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铁基双金属催化剂活化过硫酸盐去除水中抗生素研究进展

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摘要: 近年来,抗生素残留物在多种水体中被普遍检出,对水生态环境和人类健康造成严重威胁. 基于活化过硫酸盐高级氧化作用去除水中抗生素污染物,以其氧化性强、选择性高和 pH 适用范围宽等特点成为研究热点. 低成本、高稳定性和催化性能优异的铁基双金属材料能有效活化过硫酸盐,它弥补了单一铁元素活化剂易失活、效率低和容易产生二次污染等缺陷. 针对尖晶石铁氧体、铁基层状双金属氢氧化物和铁基普鲁士蓝类似物 3 种典型铁基双金属催化剂,开展其活化过硫酸盐降解抗生素的研究分析,系统讨论了铁基双金属活化过硫酸盐的几种内在驱动机制,并分别对自由基、单线态氧和高价金属的产生,电子转移和过硫酸盐直接氧化过程进行了梳理. 最后,总结了活化过硫酸盐技术处理氟喹诺酮类、磺胺类、四环素类与 β-内酰胺类抗生素等 4 种典型抗生素的一般降解途径,为今后研究铁基双金属催化剂及其改性、衍生物和复合物等在活化过硫酸盐技术中的应用提供参考.

关键词:铁基; 双金属; 过硫酸盐; 驱动机制; 降解途径
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Iron-based Bimetallic Catalysts for Persulfate Activation to Remove Antibiotics in Water: A Review

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Abstract: In recent years, antibiotic residues are commonly detected in a variety of water bodies, causing serious threat to water ecosystems and human health. The removal of antibiotic contaminants from water based on the advanced oxidation process of activated persulfate has become a hot research topic due to its strong oxidative properties, high selectivity, and wide pH applicability range. Iron-based bimetallic materials with low cost, high stability, and excellent catalytic performance can effectively activate persulfate, which makes up for the defects of being a single iron activator, such as easy deactivation, low efficiency, and producing secondary pollution easily. Three typical Fe-based bimetallic catalysts, namely spinel ferrite, Fe-based layered double hydroxides, and Fe-based Prussian blue analogues, were investigated and analyzed for their activation of persulfate for antibiotic degradation. Several intrinsic mechanisms of persulfate activation by Fe-based bimetallic catalysts are systematically discussed, including the generation of free radicals, singlet oxygen, and high-valent metals; the process of electron transfer; and the direct oxidation process of persulfate. Finally, the general degradation pathways of four typical antibiotics, including fluoroquinolones, sulfonamides, tetracyclines, and β-lactam antibiotics, are summarized to act as a reference for future studies on the application of Fe-based bimetallic catalysts and their modifications, derivatives, and complexes in the activating technology of persulfate.

Key words: iron-based; bimetallic; persulfate; driving mechanism; degradation pathways

抗生素被广泛用于促进动物生长和保护人类免受细菌感染侵害. 根据其化学结构,常见的抗生素包括磺胺类、四环素类、氟喹诺酮类、大环内酯类和 β-内酰胺类等. 2000~2015 年,全球抗生素消耗量增加了 65%,期间,我国抗生素总使用量约占全球使用总量的 50%,预计 2030 年,此占比下降至 43%,但我国仍然是世界抗生素的最大消费国[1]. 抗生素滥用会导致各类耐药性细菌的大量暴发,抗生素母体化合物及其代谢产物会随着医疗污水、制药废水、污水处理厂尾水、畜禽及水产养殖废水和农业径流等进入环境中,对生态环境和人类健康带来严重威胁[2,3]. 目前,常见的抗生素去除技术主要有吸附、生物处理和化学处理等. 吸附法作为一种物理分离技术,只能将抗生素从水中分离出来,无法实现污染物的降解去除[4]. 受制于抗生素对细菌活性的强抑制作用,生物处理技术对此类污染物的降解能力非常有限[5]. 相比而言,高级氧化工艺(advanced oxidation processes, AOPs)可以产生高活性物种[硫酸根自由基($SO_4^{-\cdot}$)、羟基自由基($\cdot OH$)、超氧自由基($\cdot O_2^-$)、单线态氧($^1O_2$)、臭氧(O_3)和氯离子(Cl^-)等],将抗生素逐步分解为小分子无毒、低毒

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或可生物降解的物质[6]. 芬顿技术是目前研究最广泛的废水处理 AOPs,但对 pH 要求苛刻,且反应过程会产生大量含铁污泥,限制了它的大规模应用,而基于过硫酸盐的类芬顿 AOPs 有望解决这些问题[6]. 常见的过硫酸盐包括过氧单硫酸盐(peroxymonosulfate, PMS)和过氧二硫酸盐(peroxodisulfate, PDS),通过被铁、银、铜、钴、镍、锰、钒和铈等过渡金属离子激活产生高活性物种[7],实现对污染物的氧化降解,是一种经济高效的处理方法.

在常见的过渡金属离子中,铁离子以低毒性、价态丰富和优异的活化性能,成为均相催化反应中应用最广泛的金属离子[8]. 然而,该均相催化体系在规模化应用时,依然面临铁离子失活、难回收、产生铁盐沉淀和造成二次污染等问题. 固相铁基催化剂则能有效地将金属离子固定在分子结构中,弥补均相催化反应的缺陷[9]. 单一铁元素在活化过硫酸盐时,由于缺乏电子供体使得高价态铁不能被还原,从而无法形成循环反应,难以维持氧化降解反应的高效进行. 引入其他金属元素,一方面能够为铁离子提供电子供体,实现金属离子再生[10]; 另一方面,金属离子间协同活化过硫酸盐,可以产生更多数量的活性物种攻击目标污染物,能大幅提升催化降解效率[11~13]. 与两种不同金属化合物物理混合形成的复合催化剂相比,双金属催化剂合成步骤更简便、金属原子结合更稳定且更容易展开进一步的改性和修饰[14~17].

