曲琛,日本京都大学能源科学研究科特定助教,日本能源学会、日本木材学会会员,《能源环境保护》青年编委。主要从事生物质的能源转化、生物质的化学成分表征、MOF 的催化剂及其环境应用等相关的研究工作。获得日本学术振兴会(JSPS)科学研究助成事业科研费等多项科研费资助。在 *ChemSusChem*、*Journal of Agriculture Food Chemistry*、*ACS Sustainable Chemistry & Engineering* 等高水平期刊发表学术论文多篇(他引达数百次)。

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金属-有机框架材料在废水脱色处理中的应用进展

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摘要:合成染料的高毒性、难降解性等引发的环境问题受到广泛关注,因此开发新型废水处理脱色剂及高效脱色工艺对染料进行无害化处理是染料脱色领域的研究重点。金属-有机框架材料(Metal-Organic Frameworks, MOFs)是金属与有机配体通过配位键自组装而成的杂化晶态多孔材料,具有高孔隙、大比表面积、丰富的活性位点等结构优势,成为染料脱色研究的热点材料。本文根据废水中的染料脱色工艺分别综述了近年来 MOFs 作为吸附剂进行吸附脱色,MOFs 作为漆酶载体进行生物降解脱色,MOFs 作为催化剂进行光催化脱色,MOFs 作为过硫酸盐活化剂进行高级氧化脱色,以及 MOFs 作为前驱物煅烧生成金属氧化物催化脱色等的研究进展。本文最后对 MOFs 在染料脱色领域的研究进行了总结,并对未来的研究方向进行了展望。

关键词:金属-有机框架材料;合成染料;脱色;光催化

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Advances in the application of metal-organic framework materials in the wastewater decolorization treatment

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Abstract: The increasing environmental problems caused by the high toxicity and recalcitrant properties of synthetic dyes have attracted significant attention. Therefore, the development of new wastewater treatment decolorizers and efficient decolorizing processes for the harmless treatment of dyes is a key research focus in the field of decolorization. Metal-organic frameworks (MOFs) are hybrid crystalline porous materials formed through the self-assembly of metals and organic ligands via ligand bonding. They possess structural advantages such as high porosity, a large specific surface area, and abundant active sites, making them popular materials for research on dye decolorization. This paper re-

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views the advances in the use of MOFs as adsorbents for adsorption decolorization, MOFs as laccase carriers for biodegradation decolorization, MOFs as catalysts for photocatalytic decolorization, MOFs as peroxodisulfate activators for advanced oxidative oxidation decolorization, and as precursors for calcination to form metal oxide catalytic decolorization. These topics are discussed with respect to the decolorization processes for wastewater treatment. Finally, this paper summarizes the research progress on MOFs in the field of dye decolorization and discusses future research directions.

Keywords: Metal-organic frameworks; Synthetic dyes; Decolorization; Photocatalytic

0　引　　言

合成染料因其成本低廉、色彩多样、着色牢固等优点被广泛应用于纺织、印刷、造纸、皮革等领域(图 1),由此带来的环境问题也日渐突出。据统计每年超过 28 000 t 的合成染料未经利用直接排放到自然界中,造其中偶氮类染料占比 50%以上,造成严重的环境问题[1-2]。研究发现偶氮类染料在特定条件下分解产生的芳香胺,经活化作用可改变人体的 DNA 结构引起病变和诱发癌症[3]。此外,大多合成染料具有高毒性、难降解性,因此排放前需无害化处理。目前工业上染料脱色工艺主要有吸附法、絮凝法、氧化法、生物法等,可有效降低染料浓度,减轻染料对环境的危害[4-6]。然而上述方法也存在一定的局限,比如吸附法中吸附剂难以回收利用,絮凝法产生的泥渣量多且脱水困难,氧化法电耗高等,因此新型脱色剂以及绿色高效脱色工艺的设计与开发仍是今后染料脱色领域的研究热点。

图 1　合成染料的应用领域

Fig. 1　Applications on synthetic dyes

金属-有机框架材料(Metal-Organic Frameworks,MOFs)是有机配体与金属离子或团簇通过配位键自组装而成的一种杂化晶态多孔材料,具有高孔隙率、大比表面积、孔径可调及可裁剪性等优势(图 2),已成为现代化学和材料领域的一大研究热点[7-8]。近年来,MOFs 材料在染料脱色领域的研究也备受关注。MOFs 既可作为优良吸附剂用于染料的脱除[9-10],同时还可用作漆酶等染料降解催化剂的载体,实现催化剂的重复利用[11-12]。此外,MOFs 本身也可作为光催化剂直接参与染料的降解[13-14]。因此,MOFs 材料在染

