DOI:10.7524/j.issn.0254-6108.2017.05.2016102507
韩春霞, 塔娜, 李城镐.染料降解产物鉴定方法及降解机理研究进展[J].环境化学,2017,36(5):1156-1165.
HAN Chunxia, TA Na, LI Chenghao. Research progress on identification methods and degradation mechanism of dye degradation products[J]. Environmental Chemistry,2017,36(5):1156-1165.

染料降解产物鉴定方法及降解机理研究进展*

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摘 要 高级氧化法(Advanced oxidation processes,AOPs)广泛应用于印染废水处理工艺中,然而该过程中产生的部分降解产物被证明具有比母体化合物更强的毒性,可能具有三致作用.另外,由于染料降解产物的不确定性、低残留性及难捕获性增加了该领域的研究难度,使其成为环境化学以及染料科学研究热点.本文汇总了应用 AOPs 降解染料的近期文献,并归纳了 GC-MS、LC-MS 等染料降解产物的重要分析和鉴定方法,同时整理和探讨了典型染料的降解途径作用机理以及可能生成的产物,并对染料降解产物鉴定方法及降解机理深入研究提出了建议.

关键词 染料, AOPs, 降解产物, 鉴定方法, 降解机理.

Research progress on identification methods and degradation mechanism of dye degradation products

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Abstract: Advanced oxidation processes (AOPs) are commonly applied for dyes degradation. However, some transformation products from the degradation processes have been proved to possess higher toxicity than the parent compounds, which have mutagenesis, carcinogenesis and teratogenesis effects. In addition, the uncertainty, low residual concentration and unavailability in capturing of dye degradation products have increased the difficulties of this research filed, which has became the hot topic in environmental chemistry and textile science. This paper summarized the recent research in the application of AOPs for dye degradation and the analysis and identification methods (GC-MS and LC-MS) for degradation products. Furthermore, detailed degradation pathways, reaction mechanisms of AOPs and possible degradation products for the important dye were discussed as well. Finally, future research about identification methods and degradation mechanism of dyes were proposed.

Keywords: dye, AOPs, degradation product, identification method, degradation mechanism.

染料根据其化学结构可分为偶氮、蒽醌、靛族、硫化、酞菁、次甲基、芳甲烷、硝基和亚硝基染料等,广泛应用于食品、医药、化妆品及纺织印染等行业.我国是印染大国,全国染料废水排放量约为(400—500)×10^4 $m^3 \cdot d^{-1}$,

2016 年 10 月 25 日收稿(Received:October 25, 2016).

* 国家自然科学基金(21167012,21667022)资助.

Supported by the National Natural Science Foundation of China(21167012, 21667022).

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约占整个工业废水的 35%[1].染料废水具有组成成分稳定、色度高、有机物浓度高、难生物降解等特点,属于难治理废水之一[2].某些偶氮染料已被证实能够导致人类膀胱癌、脾脏瘤、肝癌和试验动物的核酸异常以及哺乳动物的染色体变异[3],甚至一些染料品种已被列为致癌性测试的优先化学物质[4].由于染料生产及纺织制造过程中,大量高色度、毒性强的染料排入水体中[5]对人体健康及水生环境造成极大威胁.现阶段,许多废水处理工艺不能达到完全矿化水平[6],以致染料降解产物直接排入水中,而部分降解产物被证明毒性比母体化合物更强[7].因此,在废水处理工艺的实际应用中,除了考察染料废水的脱色率、COD、BOD 及 SS 等外,研究降解产物及降解机理,是检验废水处理技术对染料降解活性及应用前景的基础[8].

高级氧化法(Advanced oxidation processes,AOPs)以 ·OH为主要氧化剂,无选择性地与目标有机物发生氧化降解反应[9-10].目前,不少学者对染料在 AOPs 降解体系中的脱色率及降解动力学展开了全面、深入的研究[11-12],而对降解产物的分析鉴定及毒性去除率方面的报道较少[13].另外,由于染料降解产物的复杂性和不确定性、残留浓度低和难以捕获性,并且解析结构的标准物质匮乏,加之检测到的物质从 IUPAC(国际纯粹与应用化学联合会)查询不到命名[14]等原因,分析鉴定染料降解产物已成为该领域的难点和热点[15].

本文汇总了应用 AOPs 降解染料的近期文献,并归纳了 GC-MS、LC-MS 等染料降解产物的重要分析和鉴定方法.同时整理和探讨了典型染料的降解途径作用机理以及可能生成的产物.最后,对染料降解产物鉴定方法及降解机理深入研究提出了建议,以期给相关领域的研究者提供参考借鉴.