单组分铁基双金属催化剂缺乏丰富的官能团和活性结构组分,易团聚,且存在金属离子浸出问题,限制了其催化活性和实际应用[18,19]. 多数铁基双金属催化剂的合成方法灵活、成分可调、结构可控[20]且具有丰富的锚定或吸附位点[21],利用合成前驱体或衍生物、调控金属组分、修饰催化剂表面、构建缺陷和引入载体等方法,可进一步提升其催化活性、缓解纳米粒子团聚和减少金属离子浸出.

本文在介绍 3 种典型铁基双金属催化剂的基础上,重点总结了铁基双金属催化剂活化过硫酸盐降解抗生素的内在驱动机制,讨论了 4 种典型抗生素的一般降解途径,并对铁基双金属材料活化过硫酸盐的发展前景进行了展望,以期为抗生素废水处理技术应用和抗生素污染控制提供参考.

1 铁基双金属催化剂

铁基双金属催化剂具有双金属协同变价、循环活化过硫酸盐的作用,可以促进低价离子再生. 多种金属在其表面提供了更多反应活性位点,能够显著提高催化剂的化学稳定性,在保持更高氧化还原活性的同时,还能一定程度降低金属溶出率[19]. 现阶段,尖晶石铁氧体、铁基层状双金属氢氧化物、铁基双金属普鲁士蓝类似物催化剂,以其较强的活化过硫酸盐能力和优异的空间结构被应用于活化过硫酸盐体系降解抗生素.

1.1 尖晶石铁氧体

尖晶石铁氧体,通式为 XFe_2O_4(X 为一种二价过渡金属,如 Co、Cu、Mn、Ni 和 Zn 等),根据尖晶石的晶体结构(如图 1)[22],可分为正尖晶石、反尖晶石和复杂尖晶石[23]. 对于正尖晶石,X(Ⅱ)和 Fe(Ⅲ)分别占据四面体和八面体位点,如 $ZnFe_2O_4$[24]. 通常,八面体位点的间隙大于四面体位点的间隙,因此半径较小的阳离子倾向于占据 X 位点,而半径较大的阳离子则倾向于占据 Fe(Ⅲ)位点[25]. 反尖晶石中,一半 Fe(Ⅲ)位于四面体位置,而 X(Ⅱ)与另一半 Fe(Ⅲ)位于八面体位置,如 $NiFe_2O_4$[26]. X(Ⅱ)和 Fe(Ⅲ)随机占据四面体和八面体位置,则会构成复杂尖晶石.

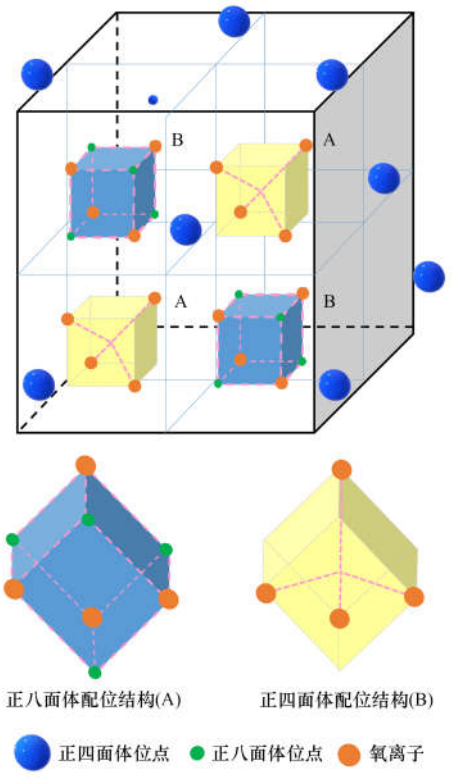


图 1 尖晶石晶体结构

Fig. 1 Crystal structure of spinel

尖晶石铁氧体以其热稳定性、宽光吸收频率、低饱和磁矩等优良理化性能,被广泛应用于水环境修复及能源领域[27]. 它属于纳米级材料,粒径小,具有高度的无序性,所具备的表面效应、量子效应和小尺寸效应是块状材料不能比拟的[22]. 在活化过硫酸盐体系中,尖晶石铁氧体表现出优异的活化性能、稳定的化学性质和耐腐蚀性,对抗生素降解具有显

著效果. Li 等[28]制得的 $CoFe_2O_4$ 可通过活化 PMS 在 30 min 内有效降解 99% 以上的磺胺甲噁唑、阿特拉津和苯甲酸. 同时，该 $CoFe_2O_4$/PMS 反应体系中，主要活性物种为 $CoFe_2O_4$ 表面和溶液中的 Co(Ⅱ)-PMS 络合物. Wang 等[29]制备的 $CuFe_2O_4$ 通过活化 PMS，能在 120 min 内去除 90% 以上的诺氟沙星，且保持优异的运行稳定性. 含不同金属的尖晶石铁氧体在处理抗生素污染物时会表现出明显差异. 据报道，铁氧体中的 X 位元素是决定催化 PDS 活性的主要因子，催化剂的还原性顺序为：$CoFe_2O_4$ > $CuFe_2O_4$ > $MnFe_2O_4$ > $ZnFe_2O_4$[30]. 然而，不同 X 位金属对 PMS 活化去除抗生素的差异尚不清楚.

目前，能强化尖晶石铁氧体活化过硫酸盐性能的负载型催化剂也被广泛研究，所用载体主要有氧化石墨烯、生物炭、金属及其氧化物和多孔碳材料等[31,32]. Meng 等[33]研究了还原氧化石墨烯(RGO)负载 $MnFe_2O_4$ 复合材料激活 PDS，RGO/$MnFe_2O_4$ 的催化性能远高于单一 $MnFe_2O_4$，80 min 内可以降解 90% 以上的四环素. Lan 等[34]发现在 Ar 气氛围利用碳纳米管(CNTs)缺陷调节 $ZnFe_2O_4$ 纳米笼后，$ZnFe_2O_4$/CNTs-Ar 复合材料活化 PDS 的催化活性是单一 $ZnFe_2O_4$ 纳米笼的 17.5 倍. 在活化 PMS 体系中，以尖晶石铁氧体中的 $CoFe_2O_4$ 为例，表 1 归纳了负载型 $CoFe_2O_4$ 降解抗生素的优异性能.

