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高级氧化技术去除水中碘代 X 射线造影剂研究进展*

向伟铭 杨绍贵** 孙敦宇 季秋忆 周文武 许晨敏 何欢 李时银

(南京师范大学环境学院, 南京, 210023)

摘要 碘代 X 射线造影剂在医学上的大量使用导致其在水环境中普遍存在, 对生态系统和人体健康构成巨大威胁. 传统的污水处理技术对碘代 X 射线造影剂去除效果不佳, 应用高级氧化技术去除水中碘代 X 射线造影剂成为研究热点. 本文系统分析了水环境中碘代 X 射线造影剂的理化性质、来源、危害及污染现状. 综述了声化学氧化、光催化、过硫酸盐活化、芬顿和电化学等 5 种高级氧化技术对碘代 X 射线造影剂的去除效果、机理及影响因素等, 并指出了各自应用优势和限制, 最后对高级氧化技术应用于碘代 X 射线造影剂的研究提出多种单一高级氧化技术协同降解的展望.

关键词 碘代 X 射线造影剂, 潜在毒性, 污染现状, 高级氧化技术, 协同降解.

Research progress of advanced oxidation technology to remove iodine X-ray contrast media in water

XIANG Weiming YANG Shaogui** SUN Dunyu JI Qiuyi ZHOU Wenwu
XU Chenmin HE Huan LI Shiyin

(School of Environment, Nanjing Normal University, Nanjing, 210023, China)

Abstract The extensive use of iodinated X-ray contrast media in medicine has led to their widespread presence in water environments, posing a huge threat to the ecosystem and human health. The traditional sewage treatment technology is not effective in removing iodine X-ray contrast agent. The application of advanced oxidation process to remove iodine X-ray contrast media in water has become the core of research. This paper systematically analyzed the physical and chemical properties, source hazards and pollution status of iodinated X-ray contrast media in water environment. The removal effect, mechanism and influencing factors of five advanced oxidation processes, including sonochemical oxidation, photocatalysis, persulfate activation, Fenton and electrochemistry, on iodinated X-ray contrast media were reviewed, and their application advantages and limitations have been pointed out, respectively. At last, it put forward the prospect of synergistic degradation, which was formed by multiple single advanced oxidation processes, for the application of advanced oxidation process on iodinated X-ray contrast media.

Keywords iodine X-ray contrast media, potential toxicity, pollution status, advanced oxidation technology, synergistic degradation.

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** 通信联系人 Corresponding author, Tel: 025-85891849, E-mail: yangsg@njnu.edu.cn

碘代 X 射线造影剂 (Iodinated X-ray contrast media, ICMs) 作为一类个人护理用品 (pharmaceutical and personal care products, PPCPs) 被大量使用, 引起人们的广泛关注. ICMs 是最常用的血管药物之一, 用于诊断人体结构并使得软组织、内脏和血管可视化. 碘原子的电子密度高, X 射线吸收效率高, 因此可以使被测器官与周围组织形成对比, 从而清晰成像^[1-2]. ICMs 高度稳定, 摄入后会在很短的时间内通过排泄进入公共排水系统^[3].

据报道, 全世界 2006 年生产 ICMs 总量就达到了 3500 t, 每位病人每次使用量约为 200 g^[4]. ICMs 通过医疗废水等排入环境中, 而由于其化学结构等原因, 传统污水净化工艺去除率极低, 因而在自然环境中分布广泛. 如今 ICMs 在全世界各地, 如德国^[3]、法国^[5]、美国^[6]、中国^[5] 等水体中均有检出, 且在环境中检测级别最高达到了 $\mu\text{g}\cdot\text{L}^{-1}$ ^[7]. ICMs 具有极性和持久性, 使其能够长期稳定存在于水生环境中, 并通过土壤渗透到地下水蓄水层中. ICMs 还显示出肾脏毒性, 影响生物体的甲状腺稳态^[8-10]. 除此以外, ICMs 可以在自然水环境中转化为有毒的消毒副产物^[11], 产生环境风险. 综上所述, ICMs 对生态系统存在潜在危险并对人体健康产生威胁^[2], 因此, 亟需对水环境中的 ICMs 进行有效去除.

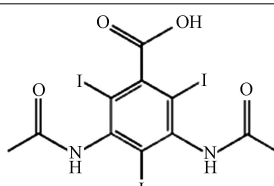
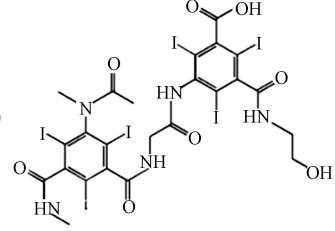
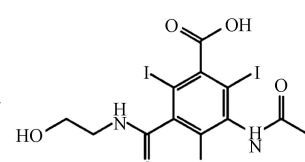
传统的污水处理工艺无法有效去除水中 ICMs, 而高级氧化技术可以有效去除水中 ICMs. 但目前国内外关于高级氧化技术应用于 ICMs 的去除的最新研究进展论述较少, 因此本文阐述了当前水环境中 ICMs 的污染状况, 综述了五种高级氧化技术去除 ICMs 的研究进展, 分析比较了各技术的优缺点, 并对今后高级氧化技术的研究方向和研究前景做出展望.

1 ICMs 的结构与性质 (The structure and properties of ICMs)

ICMs 是一类 2,4,6-三碘苯甲酸的派生物, 根据侧链基团结构的不同, 可以将其分为离子型化合物和非离子型化合物. 其中离子型 ICMs 一般含有游离的羧基, 如泛影酸、碘克沙酸、碘羟拉酸等, 而非离子型化合物的羧基被酰胺衍生物所取代, 如碘帕醇、碘美普尔、碘海醇、碘普罗胺等. 两类 ICMs 化学结构和理化性质如表 1 所示. ICMs 的沸点较高 (500—900 °C), 分子量较大 (600—1300), 具有强亲水性, 易溶于水进入生态系统中. 非离子型 ICMs 相对于离子型 ICMs 渗透性更低、毒副反应更小、生物安全性更大.