1　降解产物鉴定方法(Identification methods for degradation products)

气相色谱-质谱联用法(GC-MS)及液相色谱-质谱联用法(LC-MS)广泛应用于染料降解中间产物的分离与鉴定[5].因为 GC-MS、LC-MS 能更好地满足染料降解过程中高灵敏度、表征结构等检测需求[16].

1.1　GC-MS 技术

1.1.1　GC-MS 技术

GC-MS 分析样品应是有机溶液,需对样品进行前处理,常用的有 SPE(固相萃取)、LLE(液液萃取)及蒸发等方法,如表 1 所示.谱库检索是定性分析最为广泛的辅助手段之一[8,16],通常 GC-MS 仪器的数据系统软件都配有不同的质谱数据库和谱库检索程序,较通用的如 NIST、Willey 等.然而,高极性、热不稳定、难挥发的大分子有机化合物难以采用 GC-MS 分析.

表 1　GC-MS 在鉴定染料降解产物中的应用

Table 1　Application of GC-MS in the identification of dye degradation products

染料名称 Dye	高级氧化法 AOPs	前处理方法 Sample preparation	检测方法 Identification methods	参考文献 References
姜黄素	$H_2O_2/UV/O_2$	蒸发	GC-MS	[14]
甲基橙	$Fe/H_2O_2/UV$	LLE	GC-MS	[17]
活性橙 16	UV	LLE	GC-MS	[18]
活性蓝 160	UV/ZnO	LLE	GC-MS	[19]
活性艳红 X-3B	Fenton	蒸发	GC-MS	[20]
重氮染料	Fe^{2+}/过硫酸铵/UV	无	GC-MS	[21]
活性橙 16	TiO_2/UV	SPE	GC-MS	[22]
酸性橙 7	电-Fenton	LLE	GC-MS	[23]
亚甲基蓝	声电氧化	无	GC-MS	[24]
甲基橙	O_3	LLE	GC-MS	[25]
活性艳蓝 KN-R	湿式 H_2O_2 氧化	LLE	GC-MS	[26]

1.1.2　衍生化 GC-MS 技术

直接用 GC-MS 分析极性较大物质,在色谱柱内容易产生吸附,从而使检出值比实际值偏低,灵敏度下降[27].AOPs 处理染料废水会生成极性较大的降解产物,所以 GC-MS 检测时,对于极性大、难挥发的样品需通过衍生化转化成极性较低、更易挥发且热稳定性好的衍生物[16].

目前,常用的衍生化方法主要有硅烷化衍生法和氯甲酸酯衍生法.硅烷化试剂与化合物反应主要通

过取代羟基、羧基、巯基、氨基及亚氨基的活泼氢而进行,生成硅醚或硅酯,如图 1 所示[28].由于 N-甲基-N-三甲硅基三氟乙酰胺(MSTFA)和 N-O-双(三甲硅基)三氟乙酰胺(BSTFA)离去基团稳定,副产物挥发性好,成为目前应用最广泛的硅烷化试剂[29].蔡品品等[30]通过研究表明,MSTFA 适合非极性氨基酸和长链脂肪酸的衍生,而 BSTFA 则适合衍生极性氨基酸和短链脂肪酸.Zhang 等[31]采用 BSTFA 硅烷化 4-硝基苯酚在 UV/H_2O_2体系中生成降解产物.

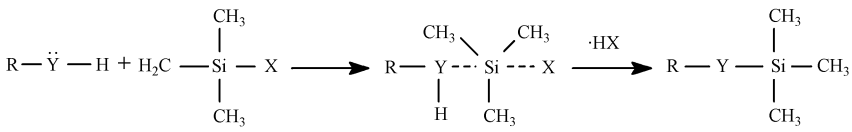

图 1 硅烷化衍生化反应

Fig.1 Derivatization by silylation using trimethylsilyl reagent

与硅烷化衍生相比,氯甲酸酯衍生法无需苛刻的无水条件,可与样品直接反应,反应活性高,且衍生时间短,室温下约 1 min 即可完成衍生反应[28,32].常用的烷基化试剂主要有氯甲酸甲酯(MCF)、氯甲酸乙酯(ECF)和氯甲酸丙酯(PCF),反应机理见图 2[33].Villasbôas 等[34]认为,较硅烷化试剂,氯甲酸酯衍生法更适用于氨基酸与有机酸的衍生.