表 1　$CoFe_2O_4$ 复合材料活化 PMS 降解抗生素性能

Table 1　Summary of $CoFe_2O_4$ composites-activated PMS for the degradation of antibiotics

催化剂	污染物	浓度	反应条件	降解性能/%	文献
$CoFe_2O_4$/氧化石墨烯	诺氟沙星	15 μmol·L^{-1}	[PMS]=0.5 mmol·L^{-1}，[催化剂]=0.3 g·L^{-1}，pH=7.0，时间=20 min，温度=25℃	100	[35]
$CoFe_2O_4$/活性炭	诺氟沙星	10 mg·L^{-1}	[PMS]=0.15 g·L^{-1}，[催化剂]=0.1 g·L^{-1}，时间=60 min，温度=25℃	100	[36]
$CoFe_2O_4$/氮化碳	左氧氟沙星	10 mg·L^{-1}	[PMS]=0.5 mmol·L^{-1}，[催化剂]=0.3 g·L^{-1}，pH=3.0，时间=20 min，温度=25℃	90	[37]
$CoFe_2O_4$/还原氧化石墨烯	氧氟沙星	40 μmol·L^{-1}	[PMS]=1.0 mmol·L^{-1}，[催化剂]=0.1 g·L^{-1}，pH=6.0，时间=30 min	100	[38]
$CoFe_2O_4$/还原氧化石墨烯	头孢唑林	40 μmol·L^{-1}	[PMS]=100 μmol·L^{-1}，[催化剂]=0.1 g·L^{-1}，pH=6.0，时间=30 min	100	[38]
$CoFe_2O_4$/石英砂	磺胺二甲基嘧啶	20 mg·L^{-1}	[PMS]=75 mg·L^{-1}，[催化剂]=10 g·L^{-1}，pH=6.8，流速=6 mL·min^{-1}	90	[39]
$CoFe_2O_4$/Al_2O_3	磺胺二甲基嘧啶	5 mg·L^{-1}	[PMS]=1.0 mmol·L^{-1}，[催化剂]=1.0 mmol·L^{-1}，pH=7.0，时间=60 min，温度=25℃	93.7	[40]

1.2　铁基层状双金属氢氧化物

层状双金属氢氧化物(LDHs)具有纳米级二维结构(如图 2)[41]，被广泛应用于能源转换、医药和环境修复等领域. 近年来，LDHs 活化过硫酸盐处理水中难降解污染物的研究日益增多，其衍生物活化过硫酸盐的潜力也被研究人员逐步开发[42]. LDHs 活化过硫酸盐主要具备以下优点：① 生产成本低，过程简单；② 化学成分灵活，可由多种过渡金属离子和功能性阴离子制备，催化活性提升明显；③ 结构稳定，对有毒重金属离子有良好的固定作用[43]；④ 形态多样，可以通过煅烧、溶剂热等不同制备方法轻松改变，以暴露更多的反应活性位点[44]；⑤ 可与不同性质的催化剂结合形成复合材料，其中“金属-金属”或“金属-碳”之间的协同作用可以显著改善氧化还原反应循环效率，减少金属浸出并增强材料的稳定性[14].

在污水深度处理过程中，使用铁基 LDHs 及其衍生物活化过硫酸盐具有明显的经济实用性和环保性[45]. 表 2 总结了近期铁基 LDHs 及其复合物活化过硫酸盐降解抗生素的一些研究结果. 此外，大多数研究利用铁基 LDHs 及其复合物降解其他有机污染物，如双酚 A[46]、酸性橙 7[47]、罗丹明 B[48]和十八胺[16]等. 铁基 LDHs 单体处理抗生素类污染物的效率有限，通过对材料进行改性、负载和制备衍生物或复合材料，可达到更好的去除效果. 此外，还可以

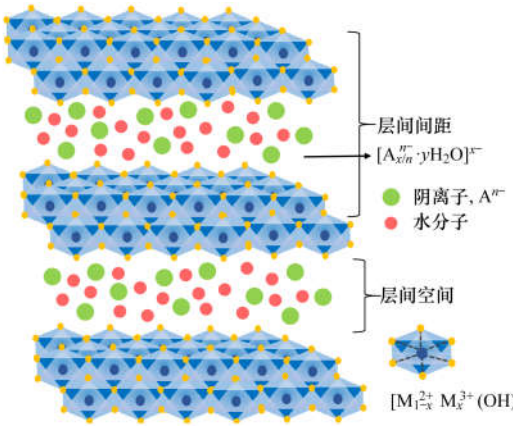


图 2　层状双金属氢氧化物结构示意

Fig. 2　Schematic of the structure of layered double metal hydroxide

表 2 铁基层状双金属氢氧化物及其复合物活化过硫酸盐降解抗生素性能

Table 2 Summary of iron-based LDHs composites activated persulfate for the degradation of antibiotics

催化剂	污染物	浓度/mg·L^{-1}	反应条件	降解性能/%	文献
FeNi-LDH	四环素	50	[PS] = 0.4 g·L^{-1}, [催化剂] = 0.5 g·L^{-1}, 时间 = 10 min	100	[46]
La/FeNi-LDH	四环素	20	[PMS] = 0.2 mmol·L^{-1}, [催化剂] = 0.04 g·L^{-1}, 时间 = 60 min	84	[53]
FeCo-LDH/活性炭	洛美沙星	10	[PS] = 1.0 g·L^{-1}, [催化剂] = 0.2 g·L^{-1}, pH = 5.0, 时间 = 60 min, 温度 = 25℃	93.2	[14]
FeCo-LDHs/PVDF 膜	四环素	20	[PMS] = 0.5 mmol·L^{-1}, [流速] = 1.2 L·h^{-1}, 时间 = 10 min	98.6	[54]
FeMg-LDH/生物炭	阿霉素	30	[PMS] = 0.75 g·L^{-1}, [催化剂] = 0.75 g·L^{-1}, 时间 = 120 min, pH = 7.0	88.8	[55]
FeCu-LDH/介孔碳	磺胺甲噁唑	25	[PS] = 0.5 g·L^{-1}, [催化剂] = 0.15 g·L^{-1}, 时间 = 150 min, pH = 5.5	84.9	[56]

在层间增加第 3 种金属形成铁基层状三金属氢氧化物及其衍生物[49~52], 实现对难降解抗生素的高效去除.

