

· 专论 ·

树脂对化工废水中有毒有机化合物的吸附作用机理与技术研究^{*}

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摘 要 超高交联吸附树脂对多种芳香有机化合物较高的吸附容量主要源于其密集的微孔和双峰孔分布。对大孔吸附树脂及超高交联吸附树脂采用不同极性功能基团进行化学修饰可以制得系列离子交换与吸附双重功能吸附树脂,该类树脂对亲水性有机污染物同时具有疏水、静电、络合等多重作用。丙烯酸酯类吸附树脂在吸附芳香磺酸盐时,树脂的骨架和功能基团对吸附过程都有重要的贡献。

关键词 树脂吸附剂, 有机污染物, 机理, 吸附

有毒有机化工废水浓度大、盐分高、污染物难以生物降解,是水污染控制的难点。树脂吸附法在处理废水的同时,可对废水中有毒有机污染物吸附、分离与回收,大大降低了处理成本,受到广泛关注。不同结构的有机污染物需要采用不同理化结构的树脂吸附剂才能有效吸附与分离,因此对树脂吸附剂结构与有机污染物吸附性能之间的匹配关系研究成为树脂吸附剂研制与应用的关键。近十余年来,作者一直致力于吸附作用机理、吸附剂及吸附技术的开发与应用^[1~18]。超高交联树脂的双峰孔分布和密集微孔特征是其高吸附容量的根本原因。双重功能吸附树脂具有离子交换与吸附双重特性,能够选择性地吸附分离高盐分水溶性芳香有机污染物。新型丙烯酸酯类吸附树脂可以解决含极性有机溶剂的高含盐废水体系中水溶性有机物吸附、分离的难题,并可以通过热水再生。系列研究成果和示范工程引起国内外同行的关注^[19]。

1 超高交联吸附树脂

超高交联吸附树脂相比大孔吸附树脂对许多有毒有机化合物具有较高的吸附容量,通常认为这是因为吸附树脂具有较高的比表面积。研究表明,大孔吸附树脂的比表面积主要集中在中孔区,而超高交联吸附树脂的比表面积主要集中在纳米级的微孔区,正是这些纳米级微孔的存在,导致超高交联吸附树脂对有毒有机污染物具有较高的吸

附容量^[18,20]。如图 1 所示。

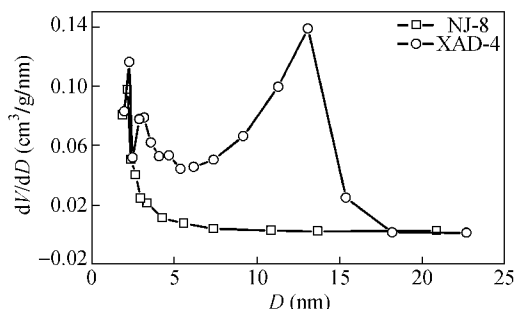


Fig. 1 Pore distribution of resin NJ-8 and Amberlite XAD-4

作者合成的超高交联吸附树脂 NJ-8 的比表面积 (906 m²/g), 与美国 Rohm & Haas 公司 Amberlite XAD-4 树脂的比表面积 (880 m²/g) 相当, 但前者的比表面积主要集中在密集的微孔区, 因而对酚类化合物的吸附容量是后者的两倍以上^[21, 22], 此项研究也得到国外同行的认同^[23]。

后续的研究表明, 通过后交联方法合成的超高交联吸附树脂不仅具有密集的微孔, 还有大孔, 呈现双峰孔分布的特征^[24], 对于分子尺寸较小的有机物分子的吸附, 有机分子进入大孔吸附树脂及双峰孔分布树脂中受到的阻力都较小, 呈现一个动力学特征。而对于分子尺寸较大的分子, 第一个吸附段出现在大孔区, 而第二个吸附段出现在微孔区, 两个吸附段之间有一个平台区, 表明较大分子进入微孔时有一定的阻力。如超高交联吸附树脂对亚甲基兰的吸附动力学行为, 第一个吸附

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平台出现在大孔区和中孔区,而第二个吸附平台出现在微孔区^[25].如图 2 所示.