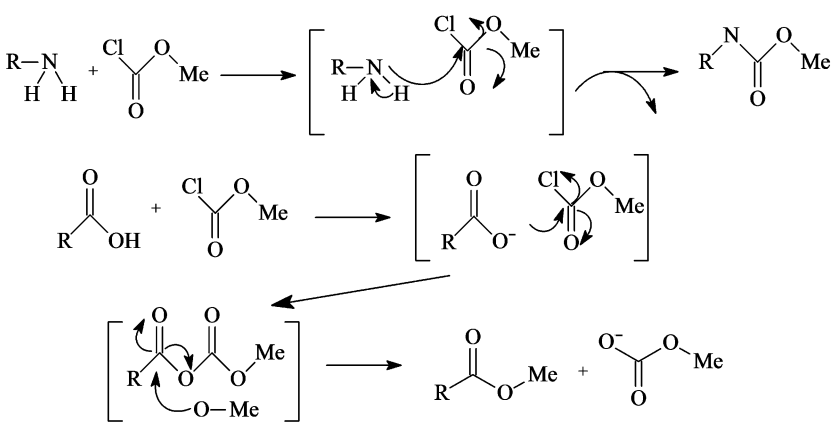

图 2 氯甲酸甲酯衍生胺类和羧酸类物质的反应

Fig.2 MCF derivatization of amine and carboxylic acid

1.2 LC-MS 技术

LC-MS 分析样品,水溶液可直接进样,只要样品中目标物浓度大于其检出限[8],无需进行前处理.并且,LC-MS 技术不受化合物沸点的限制,可对热稳定性差的试样进行分离、分析,其应用见表 2.Hisaindee[16]认为 LC-MS 检测极性大、分子量大的物质,无需要进行衍生处理,并提出 LC-MS 更适合检测 AOPs 处理的染料降解产物的观点.但是,其定性能力差,所以在实际应用中存在较大的限制.

表 2 LC-MS 在鉴定染料降解产物中的应用

Table 2 Application of LC-MS in the identification of dye degradation products

染料名称 Dye	高级氧化法 AOPs	前处理方法 Sample preparation	检测方法 Identification methods	参考文献 References
亚甲基蓝	类 Fenton	无	LC-MS	[6]
分散红 1	光-Fenton	SPE	LC-MS	[13]
亚甲基蓝	TiO_2/UV	无	GC-MS,LC-MS	[24]
酸性橙 7	TiO_2/UV	无	LC-MS	[35]
考马斯亮蓝	AOPs	无	LC-MS	[36]
罗丹明 B	UV-LED/TiO_2	无	LC-MS	[37]
1-重氮基-2-萘酚-4-磺酸	Fenton	SPE	LC-MS	[38]
罗丹明 B	光-Fenton	无	LC-MS	[39]

2　降解途径及机理(Degradation pathways and mechanism)

2.1　降解途径

Devi 等[21]在类-Fenton 体系 pH=3、各影响因素最佳条件下,用 GC-MS 测定两种重氮染料的降解产物,并基于检测到的物质结构,推测了两种染料可能降解途径,如图 3 和图 4 所示.该研究认为 BB(俾斯麦布朗,Bismark Brown)降解从偶氮基的氧化开始;而 BY(嫩黄,Brilliant Yellow)分子结构中烯基优先于偶氮基被氧化.Chen[22]认为 UV/TiO_2体系下 RO16(活性橙 16,Reactive Orange 16)降解主要通过以下几个步骤:(1)链接苯环与磺酸基的 C—S 键断裂;(2)苯环开环裂解;(3)C—C、C—N 键断裂;(4)偶氮基发生断裂.GC-MS 检测到乙酰胺为最终矿化产物,其他降解产物及途径如图 5 所示.Zhao 等[23]研究了电-Fenton体系下 AO7(酸性橙 7,Acid Orange 7)的降解途径,并采用 GC-MS 检测降解产物.AO7 的降解脱色从偶氮基的断裂开始,之后通过一系列降解步骤生成萘系化合物、苯系化合物及脂肪酸等,最终由机酸矿化为 CO_2、H_2O,主要降解过程如图 6 所示.Ma[6]、Houas[24]、马文娇[40]等采用 IC、GC-MS 及 LC-MS 等分析手段检测了 MB(亚甲基蓝,Methylene Blue)在不同降解体系中的降解产物,并推测了可能降解途径.根据以上文献的研究结果整理和归纳了 MB 可能降解途径,如图 7 所示.樊迪[25]利用紫外分光光度计、傅里叶红外光谱仪和 GC-MS 将 MO(甲基橙,Methyl Orange)的臭氧氧化过程中的产物进行了分析,得出 MO 分子逐渐被氧化成酚、醛、醌、羧酸和酰胺,最终被矿化成 H_2O 和 CO_2,并根据实验结果及相关理论提出了可能的降解机理,见图 8.

