

# 过硫酸盐高级氧化技术通过非自由基途径降解有机污染物的研究进展

江逸帆, 张鑫宇, 刘 琼\*

武汉工程大学化学与环境工程学院, 绿色化工过程教育部重点省重点实验室, 新型反应器与绿色化学工艺湖北省重点实验室, 湖北 武汉

收稿日期: 2023年4月17日; 录用日期: 2023年5月22日; 发布日期: 2023年5月31日

## 摘 要

水体中大量存在的有机污染物已经对生态系统造成不可避免的伤害。非自由基途径在过硫酸盐高级氧化技术中表现出选择性高、pH稳定性好、抗干扰能力强等优点, 成为近十年来的一个热门话题。但因非自由基途径多样, 机制复杂, 尚需深入了解。本文主要介绍了近年来单线态氧、表面结合氧化物、表面结合自由基、电子转移和高价金属等五种非自由基途径在过硫酸盐体系降解有机污染物的研究进展、研究成果和识别方法。最后对非自由基途径的发展进行了展望。

## 关键词

过硫酸盐, 非自由基途径, 降解

# Research Progress of Advanced Oxidation of Persulfate to Degrade Organic Pollutants by Non-Free Radical Pathway

Yifan Jiang, Xinyu Zhang, Qiong Liu\*

Hubei Key Laboratory of Novel Reactors and Green Chemical Processes, Key Laboratory of Green Chemical Processes of Ministry of Education, College of Chemical and Environmental Engineering, Wuhan Institute of Technology, Wuhan Hubei

Received: Apr. 17<sup>th</sup>, 2023; accepted: May 22<sup>nd</sup>, 2023; published: May 31<sup>st</sup>, 2023

## Abstract

A large amount of organic pollutants in water has caused inevitable damage to the ecosystem.

\*通讯作者。

文章引用: 江逸帆, 张鑫宇, 刘琼. 过硫酸盐高级氧化技术通过非自由基途径降解有机污染物的研究进展[J]. 自然科学, 2023, 11(3): 483-495. DOI: 10.12677/ojns.2023.113058

Non-free radical pathway has become a hot topic in the past decade due to its advantages of high selectivity, good pH stability and strong anti-interference ability in persulfate advanced oxidation technology. However, due to the variety of non-free radical pathways and complex mechanisms, further understanding is needed. In this paper, the research progress, achievements and identification methods of organic pollutants in persulfate system by five non-free radical pathways including singlet oxygen, surface-bound oxides, surface-bound free radicals, electron transfer and hypervalent metals were reviewed. Finally, the development of non-free radical pathways is prospected.

## Keywords

Persulfate, Non-Free Radical Mechanism, Degradation

Copyright © 2023 by author(s) and Hans Publishers Inc.

This work is licensed under the Creative Commons Attribution International License (CC BY 4.0).