表 1 常见 ICMs 的物理化学性质

Table 1 The physical and chemical properties of common ICMs

碘代 X 射线造影剂 ICMs	CAS	结构式 Structural formula	相对分子质量 Relative molecular mass	熔点/°C Melting point	溶解度/(g·L ⁻¹) Solubility	沸点/°C Boiling point (760 mmHg)	类型 Type
泛影酸 Diatrizoate	50978-11-5		613.91	>300	20 °C 6×10^5	—	离子型
碘克沙酸	59017-64-0		1268.88	302	25 °C 3.27×10^{-8}	887.9	离子型
碘羟拉酸 Ioxithalamic Acid	28179-44-4		643.94	253—255	—	582.8	离子型

续表 1

碘代X射线 造影剂 ICMs	CAS	结构式 Structural formula	相对分子质量 Relative molecular mass	熔点/°C Melting point	溶解度/(g·L ⁻¹) Solubility	沸点/°C Boiling point (760 mmHg)	类型 Type
碘帕醇 Iopamidol	60166-93-0		777.08	—	—	785.3	非离子型
碘美普尔 Iomeprol	78649-41-9		777.09	263—265	—	813.2	非离子型
碘海醇 Iohexol	66108-95-0		821.14	254—256	20 °C 7.96×10 ⁻¹	891.5	非离子型
碘普罗胺 Iopromide	73334-07-3		791.11	—	—	840.9	非离子型

注: 数据来源(data source): <https://baike.molbase.cn/>; <http://msds.chemicalbook.com/>; <http://search.ichemistry.cn/>.

2 水环境中的 ICMs 来源及其消毒副产物危害 (Source and harm of ICMs disinfection by-products in water environment)

ICMs 在污水处理厂浓度具体情况如表 2 所示, 进出水浓度变化不大, 说明传统污水处理厂工艺对 ICMs 去除效率不高. 除此以外, 某些高级的污水处理技术中加入臭氧去除, 但是臭氧对 ICMs 的去除率范围为 35%—55%; 而对于离子型 ICMs 去除率更低, 去除率仅为 20%, 仅碘普罗米去除率较高, 可以被降解 60%—70%^[12-14]. 由于使用频率高、注射量大、生物降解性低以及污水处理厂的减排率低, ICMs 普遍存在于水生环境中, 在地表水^[13]、城市^[15]和医院废水^[5]、地下水^[16]或饮用水^[17]中检测限高达几十甚至几百 $\mu\text{g}\cdot\text{L}^{-1}$. 因此 ICMs 主要来源于城市污水处理厂无法完全有效处理的医疗废水.

表 2 污水处理厂进出水 ICMs 检出浓度

Table 2 Detected concentrations of ICMs in the influent and effluent water of sewage treatment plants

ICMs	进水含量/($\mu\text{g}\cdot\text{L}^{-1}$) Concentration at influent	出水含量/($\mu\text{g}\cdot\text{L}^{-1}$) Concentration at effluent	进出水浓度减少量/($\mu\text{g}\cdot\text{L}^{-1}$) Reduction of concentration	参考文献 Reference
碘帕醇	4.3	4.7	0	[18]
泛影酸	3.3	4.1	0.8	[18]
碘美普尔	1.6	1.3	0	[18]
碘海醇	0.55	0.74	0	[19]
碘普罗胺	0.1	0.025	0.075	[19]
碘羟拉酸	0.17	0.16	0.01	[4,18]
碘他拉酸	0.18	0.14	0.04	[4,18]

由于 ICMs 极易在环境中赋存, 因此它的毒性及毒理引起了人们广泛的关注^[2]. ICMs 虽然本身毒性不高, 但是极易与自然水体中的物质发生反应, 生成有毒的消毒副产物 (disinfection by-products, DBPs)^[8,20-21]. Wendel 等^[22] 发现了碘帕醇和水中的氯结合后会形成具有急性毒性的副产物, 且在中国仓鼠卵巢细胞中研究了氯化过程中含碘帕醇溶液的细胞毒性变化, 发现氯化过程可增强碘帕醇的细胞毒性. Matsushita 等^[23] 进一步通过具有代谢活化作用的 Ames 测试仪 T498 菌株以及活性-结构定量关系 (Quantitative Structure-activity Relationship, QSAR) 分析模型, 发现了碘帕醇和水中的氯结合可以形成过渡产物 (Transformation Products, TPs), 且其会诱发生物细胞突变. Hu 等^[24] 测量了在 pH=7 时, 碘海醇的氯化反应遵循第三级动力学, 最大表现速率常数为 $3.78 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$, 发现了溴可以抑制氯化过程中碘海醇的降解. 但是, 在存在溴化物的情况下, 氯化过程中碘海醇向有毒碘代 DBPs 的转化显著增加, 与氯化相比, 溴化导致更高毒性的碘代 DBPs 形成.

综上所述, 碘代 X 射线造影剂分布广泛, 环境内浓度相对较高, 虽然其本身物理化学性质稳定, 但是极易与自然环境中其他物质形成 DBPs, 并进一步形成剧毒的污染物. ICMs 降解过程产生的 DBPs 毒性具体情况如表 3 所示. 其中卤代乙腈类和卤代乙酰胺类的 DBPs 细胞毒性较高, 中国仓鼠卵巢细胞 (Chinese hamster ovary, CHO) 最低致死浓度和半致死浓度达到了 $10^{-7} \text{ mol} \cdot \text{L}^{-1}$, 最低达到了 10^{-8} . 除此以外, 溴代和碘代 DBPs 毒性一般比氯代 DBPs 要强.