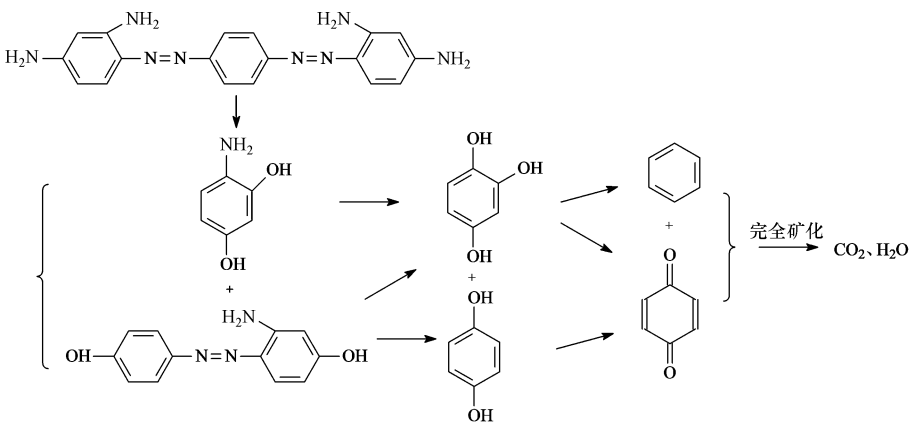

图 3　BB(俾斯麦布朗,Bismark Brown)降解途径[21]

Fig.3　Degradation pathway of Bismark Brown[21]

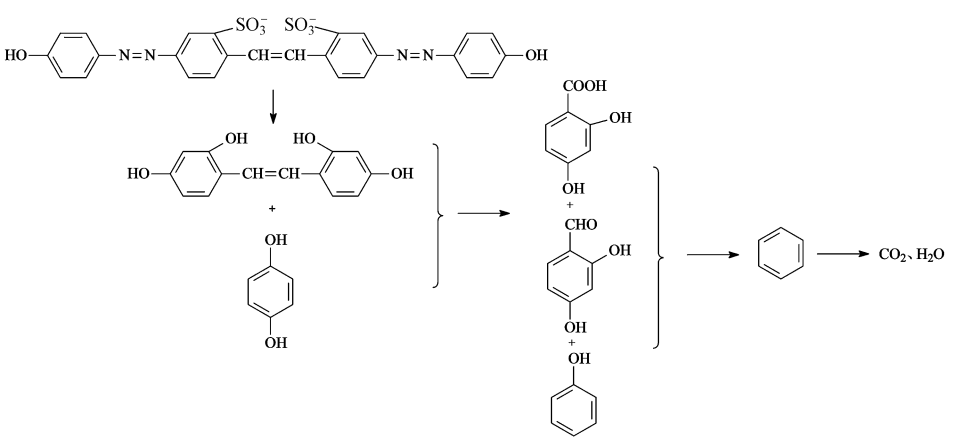

图 4　BY(嫩黄,Brilliant Yellow)降解途径[21]

Fig.4　Degradation pathway of Brilliant Yellow[21]

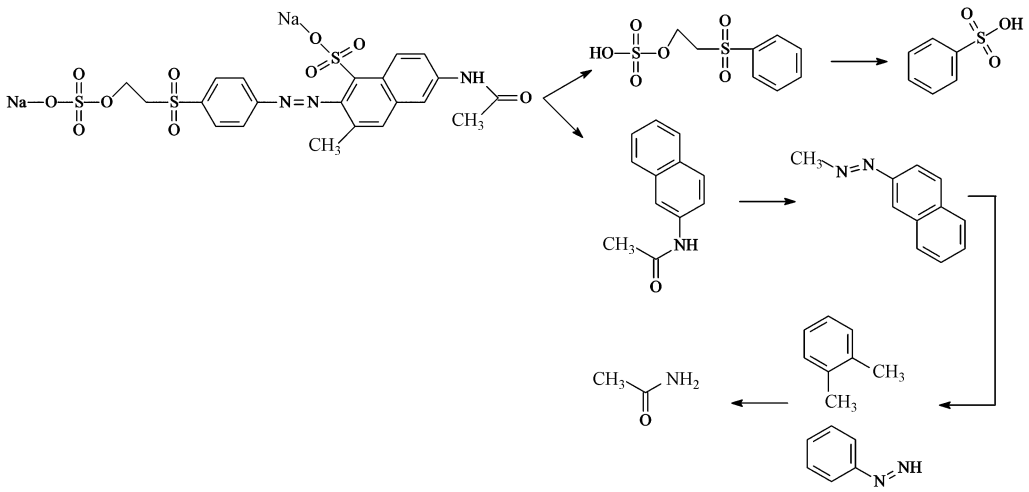

图 5 RO16(活性橙 16,Reactive Orange 16)降解途径[22]

Fig.5 Degradation pathway of Reactive Orange 16[22]