<http://creativecommons.org/licenses/by/4.0/>



Open Access

## 1. 引言

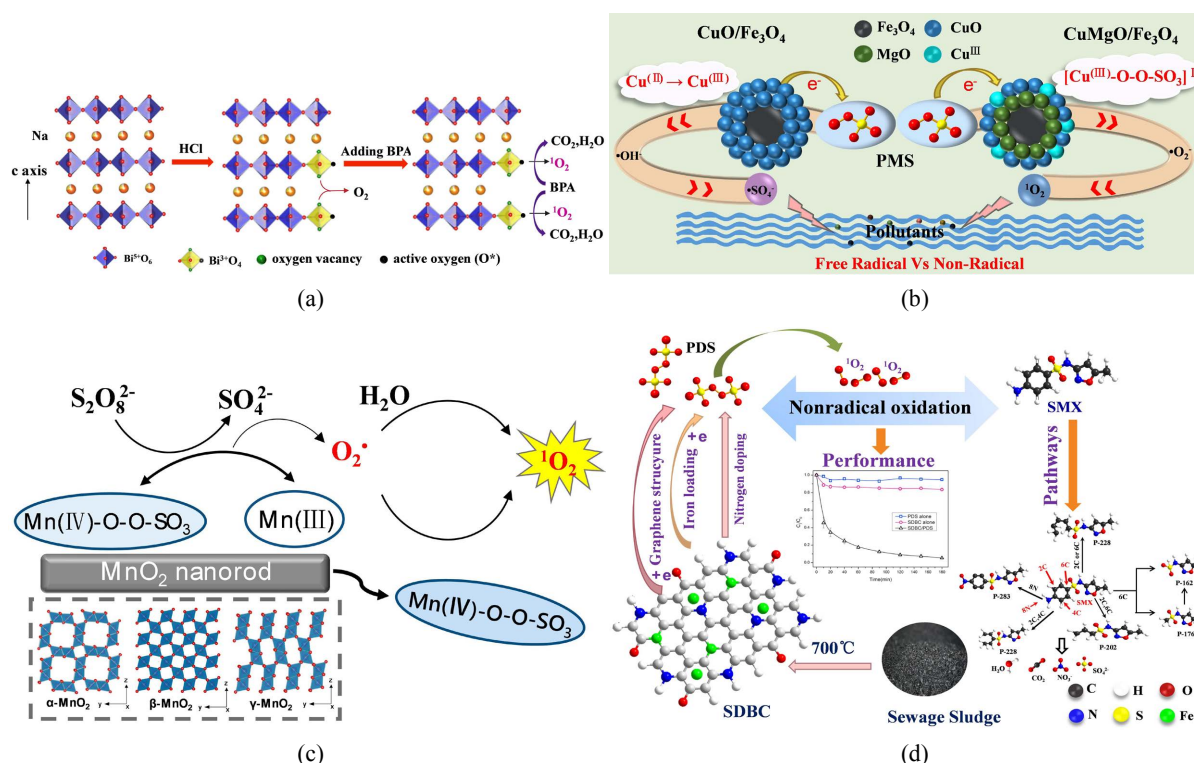
废水是已经被生活、工业和商业活动污染的水[1], 需要经过处理才能排放到其他水体中, 以避免更多的地下水污染。废水中可能含有重金属、有机污染物、无机污染物和新兴污染物等多种污染物[2]。几十年来, 人们一直在研究各种污染物, 但这些新出现的污染物主要来自制药、个人护理产品、激素和化肥行业等。当各种各样的内分泌干扰物(EDCs), 如增塑剂、除草剂、杀虫剂、药品和个人护理产品(PPCPs)、食品添加剂和甜味剂等从工业废水排放到水资源, 最终出现在饮用水中, 这一现象引起了科学界的极大关注[3]。污染物的产生主要有以下几个原因: 1) 生产和消费总量多: 中国人口快速增长, 中国是最大的EDCs、PPCPs 生产国与消费国之一, 年生产总量达几百万吨[3]。2) 产生途径多: 药物生产过程中的浪费, 药物使用时的不完全吸收, 以及药物处理时污水处理厂的不完全降解[4] [5], 都可能直接或间接的产生污染。3) 污染物的假持久性: 大量、广泛、不间断的使用各种护理用品和药物[6], 造成污染物的假持久性[7]。污染过程往往是动态的、隐匿的、累积的和不可逆的, 大多数有机污染物具有低溶解度、生态毒性、致突变性甚至致癌性, 可能对人类健康和生态系统造成威胁[8] [9]。因此污染物的完全降解就显得格外重要。近年来过硫酸盐高级氧化技术( $\text{SO}_4^{\cdot-}$ -AOPs)因其高效、温和的条件和能够完全矿化污染物的能力而受到研究者的青睐[8] [10]-[16]。过硫酸盐(PDS/PMS)活化产生的 $\text{SO}_4^{\cdot-}$ 和 $\cdot\text{OH}$ 自由基, 可以有效、非选择性地氧化有机污染物。然而,  $\text{SO}_4^{\cdot-}$ 和 $\cdot\text{OH}$ 在水溶液中不可避免地会与共存的有机物和无机底物发生反应, 过度的消耗过硫酸盐, 不能有效地降低其利用效率[17]。非自由基途径和自由基途径相比具有受环境影响较小, 选择性更强, 可以抑制有毒物质的产生等特点, 更适合应用在实际水体中[18]。

