavity-specific recognition of lysozyme	25℃, the maximum adsorption capacity is 130.0 mg·g^{-1}	[71]

3 结语与展望

传统壳聚糖吸附剂是自然界中少有的带有正电荷的纤维结构物质，无毒无害且易于制取，广泛应用于食品、医学和工业等领域，但存在机械强度弱、耐化学性差和结晶度高等缺点，极大地限制其作为吸附剂的效率。将其与磁性粒子结合形成微球，可使吸附剂结晶程度降低、化学稳定性和热稳定性提高；在此基础上进一步对微球进行改性，壳体上的活性基团发生变化或者接枝官能团，使其具有更多的物化性质，能够有效地扩大吸附剂的使用范围，形成有更高的选择性识别、吸附速度、分离效率的新型吸附材料。

综合国内外关于磁性壳聚糖微球 (MCM) 的改性及其在水处理方面的研究进展，可从以下几方面进行考虑：(1) 在现有基础上，尽量开发更多的无毒、绿色的交联剂应用于制备过程；(2) 探索新型纳米多孔复合微球，将两种或多种简单易得、无毒无害的物质与壳聚糖结合，从而制备复合微球的壳体，提高整体适应性，去除复杂体系、含量微小的有毒有害杂质；(3) 探索更多的材料用于修饰磁性粒子，在不改变其磁性结构的情况下提高其稳定性、聚集行为和分离效率；(4) 利用多模板分子印迹技术制备 MCM，使其能够同时识别和吸附不同目标分子，适用于更多的应用环境；(5) 将多种改性方法结合，例如将氨基、羧基、季铵盐等与自由基接枝共聚，引入新的官能团后交联，降低溶胀性的同时提高产物的吸附效率，以期制备出应用范围更广的 MCM，对国家统筹推进资源开发与环境协调发展，推动实现能源绿色低碳转型起到推动作用。

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