表 3 常见 ICMs 降解过程 DBPs 的细胞毒性

Table 3 Cytotoxicity of DBPs in common degradation process of ICMs

消毒副产物类别 Disinfection byproducts category	消毒副产物 Disinfection byproducts	CHO 细胞最低致死浓度/ ($\text{mol} \cdot \text{L}^{-1}$) Lowest toxic concentration	CHO 细胞半致死浓度/ ($\text{mol} \cdot \text{L}^{-1}$) The $C_{1/2}$ value	参考文献 Reference
碘代三卤甲烷 Iodo-trihalomethanes	碘代二氯甲烷	—	4.0×10^{-3}	[8]
	碘代溴氯甲烷	—	2.4×10^{-3}	
	氯代碘甲烷	—	4.0×10^{-3}	
	三碘甲烷	—	4.0×10^{-3}	
卤代酸 Haloacids	碘乙酸	5.0×10^{-6}	3.0×10^{-6}	[8,25-26]
	溴碘乙酸	2.5×10^{-4}	9.0×10^{-4}	
	二溴乙酸	7.5×10^{-4}	—	
	氯乙酸	3.0×10^{-4}	—	
卤代乙腈 Haloacetonitriles	溴氯乙酸	3.0×10^{-3}	—	[27]
	碘乙腈	1.0×10^{-7}	3.3×10^{-6}	
	溴乙腈	1.0×10^{-6}	3.2×10^{-6}	
	二溴乙腈	1.0×10^{-6}	2.9×10^{-6}	
	溴氯乙腈	7.0×10^{-6}	8.5×10^{-6}	
卤代乙酰胺 Haloacetamides	二氯乙腈	1.0×10^{-5}	5.7×10^{-5}	[28]
	碘乙酰胺	5.0×10^{-7}	1.4×10^{-6}	
	二碘乙酰胺	2.5×10^{-8}	6.8×10^{-7}	
	溴乙酰胺	5×10^{-7}	1.9×10^{-6}	
	溴氯乙酰胺	1.0×10^{-6}	1.7×10^{-5}	
	氯乙酰胺	7.5×10^{-5}	1.5×10^{-4}	

3 水环境中 ICMs 的污染现状 (Pollution status of ICMs in water environment)

由于 ICMs 的理化稳定性、高度亲水性等, 在全球范围内均有检出, 其中城市污水处理厂进出水、河流地表水等浓度较高. Xu 等^[13] 测出太湖和黄浦江的总 ICMs 浓度范围分别为 $88.7-131 \text{ ng} \cdot \text{L}^{-1}$ 和 $102-252 \text{ ng} \cdot \text{L}^{-1}$. Ens 等^[29] 用仪器分析了泛影酸盐和碘帕醇在饮用水中的浓度, 分别为 $(28 \pm 20) \text{ ng} \cdot \text{L}^{-1}$ 和 $(19 \pm 9) \text{ ng} \cdot \text{L}^{-1}$. 由于 ICMs 的结构稳定, 它们无法在传统的污水处理厂中有效去除, 从而被排放到环境中. Kormos 等^[30] 在德国 Mainz 市政污水处理厂出水中, 检测出碘帕醇浓度为 $(1.87 \pm 0.52) \mu\text{g} \cdot \text{L}^{-1}$;

Echeverria 等^[31] 在西班牙 Tarragona 城镇污水处理厂进水检出碘普罗胺浓度为 6.8—8.9 $\mu\text{g}\cdot\text{L}^{-1}$, 出水检出其浓度为 6.7—7.1 $\mu\text{g}\cdot\text{L}^{-1}$. Kovalova 等^[32] 在比利时 Gent 医药废水中检出泛影酸盐浓度进水为 (814±28) $\mu\text{g}\cdot\text{L}^{-1}$, 出水为 (292±17) $\mu\text{g}\cdot\text{L}^{-1}$. 因此 ICMs 在传统的污水处理工艺下难以被去除, 从而排放到环境中.

表 4 所示可见在各国家各个地区均有分布. 医院原水 ICMs 检出浓度较高, 达到了 $\text{mg}\cdot\text{L}^{-1}$. 污水处理厂、水回收厂、地表河流也均有 ICMs 检出, 如德国莱茵河碘海醇检出浓度达到了 $\mu\text{g}\cdot\text{L}^{-1}$; 中国长兴岛污水处理厂、法国城市废水处理厂, 以及澳大利亚水回收厂进水泛影酸、碘海醇检出浓度都在 $\mu\text{g}\cdot\text{L}^{-1}$; 除此以外, 波罗的海也能检测出 ICMs.

表 4 不同国家水环境中 ICMs 浓度 ($\text{ng}\cdot\text{L}^{-1}$)

Table 4 Concentration of ICMs in the water environment of different countries ($\text{ng}\cdot\text{L}^{-1}$)

国家/地区 Country/Region	源水 Water source	碘帕醇 Iopamidol	碘海醇 Iohexol	泛影酸 Diatrizoic acid	碘普罗胺 Iopromide	参考文献 Reference
乌泽多姆	波罗的海	—	—	14—36	—	[33]
德国, 乌尔姆	多瑙河上游, 污水处理厂	40—470	40—125	40—190	40—125	[34]
德国, 哥廷根	莱茵河	685—885	1126—1302	—	238—298	[34]
西班牙, 巴塞罗那	略夫雷加特河	86—66.1	22.9—181	—	13.5—1813	[35]
西班牙	饮用水处理厂	—	0.5—5.0	—	0.4—1.0	[36]
法国	医院原水	—	1.91×10^6 — 3.81×10^6	—	—	[5]
法国	城市废水处理厂	500—6500	3310—8770	—	500—2360	[14]
澳大利亚, 珀斯	水回收厂进水	240—610	790—9200	980—2910	280—670	[37]
中国, 江苏	太湖	—	86.0—91.6	—	2.3—28	[13]
中国, 上海	黄浦江	1.0—90.7	73.6—100	—	7.1—51.4	[13]
中国, 长兴岛	自来水	11—13	23—25	—	5.1—6.3	[7]
中国, 长兴岛	饮用水厂进水	15.3—16.7	29—33	—	8.1—8.9	[7]
中国, 长兴岛	污水处理厂进水	8000—10000	2000—2400	—	125—1110	[7]

目前, 关于我国水环境中 ICMs 污染的调查研究刚刚起步, 主要是同济大学尹大强教授团队^[7] 对 ICMs 分布、环境赋存浓度和其迁移转化规律等进行研究. 其中不容乐观的是, 尹大强团队对江苏太湖、上海黄浦江以及长兴岛等地表水、饮用水厂、污水处理厂、居民自来水等进行取样之后, 发现了地表水、污水处理厂、中国饮用水厂和居民自来水中都能检测出多种 ICMs, 其中饮用水厂和自来水中检出的浓度相差不大, 说明饮用水厂也无法用工艺去除水中所含 ICMs, 导致居民通过饮用水直接摄入的 ICMs.