## 2. 非自由基途径

非自由基途径通常具有几个明显的优势: 1) 在去除富电子有机污染物方面具有更高的选择性[19]。2) 对卤化物离子和 NOMs 等水基质具有更高的耐受性[20]。3) 抑制卤化物消毒副产物的产生。非自由基氧化剂与卤化物离子具有低反应性[21]。因此, 非自由基过硫酸盐活化在废水中微量有机污染物的氧化中具有很好的应用潜力。非自由基途径一般可以分为单线态氧、表面结合氧化物、表面结合自由基、电子转移和高价金属五种。

## 2.1. 单线态氧

与经典的  $\text{SO}_4^{\cdot-}$  和  $\cdot\text{OH}$  相比,  $^1\text{O}_2$  是一种选择性氧化剂, 它与胺、硫化物和苯酚等富电子化合物的反应活性较高, 与饱和醇的反应活性较低[22]。此外,  $^1\text{O}_2$  的氧化势相对温和, 半衰期适中, 氧化机制不同[19]。过硫酸盐多相催化体系中  $^1\text{O}_2$  主要通过 PMS 的自分解(式 1) [23]、晶格氧的释放(图 1(a)) [24]、 $\text{O}_2^{\cdot-}$  的转化(图 1(b), 图 1(c)) [25] [26]等其他途径(图 1(d)) [27]生成。



**Figure 1.**  $^1\text{O}_2$  formation path: (a) lattice oxygen release of Bi(V)/Bi(III) composites [24], (b) (c)  $\text{O}_2^{\cdot-}$  conversion [25] [26], (d) activation of PMS by carbon-based materials to generate  $^1\text{O}_2$  [27]

**图 1.**  $^1\text{O}_2$  生成途径: (a) Bi(V)/Bi(III)复合材料晶格氧的释放[24], (b) (c)  $\text{O}_2^{\cdot-}$  的转化[25] [26], (d) 碳基材料活化 PMS 生成  $^1\text{O}_2$  [27]

研究者们发现可以通过调节特定的参数来有效产生  $^1\text{O}_2$ 。Bu 等人[28]对不同 BiOBr 基催化剂活化 PDS 降解双酚 A 进行了全面的研究。研究发现, 在碱性条件下氧空位多的 BiOBr 可以产生更多的  $^1\text{O}_2$ , 从而更有效活化 PDS 降解双酚 A。结果表明, 可以通过调节氧空位的含量和溶液体系的 pH 值来调控  $^1\text{O}_2$  产生的量。Yao 等人[29]开发了一个简单的策略, 通过调整双金属沸石咪唑骨架( $\text{Zn}_x\text{Co}_{1-x}\text{-ZIFs}$ )的 Zn/Co 比值, 在原子水平上调节 Co-N-C 催化剂的组成和配位, 通过催化剂设计来实现污染物的选择性氧化, 有效生产  $^1\text{O}_2$ 。  $\text{Zn}_4\text{Co}_1\text{-C}$  在苯酚/苯甲酸(苯酚/BA)混合溶液中对苯酚的选择性去除率为 98%。密度泛函理论计算和实验结果表明,  $\text{Zn}_4\text{Co}_1\text{-C}$  中生成了更多活性的  $\text{CoN}_4$  位点, 有利于过氧单硫酸盐活化生成  $^1\text{O}_2$ 。