1.3 铁基双金属普鲁士蓝类似物

普鲁士蓝类似物(PBA)以其三维开放框架、高比表面积、可控结构和过氧化物酶活性高等优势(如图 3), 被证实具有出色的催化性能. PBA 及其衍生物、复合材料应用于电化学能量转换和存储、电化学或生物传感器、吸附和芬顿高级氧化技术等领域, 展现出优异特性[20], 引起研究学者的广泛关注[57,58]. 有学者基于 PBA 可激活 H_2O_2 的机制, 尝试将 PBA 材料应用于活化过硫酸盐高级氧化体系, 如 Zhao 等[59]证明了 CoFe-PBA 在高自旋状态下可以有效活化 PMS 降解有机污染物. 此外, Li 等[60]则以 CoFe-PBA 作为前驱体, 煅烧得到多孔 $Fe_xCo_{3-x}O_4$ 纳米笼用于活化 PMS, 发现双金属催化剂的量比对材料性能有至关重要的影响.

目前, 利用 PBAs 及其衍生物活化过硫酸盐降解抗生素的研究不多, 主要以成本较低, 更适合规模化应用的铁基双金属 PBA 及其复合材料为主. Zeng 等[61]以 CoAl-LDH 为原料, 合成了 CoFe-PBA@CoAl-LDH 纳米片, 使用该材料活化 PMS 仅需约 8 min 即可降解 98% 的磺胺甲噁唑. 虽然铁基 PBAs 单体具有氧化还原点位多、离子通道空隙大、自身结构稳定和易发生电子转移等优点, 但 PBA 材料的晶格结构不完整, 结构骨架的水稳定性差, 晶格水和实际水体的复杂成分, 会导致 C—N 键断裂、金属离子浸出和材料失效等问题[62]. 在铁基双金属 PBA 活化过硫酸盐降解抗生素领域, 多数研究集中在将其作前驱体或制备原材料, 导致制备工艺步骤繁多, 合成产率低.

因此, 针对铁基双金属 PBA 材料的优化研究值得深入探索, 对材料直接改性、引入载体(碳基、金属氧化物、多孔基底和膜基底等)或施加外部能量辅助, 都可提升催化活性、增强稳定性和减少二次污染. Pi 等[63]将一种 CoFe-PBAs@RGO 纳米复合材料用于活化 PMS 体系降解盐酸左氧氟沙星, 循环使用 5 次以后, 材料仍保持较高的催化活性和化学稳定性. Guo 等[17]利用紫外-可见光辅助 CuFe-PBA 活化 PMS, 可有效去除水中洛美沙星, 反应后溶液中金属浸出量很低. 该团队还制备了 CoFe-PBA@聚偏二氟乙烯(PVDF)催化膜, 在高效去除磺胺醋酰的同时还可重复使用, 提升了 PBA 纳米粒子的应用潜力[64].

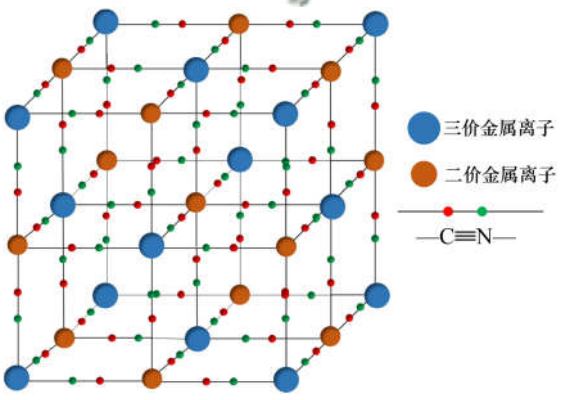


图 3 双金属普鲁士蓝类似物结构示意

Fig. 3 Schematic of the structure of bimetallic Prussian blue analogs

综上, 3 种铁基双金属催化剂在实现激活过硫酸盐的过程中各具优势, 同时也存在一定的问题. 相比于铁基 LDHs 和 PBAs, 尖晶石铁氧体的磁性能, 使其在材料再生和回收方面具有独特优势, 但其合成过程复杂, 煅烧过程耗能较高. 而铁基双金属 LDHs 和 PBAs, 利用简单的共沉淀或溶剂热法即可合成, 能灵活实现金属配比调控. 其中, LDHs 的表面积大、活性位点丰富, 金属分散性优异, PBAs 独具丰富的孔道结构, 电子转移性能优异, 但二者的稳定性受 pH、无机盐离子和氧化还原条件等环境因

素的影响较大. 由于 3 种铁基双金属催化剂均易于改性,有良好的调谐性,对其进行选择性掺杂、位置置换、结构反转、缺陷引入和复合材料耦合等,可逐步实现材料再生回收、提升催化降解性能、增强稳定性和减少有毒金属离子浸出.

2　铁基双金属活化过硫酸盐驱动机制

由于铁基双金属催化剂的复杂性和 PMS-AOPs、PDS-AOPs 中存在各种诱导因素,铁基双金属催化剂的活化机制仍存在争议. 利用淬灭剂捕获活性物种,反推它们的贡献率是较为常用的手段. 但淬灭剂的选择与投加浓度难以把控,过少的淬灭剂无法实现活性物种的完全淬灭,高浓度的淬灭剂则会在活化过硫酸盐过程中引发许多混杂效应,如加速过硫酸盐分解、干扰活性物种的产生和非目标活性物种的淬灭[65]. 因此,仅凭活性物种捕获实验推断的过硫酸盐活化机制可信度较低.

目前,利用电子顺磁共振谱(EPR)、荧光显微镜等技术,对活性物种捕获实验所得结论进行验证,可初步揭示铁基双金属催化剂活化过硫酸盐的一般机制[66],主要包括:自由基驱动机制、单线态氧驱动机制、电子转移驱动机制、高价金属驱动机制和直接氧化驱动机制,如图 4 所示.