4 高级氧化技术去除水环境中 ICMs (Advanced oxidation technology to remove ICMs in water environment)

基于 ICMs 在水环境中的广泛分布及其生态毒理危害, 对其去除技术的研究十分必要. 传统城市污水处理厂一般运用生物处理技术处理废水, 但是应用该技术很难将 ICMs 有效去除. 因此国内外学者采用多种去除技术提高处理效率, 消除水环境 ICMs^[38-41]. 其中高级氧化技术 (Advanced oxidation processes, AOPs) 又称为深度氧化技术, 以产生具有强氧化能力的自由基为特点, 在高温高压、电、声、光辐照、催化剂等反应条件下, 使大分子难降解有机污染物被降解为低毒或无毒的小分子物质. 根据产生自由基的方式和反应条件的不同, 可将其分为声化学氧化、光催化技术 (Photocatalysis)、过硫酸盐 (Persulfate, PS) 活化技术、电化学高级氧化技术 (Electro-chemical advanced oxidation processes, EAOPs)、芬顿 (Fenton) 氧化^[42-45] 等. AOPs 可以直接氧化有机污染物成为小分子物质, 到达提高污染物的生物降解性的目的. 同时, 它还可以进一步矿化小分子有机物, 在去除微量有害化学物质 (如 PPCPs) 方面具备很大的优势, 具有良好的应用前景^[42].

4.1 声化学氧化

声化学氧化对多种有机污染物和无机污染物具有良好的去除效果^[46-50]。超声波降解有机物的反应机理相当复杂,一般认为超声波辐射有机物时,水溶液中产生的空化气泡在瞬间 (ns- μ s) 崩溃,使处于正常温度和压力的液体环境在微观局部产生异常的高温高压 (>5000 K, >50 MPa),从而使难以常规降解的有机物被全部或部分降解。Ning 等^[51]利用超声辐射技术去除水中 ICMs,超声频率恒定为 20 kHz。且通过能量贡献计算,超声热裂解占 30%,而自由基攻击占 70%。同时也发现了 H_2O_2 的加入可以将整个体系的降解效率提高 2 倍,说明 HO \cdot 是主要的活性自由基。基于超声辐射降解条件和机理,对声化学降解水中 ICMs 研究较少。其耗能大,易造成二次污染(噪声污染),很难在实际废水处理中被应用。其主要机理如图 1 所示,进入微泡中的水分子发生断裂,产生高活性的氢自由基 (\cdot H) 和羟基自由基 (HO \cdot),会和水中其它的分子或自由基相互反应,又有因高温高压而发生的热裂解断键等各种因素共同作用,最终将有机物降解甚至去除^[52]。

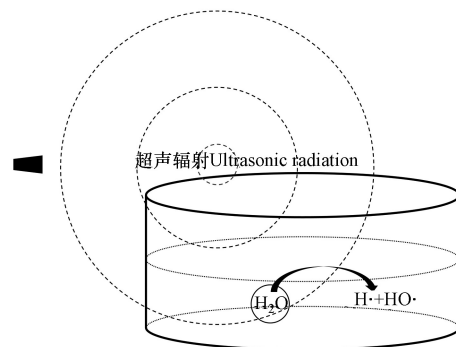


图 1 超声辐射技术降解有机污染物机理

Fig.1 Degradation mechanism of organic pollutants by ultrasonic radiation technology

4.2 光催化技术

光催化技术是一种利用光源能量光催化剂的价带电子跃迁至导带,从而使得电子空穴分离。自由电子具有还原性,空穴具有氧化性,从而产生具有高化学活性的自由基,最终降解水中有毒有害物质的绿色技术。其主要机理是材料价带 (VB) 电子被激发跃迁至导带 (CB),水中氧气 (O_2) 的得电子被活化成为超氧根自由基 ($O_2^{\cdot-}$); 价带上水分子 (H_2O) 和氢氧根离子 (HO^-) 被空穴 (h^+) 氧化得到羟基自由基 (HO \cdot),而有机污染物最终被 $O_2^{\cdot-}$ 、HO \cdot 和 h^+ 去除。由于其降解能力出众,光催化技术也被应用于水环境中 ICMs 的去除。Doll 等^[53]研究了紫外光催化 TiO_2 (P25 和 Hombikat UV100) 降解水中碘美普尔和碘普罗胺。动力学分析得出,由于 Hombikat UV100 对碘美普尔和碘普罗胺具有比 P25 更高的吸附容量,所以 Hombikat UV100 对这两种 ICMs 催化降解效果更好。该课题组^[54]又进一步研究了 P25 和 Hombikat UV100 在天然有机物 (NOM) 存在下,对碘美普尔 ($6\text{ mg}\cdot\text{L}^{-1}$) 光催化降解的影响。发现即使存在天然有机物对降解过程影响,碘美普尔也能够被光催化技术降解掉 93%。Sugihara 等^[55]通过紫外光催化 TiO_2 降解 $20\text{ }\mu\text{mol}\cdot\text{L}^{-1}$ 泛影酸钠,60 min 约降解 80%。Paganini 等^[56]通过铈掺杂的氧化锌光催化剂,在模拟太阳光下降解水中 ICMs。碘帕醇 ($10\text{ mg}\cdot\text{L}^{-1}$) 和泛影酸盐 ($10\text{ mg}\cdot\text{L}^{-1}$) 完全降解的时间为 2 h。Duran-Alvarez 等^[57]研究了纳米结构的 Ag_2O/TiO_2 光催化降解水中碘普罗胺。Ag 的存在减少了电子空穴复合率,使得 $50\text{ }\mu\text{g}\cdot\text{L}^{-1}$ 碘普罗胺 5 h 矿化率大于 65%。本课题组^[58]研究了在模拟太阳光下,通过光催化剂 BN/ Bi_2MoO_6 降解水中 $20\text{ mg}\cdot\text{L}^{-1}$ 的碘海醇,150 min 的去除率达到 90%,矿化率达到了 57.5%。其具体机理如图 2 所示, Bi_2MoO_6 带隙 (E_g) 为 2.31 eV,与一般氢能级 (vs. NHE) 相比,其 VB 和 CB 分别为 -1.20 V 和 1.25 V ; BN 的 E_g 为 3.98 eV,其 VB 和 CB 分别为 1.44 V 和 -2.54 V 。BN 的 CB 电子会迁移到 Bi_2MoO_6 的表面以阻碍了电子空穴复合。同时,BN 可以降低 Bi_2MoO_6 在 VB 中的杂化电子密度,有利于电子从 VB 到 CB 的激发。因此,复合材料可以有效地促进电子空穴的分离。因此,BN 与 Bi_2MoO_6 复合可以有效地促进电子空穴的分离,从而达到提高光催化效率的目的。