$^1\text{O}_2$  识别方法(表 1)主要有 1) 捕获剂实验, 在特定的  $^1\text{O}_2$  捕获剂下, 根据降解效率是否发生改变来确认, 常用的猝灭剂有: 糠醇(FFA), L-组氨酸和叠氮化合物( $\text{NaN}_3$ ) [30] [31] [32]; 2) 判断是否可以和空气中的氧气发生反应产生  $^1\text{O}_2$ , 可以通过在  $\text{N}_2$  氛围/惰性气体(目的是为了除氧)下反应, 根据降解效率是否发

生改变来确认[33]; 3) EPR 实验, 在水做溶剂的反应体系下加入 TEMP 捕获剂, 根据是否有特征  $^1\text{O}_2$  的信号来确认[30] [34]; 4) 更换溶剂, 将水更换成重水( $\text{D}_2\text{O}$ ), 根据降解效率和 EPR 信号是否发生改变来确认[35], 文献报道  $^1\text{O}_2$  在  $\text{D}_2\text{O}$  中的寿命比水中更长[36]; 5) 测试  $^1\text{O}_2$  的加和产物, 通过高效液相色谱和质谱(HPLC-MS)连用来确认[37]。

**Table 1.** Identification pathways of  $^1\text{O}_2$  in different literatures

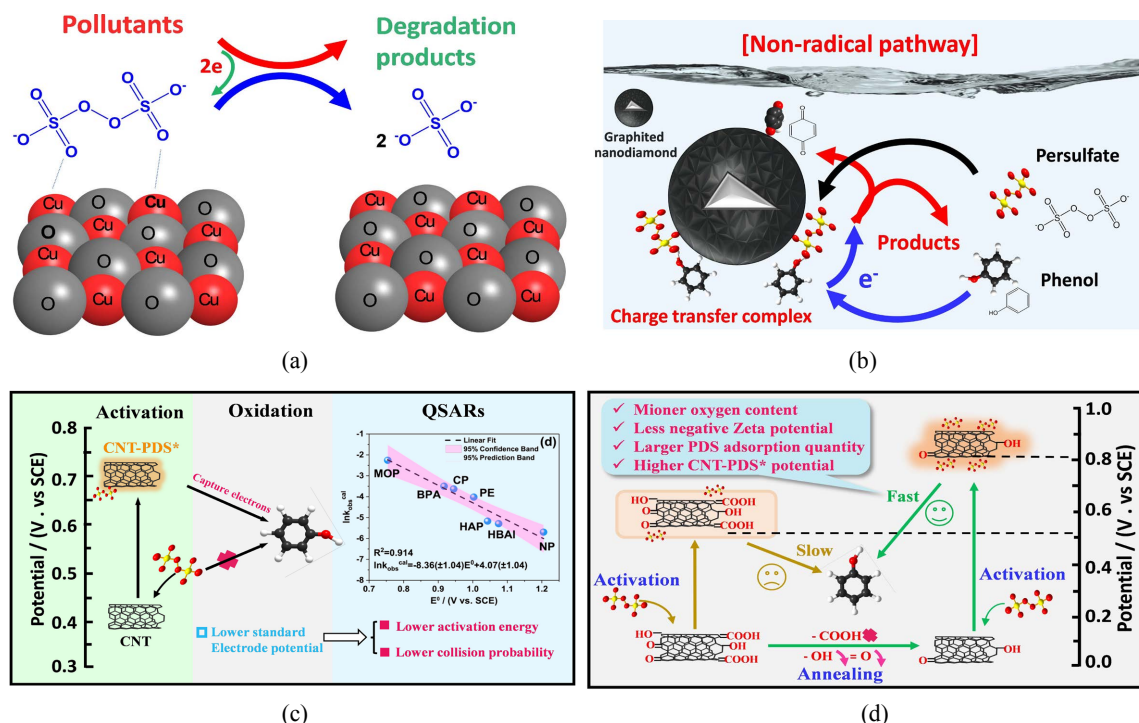
**表 1.** 不同文献中  $^1\text{O}_2$  的识别方法

| 序号 | 材料                                   | 降解污染物      | 过硫酸盐 | 识别方法                                                            | 参考文献 |
|----|--------------------------------------|------------|------|-----------------------------------------------------------------|------|
| 1  | $\text{La}_2\text{CuO}_{4-\delta}$   | 双酚 A (BPA) | PMS  | 捕获剂( $\text{NaN}_3$ )和 EPR( $\text{TEMP}-^1\text{O}_2$ )实验      | [38] |
| 2  | 碳纳米管(CNTs)                           | 2,4-二氯苯酚   | PDS  | EPR 和 HPLC-MS 实验                                                | [37] |
| 3  | $\text{CoFe}_2\text{O}_4/\text{HPC}$ | BPA        | PMS  | 捕获剂(L-组氨酸)和 EPR 实验                                              | [39] |
| 4  | i-rGO-NS                             | 对羟基苯甲酸甲酯   | PMS  | 捕获剂(L-组氨酸)和 EPR 实验                                              | [40] |
