Research progress of modified macroporous adsorption resin in adsorption separation

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Abstract: Macroporous adsorption resin (MAR) is widely used in molecular adsorption and material separation due to its unique porous nature, surface activity and easy modification. Although there may be multiple synergistic effects in the adsorption process, its adsorption capacity is weak, and it is difficult to meet the problem of separation and purification of complex samples. The functional modification of macroporous adsorption resin is an ideal way to improve its separation efficiency and selectivity. In this paper, recent advances in the preparation of modified macroporous adsorption resins and their application in adsorption separation are reviewed, which provides a reference for further research.

1. Introduction
Macroporous adsorption resin (MAR) is a new type of high molecular polymer adsorption functional material that has been rapidly developed in recent years, because its high degree of cross-linking, spatial network structure, porosity, large specific surface area, etc. It has important application value in the field of adsorption and separation of natural products and sewage treatment. However, there are many kinds of commercialized MARs. For different sample components, the workload is huge when predicting and screening MARs with the best separation efficiency. In addition, the preparation process of MARs is special, the structure is complex, and the pore structure parameters vary widely. Sexuality makes it difficult to carry out theoretical research on its adsorption. However, the research on the structure-activity relationship between MARs and target molecules and its separation law is weak. It is difficult to realize the design and preparation of MARs, which makes the selectivity and specificity of MARs not strong, and the adsorption separation effect is not high.

Therefore, in order to obtain MARs with higher adsorption capacity and higher selectivity, designing resin structure for different target components, functional modification of its surface and structure, and improving adsorption performance are the hotspots and focuses of people. In this paper, recent advances in the application of functional group modified MARs to adsorb and remove different compounds have been reviewed.

2. MARs surface graft modification
The commonly used MARs are non-polar resins, and the adsorption driving force is mainly hydrophobic, and the selectivity is low. In order to improve its adsorption performance and selectivity, a specific functional group is often introduced into the MARs to achieve separation of the target components. However, the direct substitution of the benzene ring can result in less functional groups grafting, which is not conducive to modification. Therefore, Friedel-Crafts catalyzed\(^1\) and Blanc\(^2\) chloromethylation are one of the main methods for functional modification of MARs substrates.
2.1. Amino modified resin
Lou et al [3,4] grafted amino groups by reacting chlorine spheres with chloromethylated D101 [5] with excess triethylenetetramine. Ye et al [6] modified the grafted amino group with chlorosphere and hexamethylenetetramine. Li Aimin et al [7] used chlorine with a chlorine content of 18.5% to 19.0%, Wang Dexing [8] with chlorine containing 17.5% chlorine, Zhang et al [9] with a cross-linking degree of 8% and a chlorine content of 3.8 mmol/g. The ball is the substrate, Xie Xingyu et al [10] reacted with toluene to prepare a toluene ultrahigh crosslinked macroporous resin with a chlorine content of 6.38%, and then chemically treated with 2-aminopyridine. Modified, grafted amino. Ma et al [11] grafted glycidyl methacrylate onto chloromethylated polystyrene resin by surface-initiated atom transfer radical polymerization followed by 5-aminosalicylic acid and 2-(4-imidazolyl) Ethylamine is modified to graft the amino group. Xiao et al [12] modified chloromethylated polystyrene resin by 2-aminopyridine. Xu et al [13] prepared a composite functional resin by further introducing nitro and amine groups into the chloromethylated polystyrene skeleton by optimizing the conditions of the Friedel-Crafts reaction.

2.2. Phenolic hydroxyl modified resin
Huang [14] and Hu [15] prepared a phenolic hydroxyl group modified by macroporous cross-linked chloromethylated styrene-divinylbenzene copolymer by Friedel-Crafts post-crosslinking reaction and esterification reaction. Supercrosslinked polymer adsorbent. He et al [16] prepared a sorbent containing multiple phenolic hydroxyl groups from a chloromethylated polystyrene resin by Friedel-Crafts reaction. Wei et al [17] grafted phenol onto the surface of non-porous gel-type chloromethylated polystyrene by Friedel-Crafts post reaction. Qi Fengpei et al [18] used chloromethylated cross-linked polystyrene microspheres as starting materials to react with p-hydroxybenzaldehyde to prepare hydroxylated modified polystyrene microspheres.