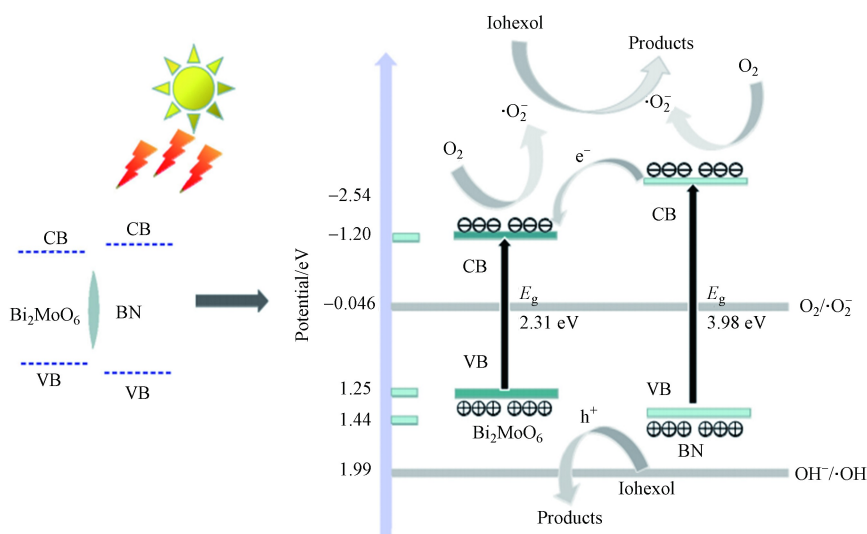


图 2 BN/Bi₂MoO₆ 模拟太阳光催化降解有机污染物机理

Fig.2 Mechanism of BN/Bi₂MoO₆ simulating solar photocatalytic degradation of organic pollutants

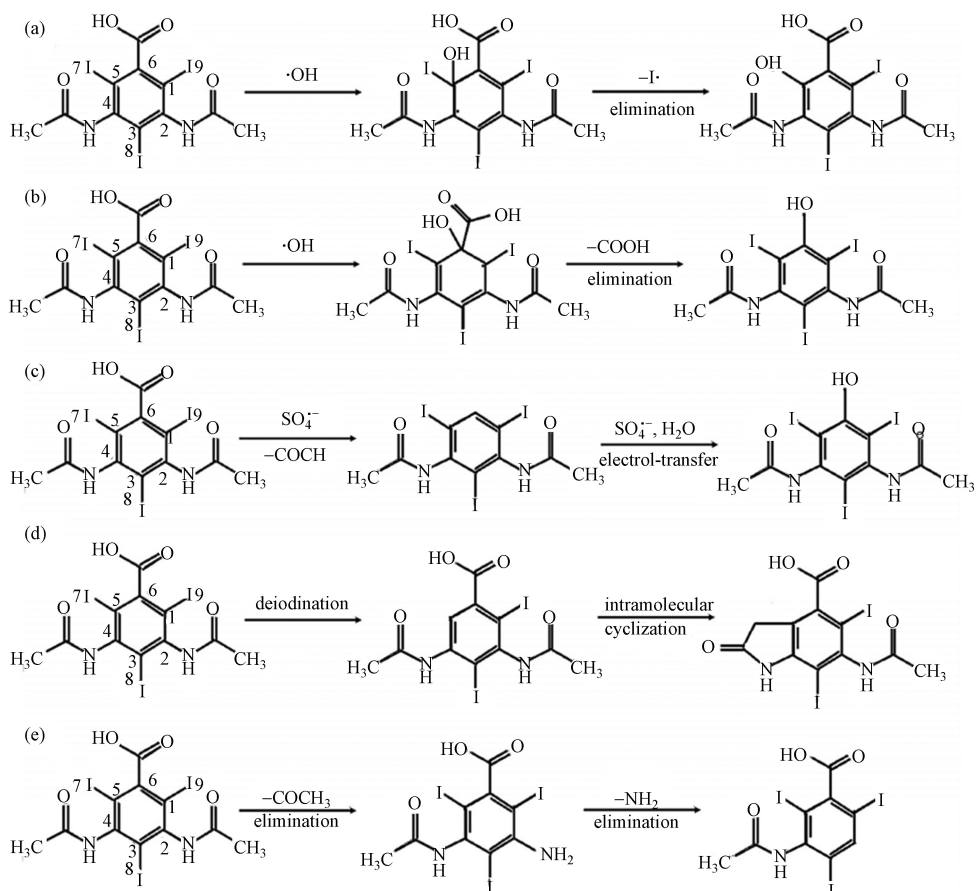
光催化对离子型或者非离子型的 ICMs 展现出较好的降解效果,且对于赋存于环境中与其他物质结合的 ICMs 也具有一定的降解效果.但是光催化降解 ICMs 的反应速率较慢、矿化率较低.

4.3 过硫酸盐活化技术

过硫酸盐活化技术可以与其它活化方式联用,具有较高的可塑性.活化过硫酸盐的方式主要有材料活化^[59-62]、紫外光活化^[63-65]、热活化^[66-68]、超声活化^[69-72]、化学结构活化^[73]、微波活化^[74]、电活化^[75].活化产生的硫酸根自由基(SO₄^{·-})的半衰期^[76-77](>3×10⁻⁵ s)较长,是O₂^{·-}和HO[·]的30倍以上,且具有较高的氧化还原电位(2.5—3.1 V)^[78],其主要机理如图3所示,过硫酸根离子被活化成为硫酸根自由基(SO₄^{·-}),SO₄^{·-}降解有机污染物,达到去除的目的.因而在环境污染物去除领域具有较好的应用前景.