| 5  | CNT                                  | 孟加拉红       | PMS  | 指示剂(FFA)、捕获剂(L-组氨酸和 $\text{NaN}_3$ )和 $\text{D}_2\text{O}$ 作为溶剂 | [41] |
| 6  | 石墨烯纳米片                               | 酸性橙 G      | PDS  | 探针(FFA)、捕获剂( $\text{NaN}_3$ )和 $\text{N}_2$ 鼓吹实验、               | [33] |

**2.2. 表面结合氧化物**

表面结合氧化物的主要机制是催化剂和过硫酸盐之间通过络合的方式结合, 结合后催化剂和过硫酸盐整体的氧化还原电位升高, 接着从污染物中提取电子, 最终达到降解的目的。Zhang 等人[42]研究发现  $\text{CuO}$  和 PDS 可以通过外球作用高效降解 2,4-二氯苯酚(2,4-DCP), 当  $\text{CuO}$  浓度为 200 mg/L, PDS 浓度为 40  $\mu\text{M}$  时, 40 分钟可完全降解浓度为 5  $\mu\text{M}$  的 2,4-DCP (图 2(a))。Lee 等人[26]研究发现, 石墨纳米金刚石(G-ND)在过硫酸盐活化方面优于其他基准碳材料, 如石墨、石墨烯、富勒烯和碳纳米管。G-ND/过硫酸盐体系对酚类化合物和一些药物有选择性反应, 其降解动力学不受氧化剂清除剂和天然有机物的抑制。线性扫描伏安法、热重分析、傅立叶红外光谱和电子顺磁共振光谱分析结果表明, 过硫酸盐和苯酚都能与 G-ND 表面有效结合, 并可能形成电荷转移络合物, 其中 G-ND 在苯酚向过硫酸盐的电子转移中起关键作用(图 2(b))。Ren 等人[27] [43]揭示了酚类化合物(PCs)非自由基氧化的实质和这一过程中主要的影响因素。结果表明, PDS 首先吸附在 CNT 上, 然后 CNT 活化 PDS 形成亚稳态  $\text{CNT-PDS}^*$  中间体。同时, 配合物有效提高了 CNT 的整体电位(+0.65 V 左右), PDS/碳配合物呈现出较高的氧化还原状态, 可将共吸附的 PCs 氧化成电位较低的产物(图 2(c))。在此过程中, 非自由基体系的氧化能力受到半波电位( $\phi_{1/2}$ , 由固有官能团决定)、PCs 的离子/分子状态和碳纳米管中氧基浓度的影响。 $\phi_{1/2}$  值较低的 PCs 更有利于将电子提供给  $\text{CNT-PDS}^*$ , 从而加速 PDS 的消耗。相反, 与  $\text{CNT-PDS}^*$  电位相比, 具有更高  $\phi_{1/2}$  值的 PC (如硝基苯酚, 羟基苯乙酮和羟基苯甲酸甲酯)将阻碍电子转移过程。PC 的负电荷离子态不利于碳纳米管表面的接近, 容易阻碍碳纳米管表面的电子穿梭过程。此外碳纳米管中氧基浓度的降低有利于 PDS 的吸附, 易于形成亚稳态  $\text{CNT-PDS}^*$ ; 其中  $\text{CNT-PDS}^*$  的非自由基氧化速率与配合物的电位呈指数相关, 表明  $\text{CNT-PDS}^*$  的非自由基氧化经历了类似于阳极氧化的机制(图 2(d))。对表面结合氧化物这一机理来说, 污染物的降解效率不仅和材料有关, 而且和污染物的半波电位(半波电位越小越容易降解) [44]、IP 值(IP 值低于 9 eV 才可发生发应) [45]的大小也有关。

