水溶液中双酚 A 吸附材料的研究新进展

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摘 要 双酚 A 是世界上生产和消费最多的化学品之一,属于一种内分泌干扰物,废水环境中的双酚 A 威胁着生态环境和人类健康。吸附法脱除水溶液中双酚 A 具有简单、便捷、高效、选择性强等优势。综述了近三年来处理水中双酚 A 的吸附材料的研究进展,介绍了矿物类材料、碳材料、高分子类材料、生活及工农业废弃物衍生材料、磁性材料和分子印迹聚合物吸附材料的制备方法、结构特点和吸附性能,并对双酚 A 吸附材料的研究方向进行了展望。

关键词 双酚 A,吸附,水溶液,吸附材料,进展

New progress in adsorption material for the removal of bisphenol A (BPA) in aqueous solution

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Abstract Bisphenol A (BPA) is one of the most widely used as chemical in production and consumption. BPA in the wastewater is a known endocrine disruptor that can exert potential negative effects on the ecological environment and human health. Adsorption has been found to be superior to the other techniques including simplicity, ease of operation, high efficiency, and good selectivity and so on. The adsorption materials applied for BPA removal in water in recent three years were summarized. The typical adsorption materials of minerals, carbon materials, polymeric materials, man's activities wastes, magnetic material and molecularly imprinted polymers materials were mainly introduced in terms of preparation processes, structure characteristics and adsorption properties. The research direction of adsorbent for BPA removal in water was outlooked.

Key words bisphenol A (BPA), adsorption, aqueous solution, adsorption material, progress

双酚 A 具有极其广泛的工业应用,主要通过制造业、工业处理不到位的废水、垃圾场渗滤液等以双酚 A 为原料生产的各种材料的废弃物而进入环境中,从而污染食物和饮用水,危害人类健康[1]。研究发现,双酚 A 能够抑制胰岛素的分泌从而导致肥胖[2]、损伤肝肾肺等器官[3],最终造成人体内分泌失调、代谢紊乱[4]。因此,有必要对污水中的双酚 A 进行去除。

目前,去除双酚 A 的方法主要有吸附法、超声光催化降解[5]、生物降解[6]、电化学催化降解[7]、纳米过滤[8]等。吸附法被普遍认为优于其他方法,因为吸附法操作简便、成本低廉、能快速有效去除污染物,且不易产生二次污染[9]。

1 双酚 A 吸附材料

1.1 粘土矿物类吸附材料

粘土矿物包括沸石、蒙脱石、坡缕石等物质,其来源丰富、价格廉价,具有比表面积大、内部微孔及介孔丰富和溶胀性能好的特点,可用有机阳离子表面活性剂改变其疏水性,增强对疏水性、弱极性双酚 A 分子的吸附。

用无机改性剂羟基铝和有机改性剂十八烷基三甲基溴化铵改性蒙脱石,合成疏水性无机-有机粘土,增强了对双酚 A 的亲和力,最大吸附量为 109.89mg/g[10]。天然沸石的比表面积大且微孔丰富,用十六烷基三甲基溴化铵改性,降低了沸石表面

基金项目:辽宁省自然科学基金(201202122)

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的负电性，对双酚 A 的吸附性增强[11]。此外，对双酚 A 的吸附量随着 HCO_3^- 浓度的增加而增大，随着 NO_3^-、OH^-、Al^{3+} 浓度的增加而减小[12]。用共沉淀法和溶胶-凝胶法制得对环境友好的疏水性蒙脱石磁性复合材料，增强对双酚 A 的有效吸引和快速隔离，达到对微量双酚 A 的富集[13]。分别制备两种新型双子吡啶表面活性剂改性蒙脱石：1，1′-双十二烷基-4，4-丙撑联吡啶溴代盐改性蒙脱石和 1，1′-双十六烷基-4，4-丙撑联吡啶溴代盐改性蒙脱石，对双酚 A 的最大吸附量分别为 222.2 和 208.3mg/g，改性蒙脱石的疏水性和与双酚 A 间的 π-π 相互作用得到提升，吸附能力显著增强[14]，但改性过程增加了实验成本。坡缕石-蒙脱石混合物廉价、丰富，具有扩展层结构，表面吸附位点丰富；机械处理制备 0.3～0.6、1.7～2.0 和≈2.8nm 三种尺寸的颗粒坡缕石-蒙脱石混合物，对双酚 A 的吸附量分别为 77.3、56.8 和 41.0mg/kg，吸附过程几乎不受溶液 pH 和离子强度的影响。所以，小尺寸、中等尺寸的坡缕石-蒙脱石混合物可作为双酚 A 的潜在吸附材料，且高温下孔道可折叠使其便于回收[15]。