Zhou 等^[79]通过模拟太阳光活化过硫酸盐降解水中泛影酸,发现SO₄^{·-}是降解过程中的主要活性物种.除此以外,与紫外光/过氧化氢(UV/H₂O₂)系统降解过程相比,动力学计算结果表明紫外光/过硫酸盐(UV/PS)系统降解泛影酸的效果更好,与UV/H₂O₂系统降解速率相比,性能提高了30%.Chan 等^[80]通过UV活化过二硫酸钾降解水中浓度为0.126 mmol·L⁻¹碘普罗胺,30 min内可以将其降解完全,且矿化率可以达到80%以上.过硫酸盐活化系统降解效率很高,因此研究人员对其降解机理开始做了许多研究.本课题组^[81]通过电磁感应无极灯(Electromagnetic Induction Electrodeless Lamp, EIEL)光降解泛影酸钠,并加入O₂、H₂O₂以及S₂O₈²⁻降解水中泛影酸钠.由于SO₄^{·-}和HO[·]能够共同作用,UV/PS系统降解效果最佳.当加入自然水体中的泛影酸钠浓度为20 μg·L⁻¹,条件为过硫酸钠浓度10 mmol·L⁻¹;初始pH=7;T=25 °C时,泛影酸钠4 min内被完全降解.通过动力学计算得到SO₄^{·-}对泛影酸钠降解反应贡献最多,占62.5%.具体反应机理如图3所示,(C)降解路径主要活性物种是SO₄^{·-},其作用机理主要为脱羧;(A)和(B)降解路径主要活性物种是HO[·],其作用机理主要为除I⁻和脱羧.

Zhu 等^[82]通过Fe(II)活化过硫酸盐降解水中碘海醇,研究了在不同碘海醇初始浓度和不同二价铁离子(Fe²⁺)和PS浓度下的自由基机理.发现了体系中SO₄^{·-}可以与水环境中的物质转化为HO[·]和Cl[·].同时Shang 等^[83]通过Fe(II)/PS系统降解泛影酸.发现了PS浓度为10 mmol·L⁻¹,n(Fe²⁺)/n(PS)比为1:10,初始pH为3.0和高温能够提高泛影酸的降解效率.Hu 等^[84]通过热活化过硫酸盐降解水中浓度为0.01 mmol·L⁻¹碘海醇.结果表明,2—3 h去除率可以达到85%.而且还研究了在自然水体中NOM存在下,该降解过程产生了一系列消毒副产物,如氮代DBPs,碘代DBPs和碳代DBPs.Wang 等^[85]通过热活化过二硫酸盐降解水中碘普罗胺.研究了温度、pH、PS浓度等对反应的影响.Farhat 等^[86]通过电活化过硫酸盐降解水中泛影酸.除此以外,通过比较得出了,加入硫酸盐阳极液的降解系统降解污染物的速率是加入硝酸盐阳极液系统的10—15倍.因此过硫酸盐活化技术运用于ICMs的降解过程是可行的,且降解速率较快且对ICMs矿化率较高.但是,大多数过硫酸盐活化方式需要消耗大量物质能量;且如果需要长时间高效降解水中污染物,需不断投加过硫酸盐,成本巨大.

图 3 EIEL/UV/PS 系统降解泛影酸路径^[81]Fig.3 EIEL/UV/PS system degradation pathway of diatrizoic acid^[81]

4.4 芬顿氧化法

芬顿氧化法是如今比较成熟的污水处理技术.其基本原理是过氧化氢(H_2O_2)在 Fe^{2+} 的活化下产生 $\text{HO}\cdot$ 从而氧化水中污染物,其反应方程式(1),(2),(3)如下.芬顿氧化法可以根据改进方式的不同分为光芬顿法(Photo-Fenton)^[87-89]、电芬顿法(Electro-Fenton)^[90-93]以及光电芬顿法(Photo-Electro-Fenton)^[94-101].其核心是芬顿试剂体系,通过改性芬顿试剂,类芬顿法也引起了广泛关注.



Zhao等^[102]通过Photo-Fenton系统降解水中碘帕醇.该研究通过比较各种活性自由基($\text{HO}\cdot$, O_2^- , CO_2^-)在 $\text{Fe(III)-oxalate}/\text{H}_2\text{O}_2/\text{UV}(350\text{ nm})$ 和 $\text{Fe(III)-oxalate}/\text{H}_2\text{O}_2/\text{visible}(450\text{ nm})$ 系统下的动力学常数,分析反应机理得出还原性脱卤是去除卤代有机污染物的一种可行方式,在降解反应中可以大大减少消毒副产物形成.Giannakis等^[103]研究了UVC/Fenton系统降解水中碘海醇($10\text{ mg}\cdot\text{L}^{-1}$)且评估了其消毒副产物毒性.分析结果得出UVC/Fenton系统降解碘海醇可以显著降低毒性,使得大肠杆菌和MS2噬菌体迅速灭活.Li等^[104]利用Photo-Fenton系统降解水中碘普罗胺,根据实验结果得出 $\text{H}_2\text{O}_2/\text{Fe(II)}$ 系统中, $10\text{ mg}\cdot\text{L}^{-1}\text{Fe(II)}$, H_2O_2 和 Fe(II) 摩尔比为3:1,以及 $\text{pH}=3$ 时, 30 min 碘普罗($1\text{ }\mu\text{g}\cdot\text{L}^{-1}$)能够被完全降解.Bocos等^[105]通过Electro-Fenton系统降解水中泛影酸.通过调整电流大小(50 mA)、减小催化剂浓度($0.05\text{ mmol}\cdot\text{L}^{-1}$)以及加大污染物浓度的方式去减缓泛影酸氧化去除过程,以便于研究其中间产物和降解路径.结果表明脱碘是氧化过程中一个重要的去除达成方式,为解决Photo-Fenton系统降解污染物速率太快而导致难以检测和分析的问题提供了新的的思路和方法.Bocos等^[106]进一步通过

Photo-Fenton 和 Electro-Fenton 耦合降解水中泛影酸. 在 Photo-Electro-Fenton 系统下, Fe^{3+} ($0.25 \text{ mmol}\cdot\text{L}^{-1}$) 和 H_2O_2 ($20 \text{ mmol}\cdot\text{L}^{-1}$) 等条件相同, $0.1 \text{ mmol}\cdot\text{L}^{-1}$ 泛影酸 2 h 可以降解完全, 速率比 Photo-Fenton 系统提高了 2 倍. 实验结果说明 Photo-Electro-Fenton 耦合系统能够提高 Fenton 试剂对 ICMs 的降解效果和速率. 也有研究团队通过类 Fenton 反应达到降解 ICMs 的目的. Banaschik 等^[107] 通过水中脉冲电晕等离子体/ H_2O_2 系统降解水中泛影酸盐. $0.5 \text{ mg}\cdot\text{L}^{-1}$ 泛影酸盐 1 h 解了 50%. Polo 等^[108] 通过 Solar radiation/ $\text{K}_2\text{S}_2\text{O}_8$ 类 Fenton 系统降解泛影酸盐. 结果发现 $25 \text{ mg}\cdot\text{L}^{-1}$ 泛影酸盐可以在光照强度为 $610 \text{ W}\cdot\text{m}^{-2}$ 光源照射的类 Fenton 系统下 280 min 降解完全.