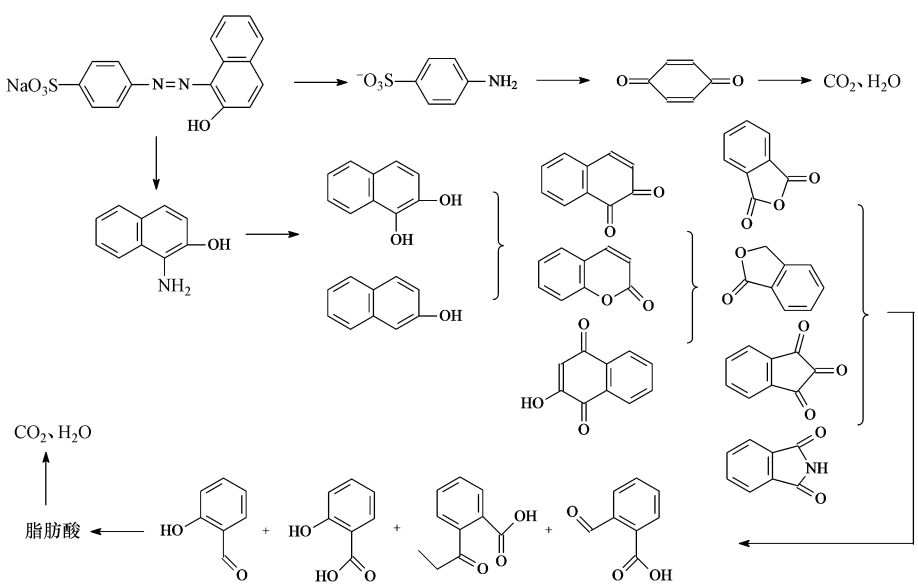

图 6 AO7(酸性橙 7,Acid Orange 7)降解途径[23]

Fig.6 Degradation pathway of Acid Orange 7[23]

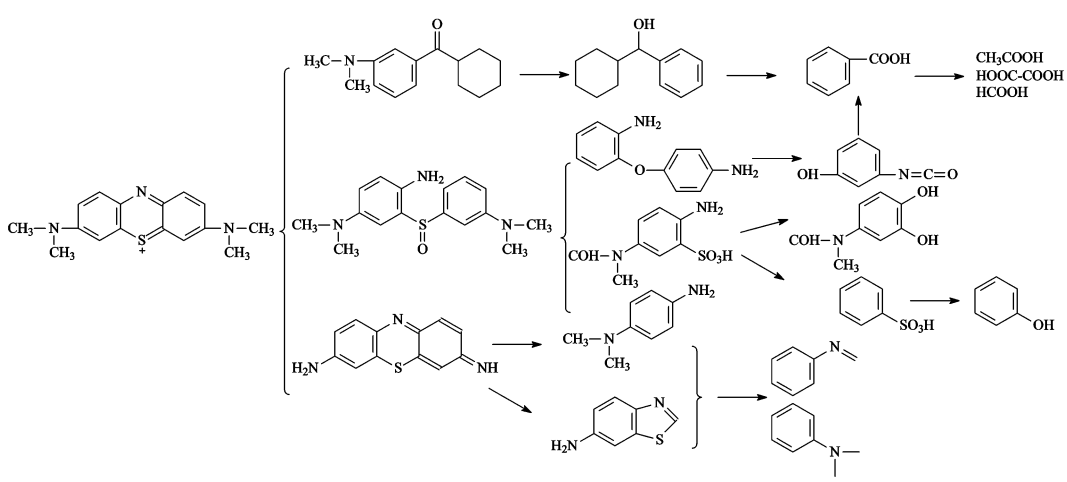

图 7 MB(亚甲基蓝,Methylene Blue)降解途径[6,24,40]

Fig.7 Degradation pathway of Methylene Blue[6,24,40]

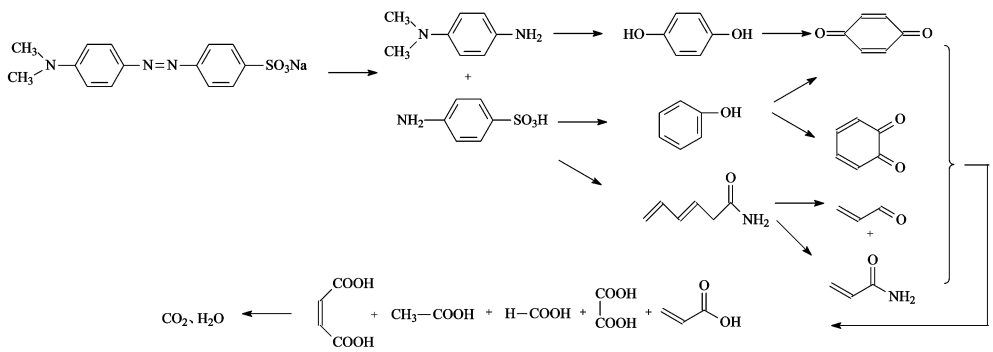

图 8　MO(甲基橙,Methyl Orange)降解途径[25]