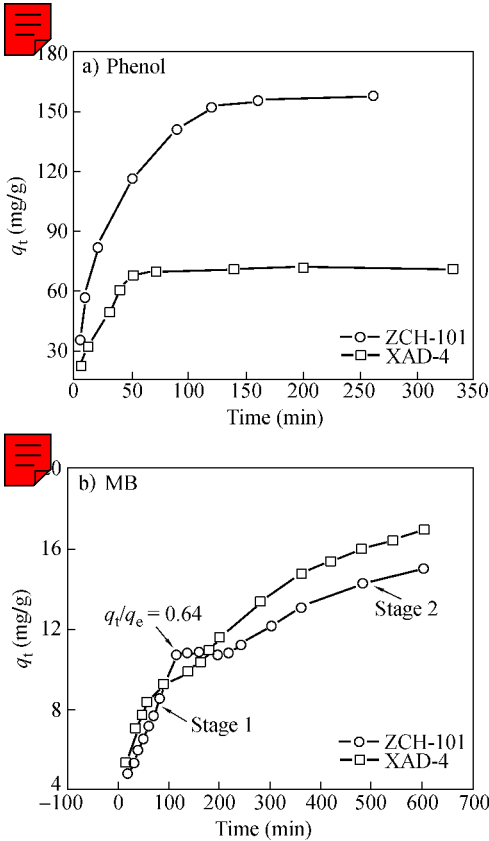


Fig. 2 Kinetic curves for adsorption of phenol (a) and methylene blue (b) by hypercrosslinked polymer resin ZCH-101 with bimodal pore size distribution and macroporous resin XAD-4

超高交联吸附树脂表面含氧官能团的来源也是科技工作者关心的问题,有文献报道,含氧官能团主要是由于反应过程中空气氧化造成.作者的研究发现硝基苯不仅是氯甲基化聚苯乙烯后交联的良好溶剂,也是温和的氧化剂,超高交联吸附树脂上含氧官能团主要是树脂上氯甲基被硝基苯氧化造成,还捕获到硝基苯还原的中间体,亚硝基苯及苯胺^[26~28].

2 离子交换与吸附双重功能吸附树脂

有毒有机化工废水通常具有浓度高、酸(碱)性强、含盐量高、难生物降解等特点,废水中有机物大多是高水溶性的疏水性离子化合物(分子中既含有亲水性基团又含有疏水性基团),依靠疏水作用为主要吸附推动力的超高交联吸附树脂和大孔树脂吸附树脂很难处理此类有毒有机化合物.针对该类有机污染物既含有较多亲水性基团,又含有较多的疏水性基团的结构特点,作者采用氨基、羧基、磺酸基、酚羟基、含氧基团、苯甲酰基等基团对大孔吸附树脂及超高交联吸附树脂进行化学修饰制得的系列新型离子交换与吸附双重功能树脂,使之对该类有机物同时具有疏水、静电、络合等多种非共价作用力^[29~35].如图 3 所示.

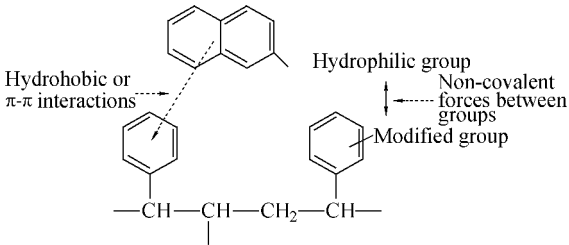


Fig. 3 Diagrammatic sketch of interactions between bifunctional polymeric adsorbent modified and adsorbate with hydrophilic groups

与修饰前树脂相比,双重功能树脂对有机污染物的吸附性能及吸附选择性有较大的提高,拓展了树脂吸附法的应用范围^[33~45].该项研究也引起国外同行的兴趣与关注^[46,47].