2.3. Other group graft modified resin
Long Yu et al [19] chloromethyl polystyrene microspheres were bonded to naphthalene and anthracene with strong conjugation effect by Friedel-Crafts reaction, and two new types of macroporous super high crosses were synthesized by post-crosslinking reaction. Copolymer resin. Cai et al [20] synthesized a novel bifunctional polymeric resin by introducing sulfonic acid groups into the surface of the resin during the cross-linking of chloromethyl low-crosslinking macroporous polystyrene resin. Li et al [21] synthesized two carbonyl-modified XAD-4 resins by chemically modifying Amberlite XAD-4 with carbon tetrachloride and benzoyl chloride. Li [22] chloromethyl macroporous polystyrene resin was used as the substrate, and a novel formaldehyde carbonyl modified self-crosslinking polystyrene resin was synthesized by Friedel-Crafts reaction. Huang Xiaojuan et al [23] used a macroporous ultra-high crosslinked polystyrene resin for nitration reaction to obtain a nitrification
modified macroporous ultra-high crosslinked polystyrene resin.

In summary, the basic path of functional graft modification of polystyrene resin is to first activate the polystyrene resin substrate, generally using chloromethylation, acylation or bromomethylation; The functional group required for the branch is a modified resin which prepares a series of functional groups.

3. Application of modified MARs

Xu et al\cite{13} used chloromethyl polystyrene resin as substrate to further introduce nitro and amine groups into the framework by Friedel-Crafts reaction to prepare phenol adsorption behavior. The results showed that the modified resin was phenol. The adsorption capacity of the compound was 412.9 mg / g, which was 16.4 to 47.7% higher than that of a commercially available resin having a similar physical structure. Wang et al\cite{24} grafted four groups of 2-pyrrolidone, 2-imidazolidinone, trimellitic anhydride and sulfamic acid onto the surface of chloromethyl polystyrene resin by Friedel-Crafts reaction, and 3-amino in sewage. The adsorption behavior of acetanilide was studied. As a result, the adsorption capacity of the modified resin on 3-aminoacetanilide in aqueous solution was improved compared with that before modification, and the modified resin of grafted 2-pyrrolidone was effective from aqueous solution. 3-aminoacetanilide was removed. Li et al\cite{22} have polyphenolic groups and hydrophobic structures for licorice in licorice, and introduced amino groups on chloromethyl polystyrene resin, which has an adsorption capacity of 45.5 mg/g, which is significantly higher than that of licorice. Adsorbent before (15.2 mg/g) without modification. Ye et al\cite{6} used chloromethylated styrene-co-divinylbenzene copolymer as substrate, modified by hexamethylenetetramine by amination reaction, and obtained a new adsorbent with amino group. Continuous modification of formylphenylboronic acid to obtain modified resin with phenylboronic acid group, the adsorption of rebaudioside A and stevioside on chloromethyl, amino and phenylboronic acid resin in chamomile was studied. It is indicated that the resin having an amino group and a phenylboronic acid group preferably adsorbs stevioside instead of rebaudioside A. Yan et al\cite{25} a porous polymer antibacterial resin containing an N-halamine functional group and subjected to an antibacterial test. As a result, the modified resin Escherichia coli (E. coli) and Staphylococcus aureus (S. aureus) have Strong antibacterial effect. Liu et al [5] used agaric catechin gallate (EGCG) and caffeine (CAF) in discarded tea to introduce amino and aniline onto chloromethyl polystyrene resin, and aniline added more to EGCG. Hydrogen bond and π-π interaction reduce the hydrophobic effect on CAF, and the adsorption performance is significantly different, thus effectively removing CAF impurities in EGCG; introducing phenol, increasing the adsorption active sites of EGCG and CAF, and improving separation ability [26].