Fig.8　Degradation pathway of Methyl Orange[25]

贺玲等[26]利用 GC-MS 鉴定 RBKN-R(活性艳蓝 KN-R,Reactive Blue KN-R)降解产物,其主要为丁二酸、已二酸、邻苯二甲酸等几种小分子有机酸,并使用三甲基氢氧化硫(TMSH)为衍生化试剂,进一步鉴定出邻苯二甲酸二甲酯,如图 9 所示.Zhang 等[31]采用 BSTFA 硅烷化 4-NP(4-硝基苯酚,4-nitrophenol)在 UV/H_2O_2体系中生成的降解产物,利用 GC-MS 测出了对苯二酚、1,2,4-三羟基苯、4-硝基邻苯三酚、4-硝基邻苯二酚,见图 10.

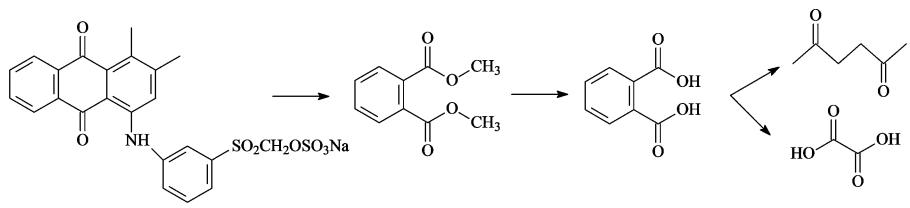

图 9　RBKN-R(活性艳蓝 KN-R,Reactive Blue KN-R)降解途径[26]

Fig.9　Degradation pathway of Reactive Blue KN-R[26]

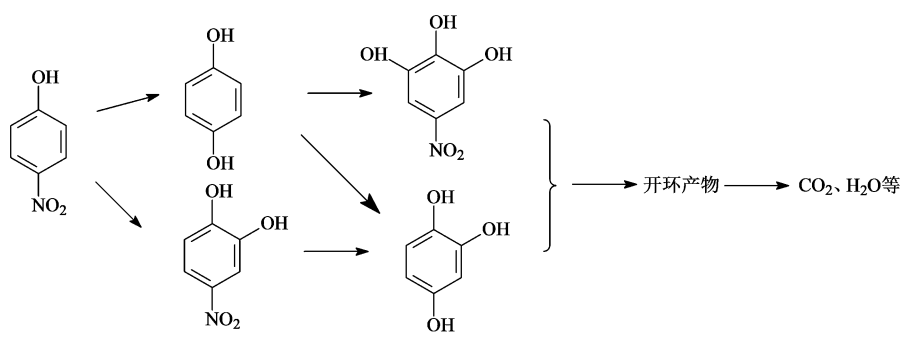

图 10　4-NP(4-硝基苯酚,4- nitrophenol)降解途径[31]

Fig.10　Degradation pathway of 4- nitrophenol[31]

Zhu 等[38]采用 Fenton 体系降解 1,2,4-acid(1-重氮基-2-萘酚-4-磺酸,1-diazo-2-naphthol-4-sulfonic acid),并利用 UPLC-(-ESI)-TOF-MS 测定降解产物,如图 11 所示.该研究认为 ·OH优先攻击偶氮基分解,1-重氮基-2-萘酚-4-磺酸为多种萘类物质,接着 ·OH进一步进攻链接偶氮基与萘环的 C—N 键,生成 N_2气体,并指出 4-羟基萘和 1-磺酸或 1,2-二氢萘的进一步氧化是可能导致降解产物含醌类结构的原因.张兴英等[39]通过 LC-MS 对 RhB(罗丹明 B,Rhodamine B)降解过程中主要产物定性检测,并推断出主要光催化降解途径.在该实验中,只检测到 RhB 的脱乙基产物,未检测到共轭生色团破坏的产物,因此推断 RhB 在类 Fenton 体系下光催化降解主要途径是逐步脱去乙基,降解途径如图 12 所示.Da silva 等[13]用 LC-MS 鉴定了光-Fenton 体系处理 DR1(分散红 1,Disperse Red 1)过程中生成的降解产物,发现多数产物都是通过 ·OH加成而得,偶氮基没被破坏.但是,也有一个产物由偶氮基被 ·OH进攻而得,降解途径见

图 13.