作者通过选用双重功能吸附树脂和大孔吸附树脂与水体中有毒有机污染物进行吸附热力学研究,发现以疏水作用为主的吸附过程往往是放热现象,系统吸附焓变小于零,吸附熵也小于零,吸附过程属于焓推动机理,低温有利于吸附.例如,大孔吸附树脂和超高交联吸附树脂对酚类及芳香

Table 1 Thermodynamic parameters and types of adsorption for aniline onto bifunctional polymeric adsorbent and macroporous resin*

Adsorbent	Q_e	ΔH (kJ/mol)	ΔG (kJ/mol)			ΔS (J/(mol K))		
			288 K	303 K	318 K	288 K	303 K	318 K
XAD-4	0.6	-19.41				-49.10	-48.71	-47.83
	0.8	-14.90	-5.27	-4.65	-4.20	-33.43	-33.83	-33.65
	1.0	-11.41				-21.32	-22.31	-22.67
LS-2	0.6	18.83				82.67	80.26	79.03
	0.8	16.04	-4.98	-5.49	-6.30	72.99	71.06	70.25
	1.0	13.88				65.49	63.93	63.46

* LS-2 represents bifunctional polymeric adsorbent, Amberlite XAD-4 represents macroporous resin

胺类化合物的吸附.如表 1 所示,在同样条件下,以静电以及静电与疏水协同作用为主要作用力的吸附过程的焓变却大于零,且吸附过程的熵变也大于零,吸附过程属于熵推动机理.如磺酸基修饰的超高交联双重功能吸附树脂对芳香胺的吸附,升高温度有利于吸附^[45].

3 丙烯酸酯类吸附树脂

丙烯酸酯类吸附树脂能够克服超高交联吸附树脂及大孔吸附树脂只能通过疏水作用吸附分离有机污染物的缺点,可以从极性有机溶剂水溶液中吸附水溶性磺酸类有机污染物^[48].当吸附质分子极性 & 水溶性较小,大孔疏水性聚苯乙烯树脂 XAD-4 的平衡吸附能力大于丙烯酸酯树脂 YWB (图 4a),此时,疏水作用在吸附过程中起到主要作用.但当吸附质分子极性 & 水溶性较大时,丙烯酸酯树脂 YWB 和离子交换树脂 D-301 的吸附能力都明显高于苯乙烯树脂 XAD-4 (图 4b),说明功能基团之间的作用力对吸附的贡献要高于疏水作用在吸附过程中起到作用^[49].

都有重要的贡献.一方面是吸附质的疏水性基团与树脂骨架之间的疏水作用;另一方面是树脂表面的功能基团(羰基与酯基)与吸附质的功能基团之间的作用力^[49,50].

通过 FTIR 和 XPS 两种仪器分析表明,在吸附过程中,酯基树脂的表面功能基团参与了吸附过程,并与吸附质发生了明显的相互作用.如图 5 所示,树脂的酯基峰和羰基峰在吸附后都发生了不同程度的移动,说明两种功能基团受到了吸附质的明显作用^[49].

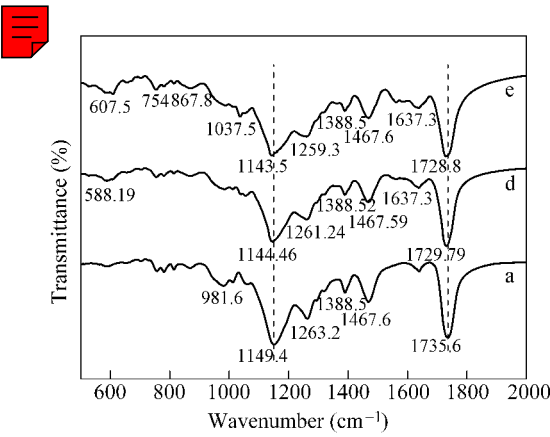
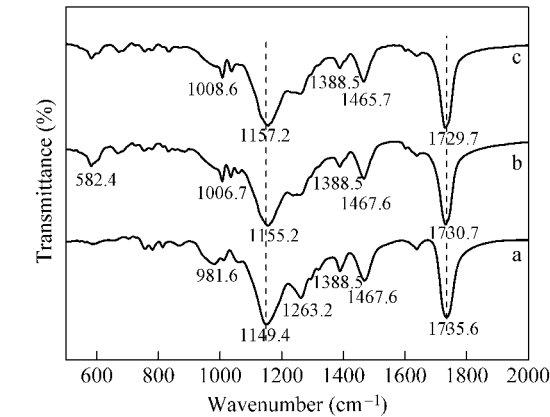