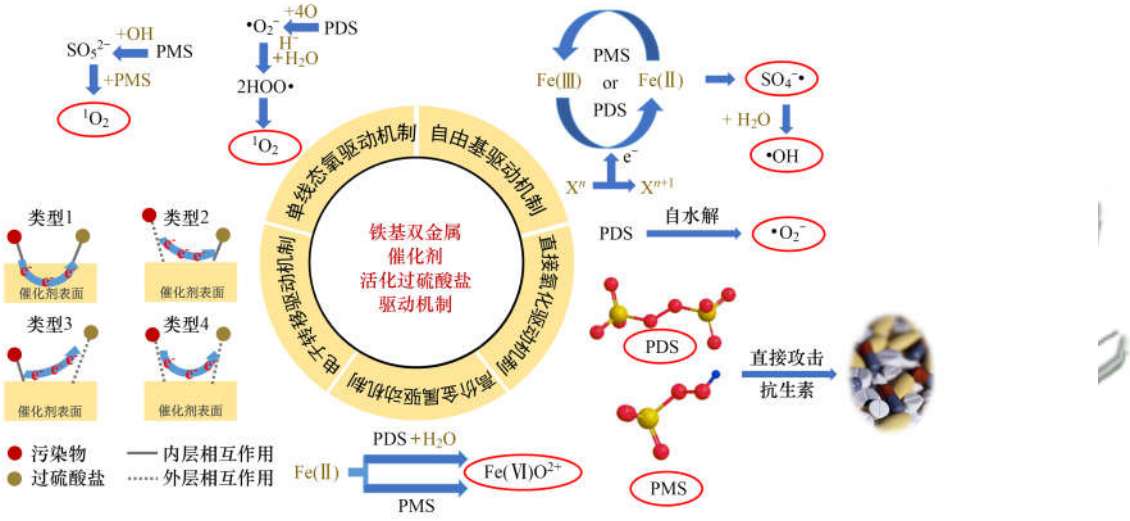


图 4　铁基双金属催化剂活化过硫酸盐的驱动机制

Fig. 4　Mechanism of persulfate activation by iron-based bimetallic catalysts

2.1　自由基驱动机制

自由基驱动机制是指催化剂中的过渡金属离子(X^{n+})与 PMS 或 PDS 发生反应,使得过硫酸盐中的—O—O—结构断裂,然后产生自由基活性物种. 以具有高氧化电势的自由基发挥主要的氧化作用,实现污染物的有效降解和矿化. 参与活化过硫酸盐降解抗生素的自由基以硫酸根自由基($SO_4^{\cdot-}$, E_0 为 2.5 ~ 3.1 V[67])和羟基自由基($\cdot OH$, E_0 为 1.9 ~ 2.8 V[68,69])为主. 铁基双金属催化剂中铁离子一般会起到产生$SO_4^{\cdot-}$的主导作用,它与 PDS、PMS 之间发生的反应也有所不同,如式(1)和式(2)所示;$SO_4^{\cdot-}$产生后会进一步与水反应生成 $\cdot OH$,如式(3)所示;进而协同氧化抗生素,如式(4)所示.

$$Fe^{2+} + S_2O_8^{2-} \longrightarrow Fe^{3+} + SO_4^{\cdot-} + SO_4^{2-} \quad (1)$$

$$Fe^{2+} + HSO_5^- \longrightarrow Fe^{3+} + SO_4^{\cdot-} + OH^- \quad (2)$$

$$SO_4^{\cdot-} + H_2O \longrightarrow SO_4^{2-} + H^+ + \cdot OH \quad (3)$$

$$SO_4^{\cdot-} / \cdot OH + \text{抗生素} \longrightarrow \text{中间产物} \longrightarrow CO_2 + H_2O \quad (4)$$

自由基驱动机制的限制因素主要是催化剂的失活问题,铁离子氧化完全,无法再启动新一轮活化过硫酸盐的反应[70]. 在铁基双金属催化剂中,其他金属离子(X^{n+})可以作为电子供体为 Fe^{2+} 再生提供动力,以促进 Fe^{2+}/Fe^{3+} 变价循环,如式(5)所示[71]. 这也是铁基双金属在活化过硫酸盐中比单一含铁材料更具优势的原因之一.

$$Fe^{3+} + X^{n+} \longrightarrow Fe^{2+} + X^{(n+1)+} \quad (5)$$

此外,还有一小部分超氧自由基($\cdot O_2^-$)可能会从 PDS 的自水解反应中产生,参与到抗生素的降解过程中,如式(6)和式(7)所示[72].

$$S_2O_8^{2-} + 2H_2O \longrightarrow HO_2^- + 2SO_4^{2-} + 3H^+ \quad (6)$$

$$S_2O_8^{2-} + HO_2^- \longrightarrow SO_4^{\cdot-} + SO_4^{2-} + \cdot O_2^- + H^+ \quad (7)$$

2.2　单线态氧驱动机制

单线态氧($^1O_2$)是活化 PDS[如式(8) ~ (10)]或 PMS[如式(11)和式(12)]过程中可能会产生的另一种活性物质[73,74],也是降解抗生素过程中一种非自由基反应路径. $^1O_2$ 分子可以在光化学过程、生物氧化或有机代谢等过程中产生和淬灭,其作用寿

命主要取决于所处溶剂状态,范围从 2 μs(超纯水中)到1 000 μs(分散于 CF_3Cl 溶剂中)[75]. 此外,$^1O_2$ 会率先选择和具有富电子双键的化合物、硫化物、苯胺和酚类化合物等物质发生反应. 因此,在活化过硫酸盐体系中$^1O_2$和$SO_4^{-}\cdot$ 相似,具有高选择性[76]. 然而,如式(8)~(12)所示,活化过硫酸盐过程直接产生的 $\cdot O_2^-$ 和 SO_5^{2-} 是生成$^1O_2$的中间产物,因此$^1O_2$浓度难以进行准确的定量分析.