1.2 碳材料类吸附材料

碳材料包括活性炭、碳纳米管和石墨烯等物质，具有较大的比表面积和孔状结构，热稳定性和化学稳定性强，表面易于改性，可用于对弱极性双酚 A 的吸附。

1.2.1 活性炭

活性炭价格低廉，对双酚 A 吸附效果较好，通过化学和物理改性可增强其吸附特性，是应用最广泛的吸附剂之一。用化学氧化热处理法和表面接枝法处理，引入温敏性聚（*N*-异丙基丙烯酰胺），制得可自絮凝化疏水粉末活性炭，改性后的活性炭比表面积增大到 1184m^2/g，促进了对双酚 A 的吸附，最大吸附量为 156mg/g[16]。用 N_2 脱气处理、酸处理和碱处理三种方法处理尺寸在 420～600μm 之间的特种煤基和木基颗粒活性炭。研究发现，酸处理制备的煤基和木基活性炭对双酚 A 吸附性能最佳，吸附量分别达 346.42 和 338.55mg/g，N_2 处理的木基活性炭可抑制双酚 A 的低聚，有利于吸附过程进行[17]。

1.2.2 碳纳米管

碳纳米管具有吸附活性强、疏水性表面大的特点，吸附平衡时间比活性炭短，对双酚 A 具有更好的吸附特性。研究单壁碳纳米管和多壁碳纳米管对双酚 A 的吸附特性发现，碱性环境有利于碳纳米管对双酚 A 的吸附，最大吸附量分别为 71 和 111mg/g[18]，并且多壁碳纳米管吸附特性较好，但溶液中碳纳米管分离困难，易造成二次污染。用超声接枝和原位包覆法制得藻酸盐-聚砜微球砜混合物，混合物的机械延展性增强，避免了多壁碳纳米管脱落危害有机生物体；由于多壁碳纳米管分散性限制，当混合物中多壁碳纳米管占 22%（wt，质量分数，下同）时，对双酚 A 的去除率最大；混合物微球用量为 4g/L 时，最大吸附双酚 A 量为 24.69mg/g[19]。在多壁碳纳米管中引入金属锑，增强对双酚 A 的协同吸附，pH＝7 时吸附率最大为 95%[20]。以 $FeCl_3$ 和自组装的胶体聚合物纳米片作为前体，通过低成本一锅法合成类竹碳纳米管，在吸附和催化的协同作用下，竹碳纳米管对双酚 A 的吸附量高达 328.6mg/g，80min 时双酚 A 几乎被完全去除，去除率高达 97%。竹碳纳米管对双酚 A 的催化降解再现性和重复性极好[21]。

1.2.3 石墨烯

石墨烯作为二维碳纳米材料，具有碳六元环结构，与双酚 A 间的 π-π 相互作用，有利于其作为吸附材料。通过改良 Hummers 法制备的氧化石墨烯对双酚 A 的吸附量较低，仅为 49.26mg/g，这可能是因为氧化石墨烯表面的含氧官能团减弱了 π-π 相互作用[22]。双酚 A 的去除率随着氧化石墨烯还原程度的增加而变大，原因在于还原过程使氧化石墨烯表面的含氧官能团减少，吸附剂与双酚 A 间的 π-π、p-p 和 n-p 相互作用增强，吸附力变大[23]。物理热剥离法得到的石墨烯吸附选择性是肼化学还原法得到的石墨烯的 2.5 倍，其对双酚 A 的最大吸附量为 96.2mg/g[24]。另外，肼化学还原法制备石墨烯过程中引入了肼，易对环境造成二次危害。化学共沉淀法磁化制得磁性石墨烯，便于吸附完成后对石墨烯的分离[25]，避免了二次污染。

1.3 高分子类吸附材料

高分子类吸附材料包括聚醚砜、树脂、纳米纤维、壳聚糖、聚苯胺等，具有比表面积大、结构稳定，对双酚 A 等有机污染物富集能力强等优点，但制备过程复杂。用干喷湿法纺纱技术将 SiO_2 接枝到薄膜上，制备具有丰富含氧基团的聚醚砜/SiO_2 复合膜，对双酚 A 的去除效果显著，可达 88%[26]。对静电纺丝聚丙烯腈聚合物溶液分别进行热稳定化、碳化、活化处理制备得到不同比表面积和不同孔径分布的静电纺丝碳纳米纤维，吸附量可达 4.82mmol/g；其中，热稳定化对静电纺丝碳纳米纤维结构的影响最大[27]。用化学、物理方法和电子喷雾技术制得