从以上研究得知, Fenton 相关技术对多种 ICMs 有一定的降解效果, 但是都需要外加能量辅助降解, 其中 Photo-Fenton 系统降解 ICMs 研究最多, 且降解效果最好. Photo-Electro-Fenton 系统也被应用于降解 ICMs, 展现出良好的降解效果和速率, 因而也是未来研究 Fenton 相关系统降解 ICMs 的一个方向. 但是 Fenton 系统存在的缺点是对环境因素要求较高, 且对物质能量投入较多, 在复杂的环境基质中降解能力较为受限.

4.5 电化学高级氧化技术

电化学高级氧化技术通过电化学反应的方式产生活性自由基, 与有机污染物反应达到降解的目的^[109]. 阳极处 H_2O 被氧化成为 $\text{HO}\cdot$. 有机污染物被 $\text{HO}\cdot$ 攻击, 同时在阳极处发生氧化反应, 同时被去除. 出于 EAOPs 处理技术能源来源简单易得, 降解速率可调控, 可用于降解水中有机污染物.

Radjenovic 等^[110] 应用掺硼金刚石阳极的三室反应器电化学系统降解水中 $100 \mu\text{g}\cdot\text{L}^{-1}$ 泛影酸盐, 其中电化学还原和氧化实验使用 $22 \text{ mmol}\cdot\text{L}^{-1}$ $\text{KH}_2\text{PO}_4/\text{K}_2\text{HPO}_4$ 缓冲液 ($\text{pH}=7.0$, 电导率 $3.7 \text{ mS}\cdot\text{cm}^{-1}$), 系统用水为 $0.7 \mu\text{m}$ 过滤器过滤后的医院废水 ($\text{pH}=7.4$, 电导率 $3.7 \text{ mS}\cdot\text{cm}^{-1}$). 分析结果得出, 降解中间产物 3, S-二乙酰氨基苯甲酸能以与泛影酸盐相似的速率从溶液中矿化, 但是 Cl^{-} 存在会导致脱碘效率下降. Korshin 等^[111] 综述了通过掺硼金刚石阳极 EAOPs 降解水中 ICMs. 结果发现该系统降解 $100 \mu\text{mol}\cdot\text{L}^{-1}$ 的碘普罗胺, 矿化率可以达到 90%, 但是降解时间超过了 7.5 h. 在其对泛影酸盐进行研究的过程中, 阴极的还原反应与泛影酸盐的脱碘反应形成了竞争关系, 因而具有不利影响. Yan 等^[112] 通过旋转圆盘电极 (Rotating Ring-disc Electrode, RRDE) 降解水中碘帕醇和泛影酸盐, 研究其在 NOM 存在下的降解效果和中间产物的迁移转化规律, 其中电化学还原条件为阴极电势 $<-0.45 \text{ V}$ (vs. SCE). 研究结果发现, 在电位 -0.65 V 至 -0.85 V 的范围内, 其电化学还原性受到质量转移控制. 结果发现 NOM 不会影响到碘帕醇和泛影酸盐的电化学还原降解, 但是同样由于阴阳极的存在, 被还原的活性碘代物质会与 NOM 会形成其它的消毒副产物. Li 等^[113] 通过 PdCl_2 和 FeSO_4 电沉积到碳纸上制备的 Pd/Fe 改性碳纸 (Pd/Fe-C) 电极在双室反应器中降解卤代乙酸类 DBPs. 结果发现在 -1.5 V (vs. SCE), $\text{pH}=3$ 且 Pd:Fe 摩尔比为 2:1 的最佳实验条件下, 初始浓度为 $500 \mu\text{g}\cdot\text{L}^{-1}$ 的三氯乙酸 (TCAA) 在 20 min 内去除率为 95%. 其中 Pd(0) 纳米粒子对原子 H^{\cdot} 的生成, 以及在氯乙酸完全脱氯的间接还原过程中起着重要作用.

EAOPs 技术优势在于矿化率高, 可去除高浓度 ICMs, 降解速率较快. 其缺点在于耗电量; 易在电极处产生氢气 (H_2) 发生安全事故; ICMs 降解后产生的 I^{-} 不但不易被去除, 而且容易产生有毒的衍生物; 自然水体中的卤素离子对 ICMs 降解反应有抑制作用. 因而对 EAOPs 降解水中 ICMs 之后的核心在于 (1) 尽可能抑制 H_2 生成; (2) 增加对电能的利用效率; (3) 阴阳电极和电解池的设计.

4.6 AOPs 协同降解技术

不同种类的 AOPs 技术各有优缺点, 因此应该使不同种类 AOPs 技术耦合协同降解水中 ICMs, 使其优势互补, 从而达到提高反应速率、降低反应条件、减少人工能源使用和物质消耗和提高矿化率的目的. 协同技术被应用于 ICMs 去除鲜有报导, 但是用于其它有机污染物的去除已有研究基础.

光催化-过硫酸盐活化 (Photocatalysis/PS) 耦合降解系统引起人们的广泛关注^[114-118]. Chen 等^[119] 研究了 Vis-RGO/ TiO_2 /peroxodisulfate 系统降解水中 PPCPs. 其中过二硫酸盐作为电子受体可以加速光催化反应的活性和速率, 且过二硫酸盐活化可以提高降解过程的矿化率. 构建的光催化剂, 既具有光催化活性又具有过硫酸盐活化的特性. 这两项系统协同互补之处在于能量来源都可以是光, 更重要的是 $\text{SO}_4^{\cdot-}$ 可以协同参与到光催化自由基反应过程中. 除此以外, 还有光芬顿-过硫酸盐活化协同技术 (UV/Fenton/PS), Feng 等^[120] 通过一种简便的溶胶-凝胶法制备了 LaFeO_3 纳米颗粒, 并通过在可见光照