$$3S_2O_8^{2-} + 4OH^- \longrightarrow \cdot O_2^- + 6SO_4^{2-} + 4H^+ \quad (8)$$

$$\cdot O_2^- + H_2O \longrightarrow HOO\cdot + OH^- \quad (9)$$

$$HOO\cdot + HOO\cdot \longrightarrow H_2O_2 + {}^1O_2 \quad (10)$$

$$HSO_5^- + OH^- \longrightarrow SO_5^{2-} + H_2O \quad (11)$$

$$HSO_5^- + SO_5^{2-} \longrightarrow HSO_4^- + SO_4^{2-} + {}^1O_2 \quad (12)$$

铁基双金属催化剂活化过硫酸盐产生$^1O_2$的过程,一般在碱性条件下,或在有碳基材料时发生. Dong 等[77]利用密度泛函理论计算发现,锚定在氮掺杂碳纳米片上的 $CuFe_2O_4$ 颗粒在其内部形成了一个内建电场,可调节电子转移过程以触发自由基和非自由驱动途径. 催化剂中的石墨 N、sp^2 杂化结构以及C═O官能团被证明是$^1O_2$产生的主要位点. Liang 等[78]开发的 FeCu 双金属共掺杂生物炭活化 PMS 体系中,$^1O_2$等非自由基控制了整个降解过程,酮基(C═O)和缺陷位点也发挥了作用. Xiao 等[79]以高度分散的 Fe-Ce 纳米立方晶作为 PMS 活化中心降解甲硝唑,取得了良好的效果,引入氮掺杂的生物炭后进一步提高了活化性能. 这主要归因于自由基协同以$^1O_2$为主导的非自由基,促进了整个降解过程.

2.3 电子转移驱动机制

基于过硫酸盐的高级氧化技术中电子转移过程也是非自由基驱动机制的组成部分[80]. 首先,过硫酸盐和污染物同时被吸附在催化剂表面,在过硫酸盐被活化过程中形成催化剂-过硫酸盐络合物. 络合物具备比催化剂更高的氧化还原电位,当其超过污染物的氧化电位时,络合物从污染物中提取电子,实现进一步降解. 电子转移过程中的过硫酸盐活化剂主要充当导电桥以促进电荷迁移. Li 等[28]结合自由基猝灭和 EPR 实验结果,提出了以 $CoFe_2O_4$ 表面和溶液中的 Co(Ⅱ)—PMS 络合物为主要介导的氧化过程.

根据污染物、过硫酸盐在催化剂表面的吸附强度,二者和催化剂结合可分为内层和外层相互作用[81]. 内层相互作用导致污染物和过硫酸盐在催化剂表面上产生更强的吸附力,直接形成化学键. 外层相互作用使污染物和过硫酸盐到催化剂表面的分子间距离更长,吸附力更弱. 根据相互作用的强度,电子转移驱动机制一般分为 4 种类型,如图 4 所示. 过硫酸盐和污染物将通过内层相互作用(类型 1)靠近催化剂表面,不受离子强度的影响. 另一部分催化剂表面只会和污染物(类型 2)、过硫酸盐(类型 3)或有机物和过硫酸盐(类型 4)发生外层反应,对离子强度的变化更敏感[82]. 但体系的氧化降解效率不受 4 种电子转移方式的影响,主要由催化剂的导电性、比表面积、孔隙、热力学相互作用、电子和质量传递等共同决定.

2.4 高价金属驱动机制

金属离子与过硫酸盐反应过程中,除了会产生自由基之外,还会生成更高价态的金属离子,同样对污染物有降解能力. Li 等[83]验证了高价铁离子[Fe(Ⅳ)]在商用零价铁活化 PMS 体系中会起到一定作用. Zhou 等[84]的研究也发现,在利用石墨相氮化碳锚定铁单原子活化 PMS 降解磺胺甲噁唑的过程中,高价铁活性物种起到一定的作用.

铁基双金属催化剂活化过硫酸盐的反应中,铁离子也可能被氧化到更高的价态,如式(13)和式(14)所示,高价态铁氧离子的氧化性使得体系中污染物有更多种降解路径. Wang 等[85]的研究发现,在酸性条件下,$PMSO_2$ 的形成和产率接近 100%. 这表明,在酸性条件下 Fe^{2+} 激活过硫酸盐发生 O—O 键裂解时,会生成 Fe(Ⅳ),而不是长期以来公认的 $SO_4^{-}\cdot$. 当 pH 值接近中性时,也发现体系中有 Fe(Ⅳ)的存在[86]. 此外,现已开发用来预测 Fe^{2+}/PMS 和 Fe^{2+}/PDS 系统中 Fe(Ⅳ)的形成和衰减的动力学模型[85],可更准确地判断高价铁离子驱动在反应中的贡献作用.

$$Fe^{2+} + S_2O_8^{2-} + H_2O \longrightarrow Fe^{Ⅳ}O^{2+} + 2SO_4^{2-} + 2H^+ \quad (13)$$