聚醚砜/聚醚砜苯乙烷微球,对双酚 A 的吸附量可通过增加微球中聚醚砜苯乙烷含量来增强[28]。

1.4　生活及工农业废弃物衍生吸附材料

由于废弃物衍生吸附材料价格低廉、易获取、吸附条件容易设计和控制,因此废弃物衍生材料可作为处理溶液中双酚 A 的理想替代吸附剂。马铃薯皮分别经 H_3PO_4、KOH 和 $ZnCl_2$ 活化后在 3 种炭化温度(400、600 和 800℃)下炭化。研究结果发现:用 H_3PO_4 活化后在 400℃下炭化制备的生物活性炭吸附特性较佳,对双酚 A 的吸附量可达 454.62mg/g[29]。用酸碱处理废弃虾蟹壳,提取出的甲壳素经脱乙酰化后制得壳聚糖对双酚 A 的最大吸附量可达 34.48mg/g[30]。用浓硫酸对废弃的椰壳纤维、椰子壳和榴莲皮进行改性处理,吸附结果表明:椰壳纤维素表面丰富的羟基、羰基,能与双酚 A 进行有效结合;对双酚 A 的吸附量和去除率分别为 4.308mg/g 和 72%,优于其他两种材料[31]。比较从制糖厂收集的处理后的稻壳灰和颗粒活性炭对双酚 A 的吸附效果:稻壳灰和颗粒活性炭的吸附率分别为 73.2%和 94%,颗粒活性炭对双酚 A 的吸附要优于稻壳灰,但稻壳灰价格低廉、来源丰富,可作为双酚 A 的吸附剂[32]。由橄榄油厂废料中制备较高比表面积、表面微孔高度非均匀分布的活性炭,研究表明:Cr(Ⅲ)和双酚 A 组成的二元系统,提高了吸附有效扩散系数,促进了活性炭对两种组分各自的去除效率[33]。

1.5　磁性吸附材料

磁性吸附材料制备复杂,但其具有特定性能,选择吸附强,易于回收且对环境友好。通过溶剂热法制备了 Fe_3O_4 纳米微球后在其表面原位组装合成聚苯胺,得到核壳磁性纳米复合微球 Fe_3O_4/聚苯胺,与双酚 A 存在 π-π 相互作用和静电相互作用,最大吸附量可达 23.0947mg/g[34]。利用共浸渍法和碳热还原法制备了掺杂磁性有序介孔碳(OMC)的纳米铁颗粒复合材料 Fe/OMC,该复合材料结构高度有序、比表面积大、磁性能优异,对双酚 A 的最大吸附量达 311mg/g,可归结为双酚 A 与 Fe/OMC 之间的氢键作用、π-π 相互作用以及纳米零价铁参与的氧化还原反应[35]。采用共沉淀法合成氧化铁纳米晶,利用超声波将氨丙基功能化的 SiO_2 修饰到氧化铁晶体表面,制备氨丙基功能化超顺磁性氧化铁/二氧化铁纳米晶材料:该材料由于修饰了 SiO_2,避免了磁性氧化铁的堆积,抑制了纳米晶的团聚,增大了比表面积,增强了与双酚 A 的结合能力和对其吸附的特性[36]。先用 NaOH 对腐殖酸预处理,再将纳米颗粒与腐殖酸以一定顺序吸附,制得尺寸为 0.15mm、不同腐殖酸比率的氧化铁-腐殖酸纳米复合体,结果表明,双酚 A 的蝴蝶结构可能有助于提高吸附效率[37]。

1.6　分子印迹聚合物吸附材料

分子印迹聚合物具有高度识别及选择吸附强的特点。以水溶性 2-丙烯酰氨基-2-甲基丙磺酸为单体、乙二醇二甲基丙烯酸酯为交联剂,通过可逆加成-断裂链转移聚合反应在碳微球上合成分子印迹聚合物,其表面疏水性得到改善,增强了对双酚 A 的吸附选择性,且分散性和重复使用性较好[38]。通过可逆加成-断裂链转移聚合制备了温磁性双重分子印迹聚合物,最大吸附率和去除率的最佳温度分别为 35 和 45℃[39]。以多孔氧化石墨烯为载体,双酚 A 为模板分子,水溶性 2-丙烯酰氨基-2-甲基丙磺酸(AMPs)和苯乙烯(St)为双功能单体,采用热聚合方法制备双功能单体协同表面分子印迹聚合物,由于 AMPs 与 St 的协同作用,其对双酚 A 的选择性吸附性能显著提高,即使在复杂的水系统中,对双酚 A 也有极好的吸附效果[40]。以酸化的天然坡缕石为载体,双酚 A 为模板分子,4-乙烯基吡啶为功能单体,加入交联剂、表面处理剂和引发剂,制备双酚 A 表面分子印迹聚合物,对双酚 A 的高亲和力、吸附选择性都高于普通分子印迹聚合物,且具有稳定的再生性能和高重复使用性,对双酚 A 的竞争吸附与特异识别明显增强[41]。

2　结论与展望

去除水中双酚 A 的吸附材料可分为矿物类、碳材料、高分子类、生活及工农业废弃物、磁性材料和分子印迹聚合物几种。吸附剂的功效主要取决于它们的特性和基质的特性。溶液 pH、初始双酚 A 浓度和吸附剂用量等也可以显着影响整体吸附过程。与未改性材料相比,化学改性通常可以提高吸附剂的吸附能力,但在改性步骤中使用化学品可能导致二次污染(改性中所用化学品的浸出问题)。此外,使用化学品进行改性也会增加处理成本。由于缺少动态吸附规模和中试规模吸附研究,因此很难预测这些吸附材料在真实环境下对双酚 A 的吸附潜力。由于多数研究缺乏对吸附材料再生成本的考察,因此,为了使吸附更加经济可行,在今后去除水中双酚 A 的吸附材料的研究中,应着眼于制备环境友好型吸附剂,增加对吸附剂再生成本的考察并扩大吸附

实验规模，推动吸附剂的实际应用。

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收稿日期:2017-04-23

(上接第 232 页)

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收稿日期:2017-09-12

修稿日期:2018-05-05