Fig. 5 Changes of FTIR spectra for ester and carbonyl groups on the matrix of acrylic ester resin before and after adsorption a) Before adsorption; b) The equilibrium adsorption concentration of 6-NaDBS on YWB is 0.194 mmol/L; c) The equilibrium adsorption concentration of 6-NaDBS on YWB is 0.735 mmol/L; d) The equilibrium adsorption concentration of KN-R on YWB is 0.145 mmol/L; e) the equilibrium adsorption concentration of KN-R on YWB is 0.338 mmol/L

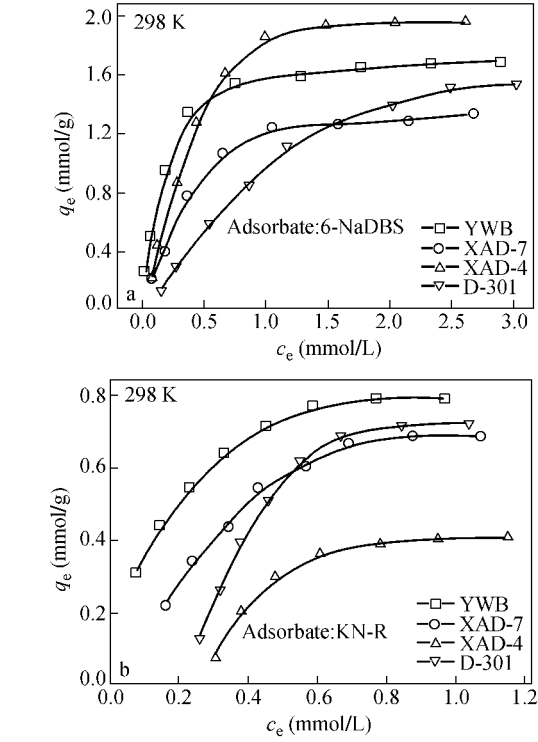


Fig. 4 Comparison of equilibrium adsorption isotherms for 6-dodecylbenzenesulfonate 6-NaDBS (a) and dye reactive brilliant blue KN-R (b) on four resins

上述两种不同的吸附行为表明,在吸附过程中,丙烯酸酯树脂的骨架和功能基团对吸附过程

由于商品化的丙烯酸酯类吸附树脂比表面积较小,吸附容量低,很少在工业废水治理中得到应用.作者通过选择合适的致孔剂进行多元共聚研制的新型丙烯酸酯类树脂 NDA-7,比表面积及对间苯二甲酸-5-磺酸的吸附容量均高于美国 Rohm & Haas 公司

Amberlite XAD-7 及日本 Diaion HP2MG. 在一定范围 水处理及资源化的成本^[51, 52].
内醇对吸附的影响很小,并可用热水脱附,降低了废

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ADSORPTION MECHANISM OF TOXIC ORGANIC COMPOUNDS IN
CHEMICAL WASTEWATER BY POLYMERIC ADSORBENTS

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Abstract Studies of authors on the adsorption and adsorption mechanisms of various organic compounds onto three types of polymeric adsorbents in aqueous solutions are reviewed. The investigations showed that the high adsorption capacity of the adsorbents to many organic compounds was ascribed not only to their high specific surface area but also their intensive micropore structure. The double-peak pore distribution mode,two-stage dynamic character and the formation mechanism of oxygen-containing groups on their surfaces are systematically studied. To bifunctional resin, the point of our study is on its industrial application. Macroporous resins and hypercrosslinked resins were modified with many different functional groups such as amidocyanogen,carboxyl,sulfonate *etc.*, to elevate their adsorption capacities. Some proposed applications of these bifunctional resins in industrial wastewater are presented. The observation on the acrylic ester resin is still on a preliminary stage in terms of its adsorption mechanism and application to organic industrial wastewater. The investigations showed that the matrix of acrylic ester resin and functional groups on its surface played an important role on its adsorption mechanism.

Keywords Polymeric adsorbent, Organic pollutant, Mechanism, Adsorption