$$Fe^{2+} + HSO_5^- \longrightarrow Fe^{Ⅳ}O^{2+} + SO_4^{2-} + H^+ \quad (14)$$

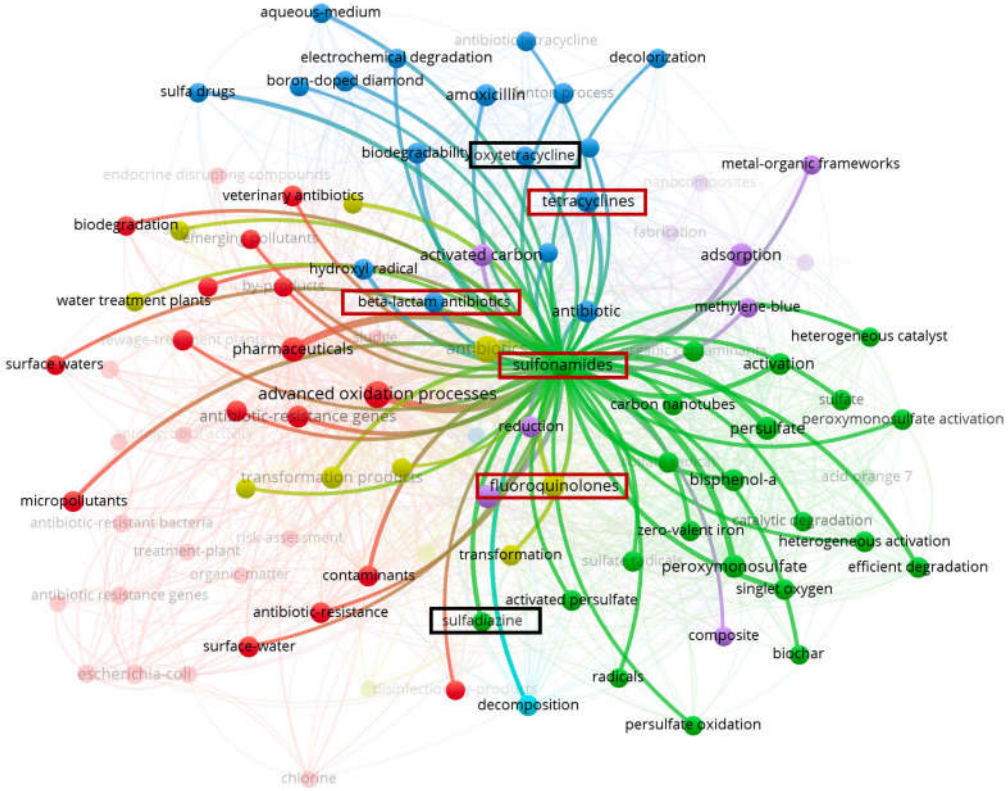
2.5 直接氧化驱动机制

在没有活化剂和外加能量的情况下,单用过硫酸盐对抗生素也有一定的降解效果. 在铁基双金属催化剂活化过硫酸盐体系中,过硫酸盐是否直接参与氧化污染物需要验证. Song 等[87]研究发现 PDS 对有机化合物具有直接选择性氧化能力. Yin 等[88]首先证明了单独 PMS 对磺胺类抗生素的直接氧化能力,揭示了 PMS 选择性和富电子污染物发生亲核反应或亲电反应,实现降解的性能和机制. 然而,仅用过硫酸盐对抗生素污染物的总有机碳(TOC)去除率很低,通过催化剂活化硫酸盐去除难降解污染物,仍是未来主要的研究方向.

3　典型抗生素的一般降解途径

在活化过硫酸盐体系中，活性物种降解抗生素的反应路径主要有加成、电子转移及氢提取等[89]. 在主要的活性物种中，$SO_4^{\cdot-}$ 的选择性降解体现在与抗生素化合物苯环部分反应时，倾向于发生电子转移，生成有机自由基阳离子，如式(15)所示[90]. 其余具有选择性的活性物种则更容易攻击抗生素污染物中的羟基(—OH)、氨基(—NH_3)和烷氧基(—OR)等电子供体位点. 当抗生素分子结构中含羰基(C═O)或硝基(—NO_2)时，不利于活性物种主导的氧化反应发生[89]. 此外，与含有烷基、醚基和不饱和结构的抗生素反应时，$SO_4^{\cdot-}$ 更可能优先发生夺氢反应[式(16)][91]和加成反应[式(17)][92].

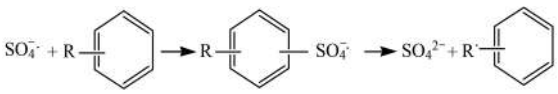
采取文献计量学对高级氧化法处理抗生素的研究进展进行分析，基于科睿唯安 Web of Science 核心数据库，搜索 2006 ~ 2022 年期间 SCI-E 文章，以“(advanced oxidation processes) AND antibiotics (所有字段)”为检索式进行筛选. 使用 VOSviewer 可视化分析软件对检索出的1 713篇文章中的关键词进行共现分析，如图 5 所示. 根据结果，发现氟喹诺酮类(fluoroquinolones)、磺胺类(sulfonamides)、四环素类(tetracyclines)和 β-内酰胺类(bata -lactams)抗生素出现的频率较高，表明这 4 种抗生素在该研究领域为热点研究对象. 图 6 展示了主要活性物种攻击这 4 种典型抗生素污染物位点机制.



圆圈大小表示出现的频率，出现的次数越多，圆圈越大

图 5　关键词共现的可视化分析

Fig. 5　Visual analysis of keyword co-occurrence



(15)

$$SO_4^{\cdot-} + RH \longrightarrow HSO_4^- + R\cdot \quad (16)$$

$$SO_4^{\cdot-} + H_2C{=}CHR \longrightarrow {}^-OSO_2OCH_2{-}CHR\cdot \quad (17)$$

3.1　氟喹诺酮类抗生素

对于氟喹诺酮类抗生素，通常会经历一系列较为相似的氧化分解过程，例如羟基取代、脱羧反应、哌嗪环分解、哌嗪基团脱落和氟释放等，最终氧化为小分子物质[93]. 这类抗生素结构中的哌嗪环最容易受到活性物种的攻击，一般会被率先氧化破坏，导致 C—N 键断裂. 其次，引起 C—C、C—F 和 C—O 键的依次断裂. 最后，污染物分子中其他化学键相继氧化断裂，从而实现污染物的降解[94].