射下非均相活化过硫酸盐降解盐酸四环素 (TC-HCl). 其自由基捕获实验表明, SO_4^- 在降解过程中的其主要作用, HO^\cdot 也参与其中一部分反应. 该工作说明 Vis/LaFeO₃/PS 系统在降解废水中的有机污染物方面具有潜在应用价值; 电化学-芬顿技术协同 (Electrochemical-Fenton), Trellu 等^[121] 通过将 TiO₂ 制成反应性电化学膜 (REM) 作为阳极, 引入到 Electro-Fenton (EF) 系统中降解醋氨酚, 结果发现 REM/EF 系统比单一 REM 和 EF 系统的降解矿化率好很多, 110 mg·L⁻¹ 初始有机碳降解率达到 77%. dos Santos 等^[122] 分别使用硼掺杂金刚石, Pt 或 IrO₂ 作为阳极, 并且使用空气扩散阴极, 采用电化学产生 H₂O₂ 进行氧化反应. 该电化学系统在电解液为 130 mL 0.05 mol·L⁻¹ 硫酸钠介质中, 降解城市废水和合成尿中的降压药卡托普利 (0.23 mmol·L⁻¹), 60 min 可以降解完毕. 协同技术体系体现出的降解速率和矿化率比单一技术优良, 且适用性更加广泛.

4.7 高级氧化方法优缺点对比

高级氧化技术是利用自由基的强氧化性去除环境中污染物的新型污染物去除技术. 单一的高级氧化技术由于其自由基产生原理不同、产生的自由基种类不同, 因此对 ICMs 去除效果不同. 声化学氧化技术去除 ICMs, 主要通过热裂解和 HO^\cdot 作用, 但其耗能高, 会造成二次噪声污染; 光催化技术能量来源于绿色的太阳光, 降解效果好, 其核心在于光催化剂的设计. 但其缺点在于自然水体复杂的物质组成会影响光催化剂的使用寿命, 且 ICMs 降解后产生的 I^- 会对反应产生一定的抑制效果. 且光催化剂大多含重金属, 金属离子溶出会造成二次污染, 无法被大规模使用; 过硫酸盐活化技术产生的硫酸根自由基半衰期长、氧化还原电位优于一般常见自由基, 且反应活性高、降解速率快, 因而对 ICMs 降解效果较好. 但是其需要添加过硫酸盐, 成本较高; 芬顿技术较为成熟, 但是其对物质能量的消耗极大, 其未来方向在于自产 H₂O₂ 的 Fenton 试剂的设计; 电化学高级氧化技术降解效率高, 矿化率高, 但是卤素原子会在阳极处抑制反应发生, 且电解水产生的氢气既消耗了能量, 又增加了安全隐患, 且成本巨大, 耗能高. AOPs 协同降解技术降解水中 ICMs 可以弥补单一 AOPs 技术的缺点, 其使得单一 AOP 技术优势互补, 是未来应用于 ICMs 降解技术的方向. 其优缺点具体如表 5 所示. 对于各种高级氧化技术成本核算, 声化学高级氧化法和光催化高级氧化法工艺成本难以估算. 过硫酸盐活化工艺与其活化方式密切相关, 成本一般小于 10 CNY·t⁻¹^[123]; Fenton 法工艺成本一般在 5 CNY·t⁻¹^[124]. 而协同高级氧化技术成本与其设计相关. 如电化学-过硫酸盐协同降解有机废水的运行费用在过硫酸盐浓度为 1.5 mmol·L⁻¹、Fe²⁺ 浓度为 2.25 mmol·L⁻¹ 的最优工艺条件下废水处理成本为 2.8 CNY·t⁻¹^[125]. 热活化-过硫酸盐协同降解有机废水费用为 8.2 CNY·t⁻¹^[126].

表 5 高级氧化技术优缺点对比

高级氧化技术 AOPs	主要活性物种 Main active species	优点 Advantages	缺点 Disadvantages	参考文献 Reference
声化学	H ⁺ 、HO [·]	自由基氧化, 超声热裂解	耗能高, 易造成二次噪声污染	[127 - 128]
光催化	HO [·] 、O ₂ ⁻	能量来源绿色可循环, 降解效果好, 矿化率高	降解速率慢, 光催化剂使用寿命容易受复杂水环境影响	[129 - 130]
过硫酸盐活化	SO ₄ ⁻ 、HO [·] 、O ₂ ⁻	降解速率快, SO ₄ ⁻ 半衰期长, 矿化率高	物质能量消耗较大, 反应中需不断投加 PS	[59, 131]
芬顿法	HO [·]	技术应用成熟, 可以实际应用	受环境因素影响较大 (pH, T)	[132 - 133]
电化学	HO [·]	降解速率快, 小分子物质阳极直接被氧化去除	阴阳极材料使用寿命, 耗能高	[134]
协同催化技术	SO ₄ ⁻ 、HO [·] 、O ₂ ⁻ 等	根据污染物灵活设计	较少	[89, 135 - 138]

5 总结与展望 (Conclusion)

ICMs 在自然界中可以稳定存在、分布广泛, 其自然降解过程中产生的消毒副产物具有较大的毒性, 且通过传统污水净化技术无法完全去除, 因此亟需开发能够消除环境污染的技术.

每一类 AOP 技术都存在着一定的优点, 且对 ICMs 有一定的去除效果, 但其缺点明显, 被广泛应用的可能性很小. 协同 AOPs 技术可以将每种单一 AOP 技术优势结合, 缺点减小. 如光催化/过硫酸盐活化协同技术, 将过硫酸根离子作为外部电子受体, 减小了光催化材料内部电场电子空穴复合率; 而在 Electrochemical-Fenton 协同技术降解机理中, 可以通过电化学反应生成 H₂O₂, 作为 Fenton 反应的原料.

因此, 协同 AOPs 技术可以作为未来 AOPs 技术的一个重要的发展方向。

随着对 AOPs 机理的进一步研究和相应配套实验装置的研发, 大型 AOPs 降解装置将被应用于污水处理厂的污染物去除过程中, 使得 ICMs 最终能够从城市废水中被去除。除了对 ICMs 污染采取相应措施以外, 希望能够研发出可替代 ICMs 的绿色可降解无污染的 X 射线造影剂, 或是在政策上对 ICMs 除应用于医疗等其它途径进行管控, 从而在源头上控制 ICMs 的污染。

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