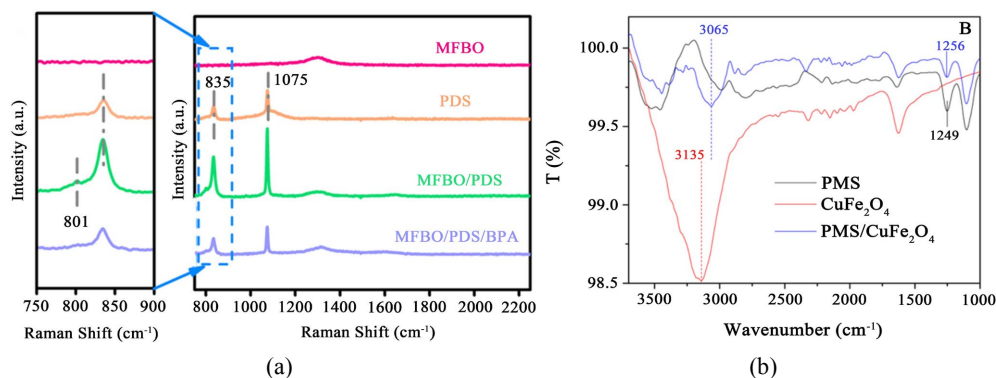
表面结合氧化物是否形成, 主要通过拉曼光谱和表面衰减全反射光谱(ATR-FTIR)两种最直接的证据来确定[27] [46]。Ma 等人[47]通过原位拉曼光谱提供了 MFBO-PDS 配合物形成的直接证据。从图 3(a)中可以看出, 除了 PDS 分子在 1067 和 835  $\text{cm}^{-1}$  处的特征峰, MFBO/PDS 体系在 801  $\text{cm}^{-1}$  附近出现了一个



**Figure 2.** Schematic diagram of the mechanism of surface binding oxides: (a) exosphere interaction of CuO and PDS [42], (b) G-ND activated persulfate degradation of phenol [26], (c) formation of complexes of CNT and PDS degradation of different pollutants [27] and (d) complexation of different CNTs and PDS [43]

**图 2.** 表面结合氧化物机理示意图: (a) CuO 和 PDS 的外球作用[42]; (b) G-ND 活化过硫酸盐降解苯酚[26]; (c) CNT 和 PDS 形成配合物降解不同污染物[27]; (d) 不同 CNT 和 PDS 的络合作用[43]

新的峰, 这可能是亚稳反应配合物中过氧化 O-O 键延长的弯曲振动所致。此外, 添加 BPA 后,  $S_2O_8^{2-}$  波段的峰强度减弱,  $801\text{ cm}^{-1}$  处出现的峰消失更加证明了亚稳反应配合物的形成。Zhang 等人[48]通过测试不同反应液的 ATR-FTIR, 确定了表面结合氧化物这一机理。如图 3(b)所示,  $1249\text{ cm}^{-1}$  的红外波段可能来自于  $HSO_5^-$  或  $SO_4^{2-}$  的 S-O 拉伸振动, 在  $CuFe_2O_4$  和 PMS 同时存在时, 该波段的蓝移分别为  $7\text{ cm}^{-1}$ 。结果表明,  $HSO_5^-$  的 S-O(OH)结构中的 OH 在与氧化物表面结合时, 从相邻的 S-O 键吸引的电子密度较小, 使其更强。表面 Cu(II)给了  $HSO_5^-$  的 OH 电子, 抑制了相邻 S-O 的电子吸引。