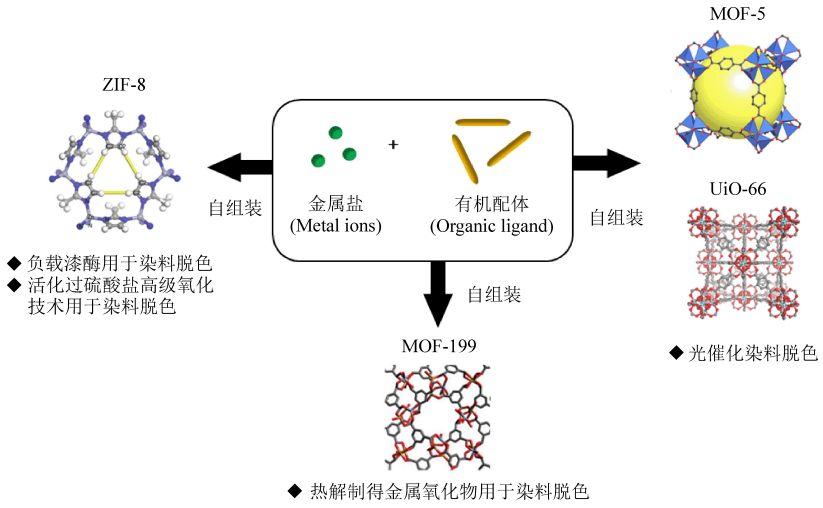

图 2　金属-有机框架材料制备示意图

Fig. 2　The illustration of various MOFs preparation

料脱色方面具有广阔的应用前景。本文根据脱色工艺分别综述了近年来 MOFs 在染料脱色领域的研究进展,最后对未来 MOFs 用于染料脱色的研究方向进行了展望。

1 MOFs 对染料的吸附研究

MOFs 可调的孔道尺寸、超高的比表面积、以及可修饰的表面性能,是染料脱除的优良吸附剂。目前 MOFs 对染料的吸附研究主要集中在吸附性能的改进及吸附机理研究。鉴于双金属 Co/Zn-MOF-5 的光催化活性优于 MOF-5[15], SONI 等[16]制备了 Co 掺杂的 Fe-MOF 对甲基蓝的吸附量可由 8.56 mg/g 增大到 23.92 mg/g。YANG 等[17]制得的 Ce(Ⅲ)掺杂 UiO-66 对甲基蓝、甲基橙和刚果红的吸附量较 UiO-66 分别高出 490%、270%和 70%。Ce 掺杂 UiO-67 对罗丹明 B(754.4 mg/g)和甲基橙(589.2 mg/g)的吸附量,远高于 UiO-67(罗丹明 B 41.3 mg/g 和甲基橙 357.3 mg/g)[18]。上述文献中的双金属 MOFs 均以传统 MOFs 为母体,在制备过程中添加一定比例新的金属盐自组装而成,由于引入了新的金属结点,双金属 MOFs 与染料之间静电相互作用增强,进而吸附性能力也随之提高。近年来,绿色环保生物基 MOFs 的合成逐渐成为研究热点,张华等[19]将乙二胺中的氨基基团引入到 MOF-5 中,制得的 EDA/MOF-5 同时具有了物理吸附性能和化学吸附性能,该功能化 MOFs 对刚果红的吸附量高达 78.36 mg/g,较 MOF-5 提高了 13.19 mg/g。IBRAHIM 等[20]引入胺基制得 UiO-66-NH_2 可增强 MOFs 与染料的静电相互作用,最高吸附 1 275 mg/g 甲基蓝和 909 mg/g 甲基橙。SALAMA 等[21]在 MOF 的制备过程中添加了环境友好的腺嘌呤,不仅能吸附阴离子型直接红 81 和阳离子型甲基蓝,还可多次重复使用。