The non-polar polystyrene type MARs and the adsorbate are mainly π-π interaction and hydrophobic interaction. The introduction of an amino group easily forms a hydrogen bond or an electrostatic interaction with the hydroxyl group on the adsorbate, and the hydrophilicity of the surface of the resin is also improved, which facilitates the entry and adsorption of the hydrophilic component; the introduction of the aniline and the nitrogen atom is more easily associated with the hydrogen-containing bond donor. The organic matter forms a hydrogen bond; the large π bond of the benzene ring can participate as a hydrogen bond acceptor to form a hydrogen bond; at the same time, the pore structure and distribution state also change, the molecular sieve principle changes, and the separation efficiency and adsorption performance also change. Therefore, the introduction of different functional groups on the surface of the polystyrene resin substrate according to different target components is an effective way to improve adsorption performance and selectivity.

4. Prospective Future

At present, the research on the modification method of polystyrene resin is mostly used in the treatment of environmental wastewater. The natural products are not much involved, but the graft modification method still has great reference value. The polarity, hydrophilicity, pore size distribution and adsorption of MARs changed after graft modification. These factors together led to the change of
adsorption efficiency of target components, which provided a way of thinking about the separation of MARs.

With the gradual deepening of natural product research, efficient separation and purification technology is an urgent problem to be solved. Conventional MARs are difficult to meet when obtaining active ingredients with low content, high added value, and difficulty in obtaining. Therefore, the design and preparation of specific MARs for the target components is a new opportunity for the separation and purification of specific active components in natural products.

References
[1] Gao B, Liu Q, Jiang L. (2008) Studies on performing chloromethylation reaction for polystyrene by micellar catalysis in aqueous surfactant solutions [J]. Chemical Engineering and Processing: Process Intensification, 47(5): 852-858.
[2] Ma Ping, Tian Lili. (2011) Blanc Chlorine Methylation Polystyrene Preparation and Conditions Screening [J]. Guangdong Chemical Industry, 38(11): 209-210.
[3] Lou Song, Chen Zhenbin, Liu Yongfeng, et al. (2012) Synthesis of Functional Adsorption Resin and Its Adsorption Properties in Purification of Flavonoids from Hippophae rhamnoides L. Leaves [J]. Ind Eng Chem Res, 51(6): 2682-2696.
[4] Lou Song, Chen Zhenbin, Liu Yongfeng, et al. (2011) New Way to Analyze the Adsorption Behavior of Flavonoids on Macroporous Adsorption Resins Functionalized with Chloromethyl and Amino Groups [J]. Langmuir, 27(15): 9314-9326.
[5] Liu Yongfeng, Bai Qingqing, Lou Song, et al. (2012) Adsorption Characteristics of (−)-Epigallocatechin Gallate and Caffeine in the Extract of Waste Tea on Macroporous Adsorption Resins Functionalized with Chloromethyl, Amino, and Phenylamino Groups [J]. J Agric Food Chem, 60(6): 1555-1566.
[6] Fayin Ye, Ruijin Yang, Xiao Hua, et al. (2014) Adsorption characteristics of rebaudioside A and steviol on cross-linked poly(styrene-co-divinylbenzene) macroporous resins functionalized with chloromethyl, amino and phenylboronic acid groups [J]. Food Chemistry, 159: 38-46.
[7] Jinnan Wang, Li Xu, Aimin Li, et al. (2010) Adsorption Study of Gallic Acid by Hyper Cross-linked Resin Modified by Amino Function Groups [J]. Chemical Journal of Chinese Universities, 31(1): 193-198.
[8] Dexing Wang. (2016) Synthesis of Amino-modified Ultra-high Crosslinking Resin and Its Adsorption of Dimethyl Phthalate [J]. Resource Information and Engineering, 31(04): 97-98.
[9] Zhang W M, Dua Q, Pan B C, et al. (2009) Adsorption equilibrium and heat of phenol onto aminated polymeric resins from aqueous solution [J]. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 346(1/2/3): 34-38.
[10] XIE Xing-yu, WANG Bin, QIN Hai-jiao, et al. (2016) Synthesis of Toluene Hypercross-Linked Macroporous Resins Modified by Aminopyridine and Their Adsorptive Properties [J]. Chemistry and Bioengineering, 1: 26-29.
[11] Ma Jingchong, Shen Jiwei, Wang Chaozhan, et al. (2018) Preparation of dual-function chelating resin with high capacity and adjustable adsorption selectivity to variety of heavy metal ions [J]. Journal of the Taiwan Institute of Chemical Engineers, 91: 532-538.
[12] Guqing Xiao, Ruimin Wen. (2019) Comparative adsorption of glyphosate from aqueous solution by 2-aminopyridine modified polystyrene resin, D301 resin and 330 resin: Influencing factors, salinity resistance and mechanism [J]. Fluid Phase Equilibria, 411: 1-6.
[13] Xu Chao, Jiang Long, Qin Xiaoli, et al. (2109) Enhancement mechanism behind the different adsorptive behaviors of nitro/amine modified hypercrosslinked resins towards phenols [J]. Journal of the Taiwan Institute of Chemical Engineers, 102: 340-348.
[14] Jianhan Huang, Xiaomei Wang, Xing Deng. (2009) Synthesis, characterization, and adsorption properties of phenolic hydroxyl group modified hyper-cross-linked polymeric adsorbent [J]. Journal of Colloid and Interface Science, 337: 19-23.
[15] Huanxiao Hu, Xiaomei Wang, Shengyong Li, et al. (2012) Bisphenol-A modified hyper-cross-linked polystyrene resin for salicylic acid removal from aqueous solution: Adsorption equilibrium, kinetics and breakthrough studies [J]. Journal of Colloid and Interface Science, 372: 108-112.