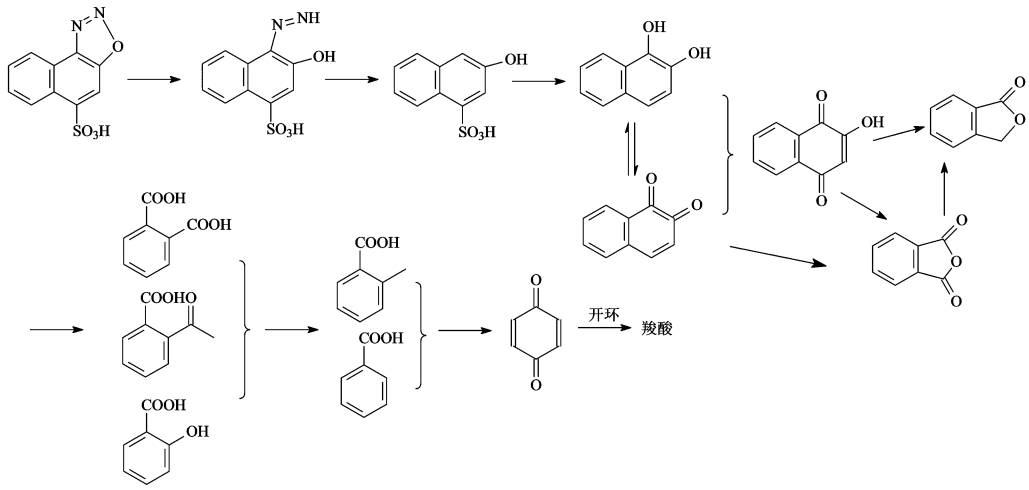

图 11 1,2,4-acid(1-重氮基-2-萘酚-4-磺酸,1-diazo-2-naphthol-4-sulfonic acid)降解途径[38]

Fig.11 Degradation pathway of 1-diazo-2-naphthol-4-sulfonic acid[38]

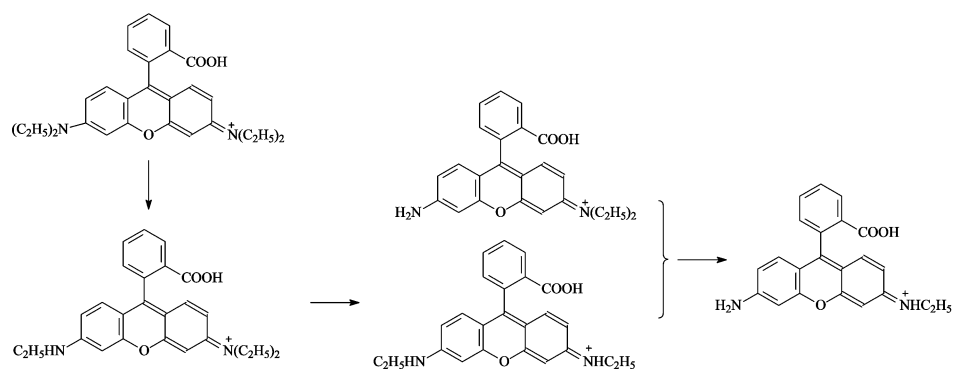

图 12 RhB(罗丹明 B,Rhodamine B)降解途径[39]

Fig.12 Degradation pathway of Rhodamine B[39]

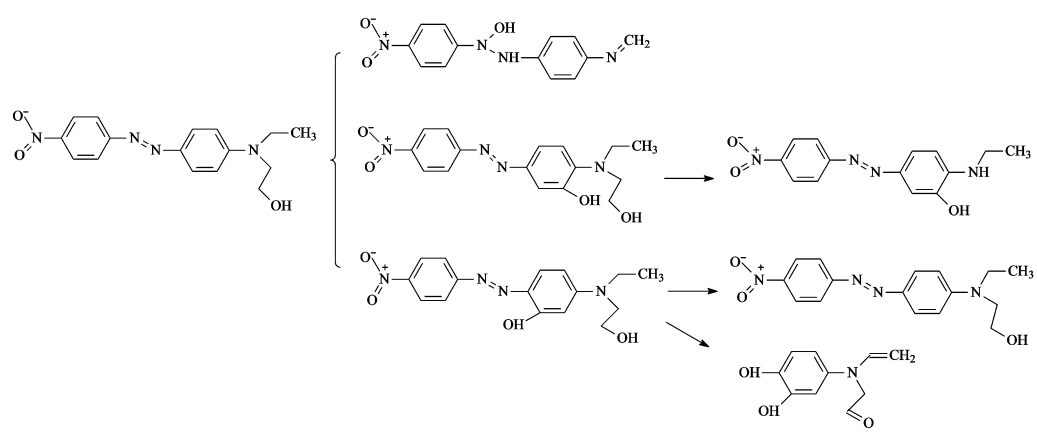

图 13 DR1(分散红 1,Disperse Red 1)降解途径[13]

Fig.13 Degradation pathway of Disperse Red 1[13]

2.2 降解机理

2.2.1 AOPs 作用机理

AOPs 中多数处理方法都借助 UV 或过氧化物,如 O_3/UV、O_3/UV/H_2O_2、UV-Fenton、UV/H_2O_2/草酸高铁铵法及非均相光催化等处理技术.在光化学反应里,染料分子吸收光量子有两种可能[41]:从基态转

化为激发态分子,而激发态的分子不稳定,容易被攻击和破坏;或激发态分子自身均裂为两个较小的分子或自由基.