MOFs 与染料之间的等温吸附曲线一般采用 Langmuir 模型(式 1)和 Freundlich 模型(式 2)对实验数据进行拟合。其中 Langmuir 模型是基于 MOFs 表面的吸附能均匀分布的单分子吸附[16,21]。Freundlich 模型则是建立在染料分子与 MOFs 表面存在相互吸引作用基础上,随染料浓度的增加吸附量呈指数增长[19]。

$$\frac{c_e}{q_e}=\frac{c_e}{q_m}+\frac{1}{bq_m} \tag{1}$$

$$\ln q_e=\ln k+\frac{1}{n}\ln c_e \tag{2}$$

其中,c_e和 q_e分别是吸附平衡时染料的浓度,mg/L 和吸附量,mg/g;q_m是 Langmuir 吸附时的最大吸附量,mg/g;b 是与吸附能有关的 Langmuir 常数;k 和 n 是与吸附能和吸附强度有关的 Freundlich 常数。

MOFs 对染料的吸附动力学的研究通常采用准一级(式 3)和准二级动力学模型(式 4)与实验数据进行拟合,进而探究吸附机理[22]。文献中大多 MOFs 对染料的吸附符合准二级动力学模型,进一步说明 MOFs 与染料之间存在化学吸附,包括氢键、π 键等化学键作用。

$$\ln(q_e-q_t)=\ln q_e-k_1t \tag{3}$$

$$\frac{t}{q_t}=\frac{1}{k_2q_e^{\,2}}+\frac{t}{q_e} \tag{4}$$

其中,q_e表示平衡吸附量,mg/g;q_t表示时间为 t 时的吸附量,mg/g;k_1为准一级动力学速率常数,1/min;k_2为准二级动力学速率常数,g/(mg·min)。

2 MOFs 负载漆酶用于染料脱色研究

漆酶(Laccase)是一种含四个铜离子的多酚氧化酶(EC 1.10.3.2),可用于废水中合成染料的降解,因其反应条件温和、催化效率高、绿色环保成为染料脱色的研究热点[23]。然而在实际工业应用中,受生产环境、经济成本等因素的制约,对漆酶的稳定性、可回收性及循环使用性提出了较高的要求。目前最优的解决方法则是把漆酶负载到载体上制成固定化酶,以提高漆酶的稳定性及可回收性[24]。MOFs 规整的孔道结构、良好的生物相容性等结构特点成为漆酶的优良载体。通过物理吸附、共价键结合、戊二醛交联等固定化方式,漆酶可与 MOFs 牢固结合,制得的固定化漆酶稳定性显著提高,大多可在较宽的 pH 及温度范围保持较高的酶活性。同时经 MOFs 固定后,漆酶可长时间保存并具有较高的催化活性。此外固定化漆酶可通过磁分离或过滤等简单操作进行回收,并可多次循环使用从而降低了生产成本。表 1 对近年来 MOFs 用作漆酶载体的文献进行了汇总。

3 MOFs 光催化染料脱色研究

TiO_2是一种传统的光催化剂,催化机理如图 3 所示,受光子激发产生光生电子和空穴,迁移到催化剂表面的电子和空穴可分别与吸附物,发生还

表 1　MOFs 固定漆酶降解染料汇总

Table 1　Summarization of research on the degradation of dyes by MOF-immobilized laccase

MOFs 载体	染料	脱除率/%	循环使用次数/相对酶活性*	参考文献
Co-MOF	活性蓝 171	88(6 mg)	12/56.50%	[25]
	活性蓝 198	77(6 mg)		
Cu-MOF-NH_2	刚果红	95	6/84.63%	[26]
CoCu-MOF	刚果红	90(1 h pH=4)	6/75.00%	[27]
	刚果红	95(5 h pH=7)		
Fe_3O_4@ZIF-8	靛蓝	100	7/36.00%	[28]
HS NMIL88(Fe)	雷玛唑亮蓝 R	100	4/-	[29]
Fe_3O_4-NH_2@MIL-101(Cr)	活性黑 5	81	5/73.00%	[30]
	茜素红 S	100	5/92.00%	
CoCu-MOF-OH	刚果红	95	6/264.02%	[31]
Cu(PABA)	直接红 31	92	10/70.00%	[32]
Cu/H_3BTC MOF**	氨基黑 10B	90	10/60.00%	[33]

注：*相对酶活性是以固定化漆酶首次测定的酶活性为标准进行计算；**Cu/H_3BTC MOF 作为类似漆酶的催化剂对染料直接进行降解脱色

原和氧化反应。由于 TiO_2 光生空穴的电位(价带)为 3.1 eV,具有强氧化性可将染料分解成可生物降解的有机物,甚至能矿化为无害的 CO_2 和 H_2O。然而,TiO_2 的禁带宽度大(3.2 eV),需在紫外照射下才能实现电子跃迁,TiO_2 还存在电子和空穴高复合率,光催化效率低等缺点。因此开发利用可见光的窄禁带光催化材料是今后研究的热点[34]。