[16] Chunlian He, Kelong Huang, Jianhan Huang. (2010) Surface modification on a hyper-cross-linked polymeric adsorbent by multiple phenolic hydroxyl groups to be used as a specific adsorbent for adsorptive removal of p-nitroaniline from aqueous solution [J]. Journal of Colloid and Interface Science, 342: 462-466.

[17] Wei Kuang, You-Nian Liu, Jianhan Huang. (2010) Phenol-modified hyper-cross-linked resins with almost all micro/mesopores and their adsorption to aniline [J]. Journal of Colloid and Interface Science, 487: 31-37.

[18] Qi Fengpei, Hu Yifan, Ou Panlin, et al. (2019) Study on the Adsorption Properties of Modified Polystyrene Microparticles Containing Polyhydroxy Compounds for Pb2+ [J]. Journal of Hunan City University (Natural Science), 4: 65-59.

[19] LONG Yu, LIAO Hui-lin, FU Yu-li, et al. (2018) Synthesis of Polystyrene Nenaphthalene Resin and Its Adsorption Property for Theophylline [J]. Fine Chemical Intermediates, 4: 47-50

[20] Cai Jianguo, Li Aimin, Shi Hongyan, et al. (2005) Adsorption characteristics of aniline and 4-methylaniline onto bifunctional polymeric adsorbent modified by sulfonic groups [J]. Journal of Hazardous Materials, 124: 173-180.

[21] Chengyong Li, Maowen Xu, Xiucheng Sun, et al. (2013) Chemical modification of Amberlite XAD-4 by carbonyl groups for phenol adsorption from wastewater [J]. Chemical Engineering Journal, 229: 20-26.

[22] Xiaoting Li, Yongfeng Liu, Duolong Di, et al. (2016) A formaldehyde carbonyl groups-modified self-crosslinked polystyrene resin: Synthesis, adsorption and separation properties [J]. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 500: 1-9.

[23] HUANG Xiao-juan, LONG Yu, FU Yu-li, et al. (2017) Study on Nitrification and Adsorption Properties of Macroporous Hypercross-linked Polystyrene Resin [J]. Fine Chemical Intermediates, 47(06): 37-42.

[24] Tao Wang, Chunhui Shena, Nan Wang, et al. (2019) Adsorption of 3-Aminoacetanilide from aqueous solution by chemically modified hyper-crosslinked resins: Adsorption equilibrium, thermodynamics and selectivity [J]. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 575: 346-351.

[25] Shulan Yan, Xiufang Yan, Xuexiang Shao, et al. (2015) Porous polymeric antimicrobial resin containing N-halamine functional groups [J]. Reactive and Functional Polymers, 96: 71-77.

[26] Xiaofeng Zhang, Yi Xu, Qing Zhang, et al. (2016) Simultaneous separation and purification of (−)-epigallocatechin gallate and caffeine from tea extract by size exclusion effect on modified porous adsorption material [J]. Journal of Chromatography B, 1031: 29-36.