另外,AOPs 法能产生大量氧化性极强的 ·OH和 O_2^- 等多种自由基,其中最主要的自由基为 ·OH,其有以下特点:(1)氧化能力极强,其氧化还原电位 E^0 为 2.80 V,仅次于氟单质(F_2)的氧化还原电位(2.87 V);(2)非常活泼(与大多数有机物反应速率常数在 10^6—10^{10} $mol^{-1}\cdot L\cdot S^{-1}$).其主要通过亲电加成、电子转移及脱氢反应[42],无选择性氧化降解大多数染料为水溶性小分子化合物、无机离子(NO_3^-、CO_3^{2-} 及 SO_4^{2-})或完全矿化为 CO_2和 H_2O[11].大量研究证明,AOPs 降解有机污染物,主要遵循 ·OH反应机理[9,11,43].

染料分子结构中主要发色基团有 N═N、C═C、N═O、NO_2、C═O 等,这些发色基团优先在光量子和 ·OH作用下受到攻击发生断裂,使染料分子开始脱色降解[44-45].其次, ·OH等由 AOPs 产生的自由基进一步进攻降解中间产物,形成多种复杂降解产物.结构中若有苯环或萘环, ·OH等进攻位点受分子结构的空间位阻效应影响[25,41],生成酚羟基化和多酚羟基化产物,形成开环产物,最终使染料矿化完全.

2.2.2　降解产物类型

AOPs 处理染料废水,其降解产物可归纳为以下几种类型:(1)去烷基产物:烷基取代的叔或季胺是染料常见的结构特征,文献报道的染料降解产物中脱烷基物质最为常见,说明脱烷基产物在染料降解中最容易生成.(2)羟基化或多羟基化产物:苯环上的侧基,如—SO_3H、—NH_2、—NO_3、卤素、烷基等基团被 ·OH取代或直接从苯环上断开,形成羟基化或多羟基化产物.(3)脱羧产物:降解过程中侧链上甲基和乙基等形成羧基化合物,其经光照后,通过能量转移和氧化脱去 CO_2,生成脱羧产物.(4)苯环开环产物:苯环形成多酚后,最终会开环,形成醋酸、草酸、蚁酸等小分子有机酸.(5)异构化产物:受空间位阻效应影响, ·OH进攻位点不同则生成结构异构化产物或在光照后部分产物会得到能量异构化.(6)一些无机离子诸如 NO_3^-、CO_3^{2-} 及 SO_4^{2-} 等.(7)最终完全矿化为 CO_2、H_2O 等.

3　结论与展望(Conclusion and prospect)

目前在 AOPs 处理染料废水过程中生成的降解产物的鉴定、降解途径及机理推测方面的研究取得了一定的成果,但由于降解产物的复杂性及检测方法的局限性,该领域的研究仍面临许多困难.(1)首先,虽然 GC-MS、LC-MS 鉴定方法较可靠和成熟,但鉴定分析中都存在无法克服的阻力.其原因为 GC-MS 样品前处理复杂,除需要结合固相萃取等前处理过程以外,GC-MS 法难以测定高极性、热不稳定、难挥发有机物以及大分子有机化合物,并且对于极性大的有机物需衍生化处理,这不仅增加了繁琐的步骤,亦加大了工作量;LC-MS 虽然能检测极性大、分子量大的物质,并且无需进行衍生处理,但是没有质谱数据库和谱库检索程序,因此也限制了 LC-MS 的应用.(2)其次,该过程中生成的降解产物极性变化大、成分复杂等特性,使富集浓缩过程以及检测难度增大,而且其较强的极性和吸附性能使之易在色谱柱上残留或致色谱柱流失,会造成色谱柱的污染.(3)降解产物途径与机理研究主要通过染料母体和测到的降解产物结构,依据理论推测出可能的降解途径和降解机理,对真正降解机理的研究和探讨还不够深入.因此,寻求和探索更简单、更科学的降解产物鉴定方法及更完整、全面地解释染料降解机理是推动该领域发展的重点所在.(4)AOPs 处理染料废水的降解产物毒理学研究及毒性去除方面的深入研究尤为重要.

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