MOFs 可调的结构、丰富的活性位点等成为光催化反应的潜在材料,自从 MOF-5 首次作为半导体材料被报道具有光催化活性以来,越来越多的学者致力于 MOFs 光催化降解染料的研究[35]。MOFs 光催化反应机理与 TiO_2 类似,其中有机配体和/或金属簇均可吸收光子产生光生电子和空穴对。Zr 基 MOFs,尤其是 UiO-66 具有优异的水稳定性和热稳定性,目前文献报道较多,研究集中在有机

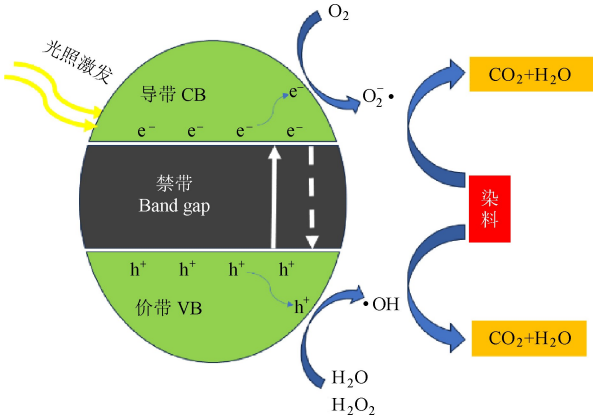

图 3　TiO_2 光催化反应机理示意图

Fig. 3　The photocatalysis mechanism of TiO_2

配体改性以提高光捕获率并降低电子空穴的复合率,以及金属掺杂降低 MOFs 禁带宽度从而能在可见光条件下实现染料的降解等。表 2 总结了近年来 MOFs 用于光催化降解染料的文献研究。

表 2　MOFs 用于光催化降解染料的汇总

Table 2　Summarization of research on the photocatalytic degradation of dyes by MOFs

MOFs 光催化剂	禁带宽/eV	光	染料	脱除率/%	参考文献
TiO_2/MIL-100(Fe)/复合锦纶	—	氙灯	活性黑 KN-B	95.20	[36]
$Cu_3(BTC)_2$	3.680	可见光	罗丹明 B	99.00	[37]
[Zn(L)(H_2O)]·H_2O (1)	3.282	氙灯	罗丹明 B	98.50	[38]
			甲基橙	83.80	
Bi-MMTAA	2.670	可见光	罗丹明 B	96.18	[39]
ZIF-8/$BiFeO_3$	2.040	可见光	罗丹明 B	99.42	[40]
		紫外光		100.00	
PDA@MOF	2.950	LED	甲基蓝	99.00	[41]

续表

MOFs 光催化剂	禁带宽/eV	光	染料	脱除率/%	参考文献
UTSA-38	2.850	紫外-可见光	甲基橙	100.00	[42]
NTU-9	1.720	可见光	罗丹明 B	100.00	[43]
			甲基蓝	100.00	
g-C_3N_4/UiO-66	3.790	可见光	罗丹明 B	~96.00*	[44]
UiO-66(1.25Ti)	3.200	模拟太阳光	甲基蓝	87.10	[45]
UiO-66-Br	3.690	氙灯	罗丹明 B	~70.00	[46]
UiO-66- NH_2	2.830			~0	
UiO-66-$(SH)_2$	2.750			~70.00	
UiO-66-$(OH)_2$	2.690			~0	
MOF-5@ rGO	-	太阳光	甲基蓝,甲基橙,罗丹明 B	>90.00	[47]
Zr-fum MOF	—	紫外光	甲基紫 2B	90.00	[48]
MOF-199	5.430	紫外光	碱性蓝 41	90.00	[49]
NNU-15(Ce)	~2.110	氙灯	罗丹明 B	99.00	[50]
NNU-15(Tb)	~2.200			90.00	
NNU-15(Dy)	~2.150			95.00	
HNU-29	1.920	氙灯	甲基蓝	92.00	[51]
$[Cu(4,4'-bipy)Cl]_n$	2.140	氙灯	甲基蓝	93.93	[52]
Fe-ZIF-8	2.200	太阳光	罗丹明 B	~100.00	[53]