3.2　磺胺类抗生素

对于磺胺类抗生素，目前已经证实有 5 种并存的降解途径. 首先，磺胺类抗生素结构中苯胺 N 的 $2FED^2_{HOMO}$ 值最大，极易受到 $SO_4^{\cdot-}$ 的攻击，产生苯胺自由基阳离子($SA^{+\cdot}$)[95]，再次经历水解过程后，最

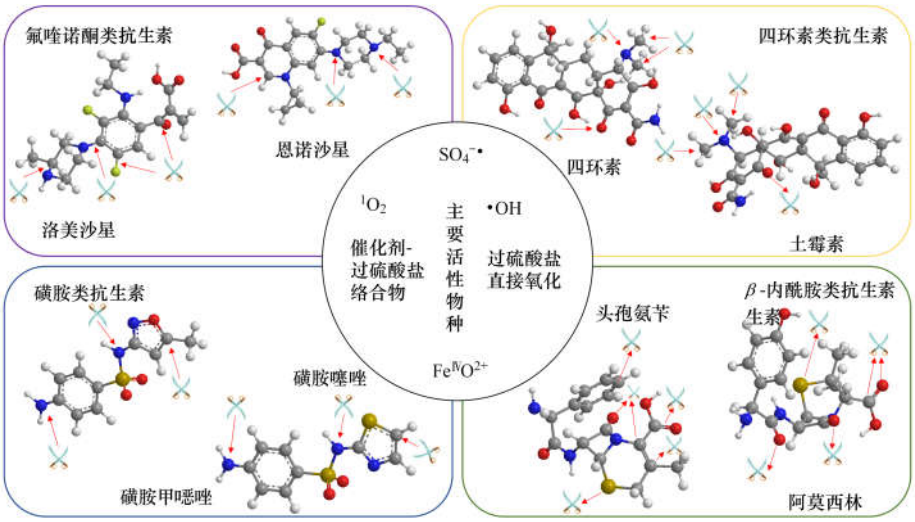


图 6 主要活性物种攻击典型抗生素污染物位点机制

Fig. 6 Mechanism of major active species attacking typical antibiotic-contaminant sites

终生成羟基化产物[96]. 其次,$SA^{+\cdot}$ 会被$SO_4^{-\cdot}$ 继续氧化,完成去质子化过程,生成一系列中间体[97,98],其中包含 N4-羟基-、4-亚硝基-和 4-硝基-等基团[97,99~101]. 其三,$SA^{+\cdot}$ 再次经历去质子化后,产生 SA—H·,然后发生二聚化反应生成偶联产物[97,101]. 其四,磺胺类抗生素的磺酰胺键(—SO_2—NH—)通常容易受到 ·OH和$SO_4^{-\cdot}$ 等自由基的攻击,发生断裂,形成氨基磺酸和 R—NH_2[96]. 这是由于磺酰胺键中的 N 也具有较高的 $2FED^2_{HOMO}$ 值,会发生电子转移. 其五,$SO_4^{-\cdot}$ 与不饱和噁唑和异噁唑衍生物通过在碳碳双键上发生加成反应,从而产生烯丙基自由基. H_2O/OH^- 进一步水解烯丙基自由基,形成羟基化噁唑[102]. 羟基化噁唑环可以通过半缩酮平衡步骤重排为羰基,该步骤在 C 单键处裂解杂环,并生成肟[103]. 肟与 H_2O 反应后,可进一步释放羟胺形成第二个羰基[104~107].

3.3 四环素类抗生素

根据对四环素类抗生素 Fukui 指数的评估,其分子中存在具有高电子密度的双键、酚和胺基团,容易受到自由基的攻击[108],因此四环素类抗生素的降解一般以去甲基化和羟基化两种路径开始[109]. $SO_4^{-\cdot}$ 是一种亲电子自由基,与富电子基团反应后,产生的中间产物会继续通过以下两种途径分解[110]:一种是二甲氨基和羟基一同脱落,在酚环上生成酮[111];另一种是中间体脱羟基后,持续被自由基和非自由基攻击,进一步被氧化成相对分子质量小的碎片[112]. 此外,四环素类抗生素还可能在脱水后[113],通过去甲基化、脱羟基化和开环过程生成相对分子质量小的中间体,直至被矿化为 CO_2 和 H_2O[114].

3.4 β-内酰胺类抗生素

β-内酰胺类抗生素在活性物种的攻击下会发生羟基化、水解、脱羧和胺氧化成羰基反应:① 羟基化反应中芳香环是活性自由基与 β-内酰胺抗生素作用的主要位点[115]. 硫原子是反应中第二个作用位点[116];② β-内酰胺类抗生素的水解几乎会发生在所有高级氧化过程中,且 β-内酰胺环的开环过程会导致其毒性降低[117];③ 脱羧过程是由 ·OH和$SO_4^{-\cdot}$[118]攻击裂解后的 β-内酰胺环结构或与 β-内酰胺环相邻的五元环开始的,提取电子后释放 CO_2[119],并进一步形成酸[120];④ 自由基能够增加攫氢反应中 α 氢原子的反应性[118,121],导致 β-内酰胺类抗生素中的 CH—NH_2 基团转化为亚胺 C═NH、C ═N 双键进一步断裂以形成羰基 C═O[122].

4 展望

(1)为提高过硫酸盐活化剂的性能,同时避免引入更多过渡金属引起二次污染,未来研究应聚焦于对铁基双金属催化剂本身的改性,例如,杂原子掺杂、缺陷位点构建、羟基氧基团引入、形貌晶型调控等. 同时,开发高稳定性、可再生回收的铁基双金属催化剂,对该技术的工程化应用也具有重要意义.

(2)活化过硫酸盐技术是多种驱动机制共存的复杂体系,研究该体系降解抗生素机制时,仅凭活性物种捕获实验所得的结论已被证明可信度低,需结合 EPR、荧光显微镜等更精准的技术进行验证分析. 此外,如何定量分析活性物种对降解效果的产生和贡献也是当前研究难点,亟需创新研究思路和技术手段突破这一瓶颈. 在工程应用方面,开发可高效产生强氧化性自由基的铁基双金属改性材料,仍是当前该领域的研究热点.

(3)高选择性降解污染物是活化过硫酸盐高级

氧化技术的特性,但对该特性的内在机制尚不清晰.理论上,降解同类污染物时,活性物种会选择性攻击特定位点,并以一种特定降解规律逐步实现污染物矿化.因此,基于过硫酸盐高级氧化处理某一类抗生素污染物的一般降解路径,值得进一步研究、总结和归纳.

(4)随着耦合高级氧化技术研究的兴起,今后可结合光催化、热活化、电化学和臭氧氧化等技术,辅助铁基双金属催化剂活化过硫酸盐,实现对污染物的协同降解,进一步拓宽该技术的实际应用范围.

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