注：* 该数据根据文献中罗丹明 B 催化反应曲线估算得到

4 其他染料脱色工艺研究

4.1 MOFs 活化过硫酸盐高级氧化技术用于染料脱色研究

基于过硫酸盐的高级氧化技术是以过硫酸盐为催化剂，通过特定的活化手段断裂 O—O 键产生硫酸根自由基(SO_4^- ·)，用于氧化和分解有机物的清洁技术，由于 SO_4^- · 较高的标准氧化电位(E^0 = 2.5~3.1 V)，较宽的 pH 使用范围和较长的半衰期(30~40 μs)等在染料脱色领域具有较强的应用前景[54]。MOFs 特有的结构可用作过硫酸盐的活化剂，促使过硫酸盐生成 SO_4^- · 降解染料。XIAO 等[55]采用 MIL-101(Fe)可快速活化过一硫酸盐(PMS)用于降解甲基蓝。TAN 等[56]制备了钴掺杂的 MOFs 可活化 PMS 降解罗丹明 B。研究发现，相比单金属 MOFs，双金属 MOFs 具有更高的催化活性，可快速活化 PMS 产生 SO_4^- ·[57]。由于制备的 MOFs 属于纳米粉状颗粒难以回收，ZHU 等[58]将 ZIF-8 固定在纳米纤维素膜(CNFs)上，不仅具有较高的 PMS 催化活性，同时还可通过简单的真空过滤对 ZIF-8/CNFs 进行回收再利用。LI 等[59]制备了磁性 Fe_3O_4/CoNi-MOF 作为 PMS 的活性剂，可利用材料的磁性进行分离回收。

4.2 MOFs 热解制得金属氧化物用于染料脱色的研究

MOFs 可调的孔道结构和可设计的金属与有机配体的组成，成为制备金属氧化物的优良前驱物。通过热解或煅烧 MOFs 可得到结构稳定的多孔金属氧化物，用作染料脱色的催化剂[60]。MINH 等[61]在 500 ℃下煅烧 Zn/Cu-BTC 制得 ZnO/CuO，该复合氧化物呈多孔八面体，比表面积高达 32.5 m^2/g。ZnO/CuO 的光催化活性高于 ZnO 和 CuO，在可见光照射下将甲基蓝完全分解。GUPTA 等[62]采用不同温度煅烧 MOF-199，其中 280 ℃时制得的 CuO-280 首先可用作 H_2S 吸附剂，在吸附能力被耗尽后，重新用于光催化反应时甲基蓝的脱除率可高达 89.0%。YANG 等[63]以 PB NCs 为前驱物，采用分段热解法制得 Fe/N 掺杂的碳磁性纳米管(Fe/N-C MNCs)，在 H_2O_2存在下对阳离子染料具有较高的催化活性，其反应机理是 Fe/N-C MNCs 活化 H_2O_2产生了强氧化性的单线态氧($^1O_2$)，进而可将染料氧化分解。

4.3 MOFs 催化还原染料脱色的研究

合成染料在溶液中被氧化或还原成低毒的小分子有机物，再进一步降解成水或二氧化碳，是比较快速有效的脱色方法[64]。文献中大多采用纳米贵金属(Au、Ag、Pt、Pd 等)作催化剂对废水中的

有机染料进行还原处理[65]。鉴于贵金属催化剂价格昂贵,LIN 等[66]以价格相对低廉的 Cu 为还原剂,制得泡沫型 MOF(HKUST-1 foam)兼具泡沫大孔性能及 MOF 微孔特性,在 $NaBH_4$存在条件下,能将甲基蓝完全分解至无色,MOFs 催化还原工艺为染料脱色提供了一种新思路。

5　总结与展望

设计新型高效染料脱色剂及脱色工艺是当前染料处理的研究重点。基于 MOFs 可功能化修饰界面、高比表面积、丰富的活性位点等优势在染料脱色领域具有广阔的应用前景。然而 MOFs 作为吸附剂对吸附染料的回收利用、MOFs 作为漆酶固定化载体的活性回收率等研究还十分有限。因此,在今后的研究中可考虑:(1)MOFs 对各种染料的无差别吸附及染料的回收;(2)设计生物相容性良好的 MOFs 用于漆酶的固定化载体;(3)MOFs 用作光催化剂时的可回收性及循环使用性;(4)通过控制 MOFs 热解条件获得高染料催化活性的金属氧化物。

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