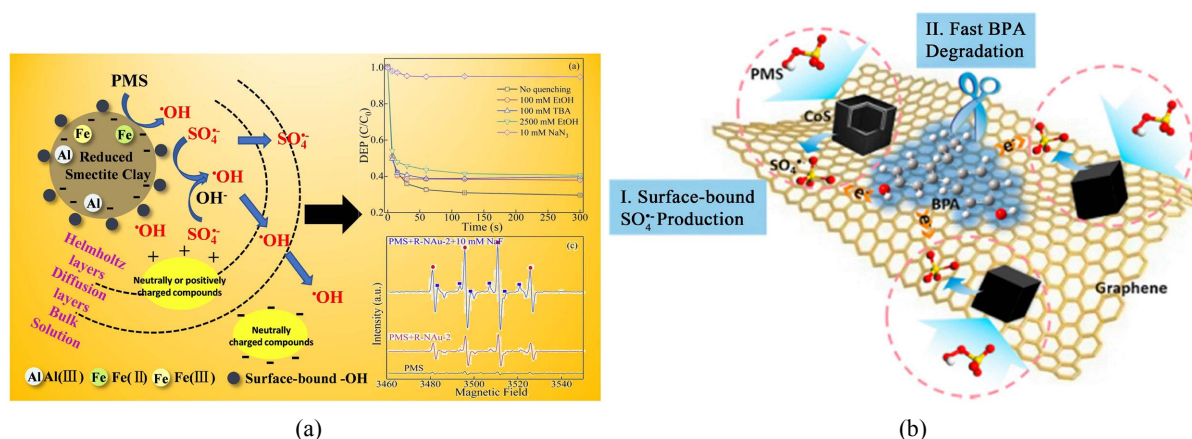
**Figure 3.** The most direct means of proving the formation of surface bound oxides are (a) Raman spectra under different systems [47], and (b) ATR-FTIR spectra under different systems [48]

**图 3.** 证明表面结合氧化物形成的最直接手段: (a) 不同体系下的拉曼光谱[47], (b) 不同体系下的 ATR-FTIR 光谱[48]

### 2.3. 表面结合自由基

表面结合自由基机理包括表面结合的  $\text{SO}_4^{\cdot-}$  和  $\cdot\text{OH}$  自由基。与自由基机理不同,生成的  $\text{SO}_4^{\cdot-}$  和  $\cdot\text{OH}$  被吸附在催化剂表面,而不是分散在溶液中[18]。此外,经典的亲水自由基猝灭剂(MeOH, TBA 等对这些体系的催化降解没有明显的淬灭作用。Liang 等人[49]采用新型负载型氧化铜催化剂,在室温(即  $20^\circ\text{C}$ )的水溶液中活化过硫酸盐(PS)氧化对氯苯胺(PCA)。氧化铜催化过硫酸盐氧化对 PCA 的破坏效果明显优于单纯的 PS 或氧化铜体系。通过对自由基机理的分析,用三种自由基清除剂(苯酚、MA 和 TBA)确定,在初始 pH 为 7 时, CuO/PS 体系降解 PCA 的过程可能不是发生在液相中,而是发生在氧化铜表面的边界层中。Chen 等人[50]制备的还原含铁蒙脱石粘土(R-NAu-2)能有效激活 PMS,在 300 s 内诱导邻苯二甲酸二乙酯(DEP)的快速降解。化学探针、自由基猝灭和电子顺磁共振(EPR)结果证实,  $\cdot\text{OH}$  和  $\text{SO}_4^{\cdot-}$  活性物种主要结合在粘土表面,而不是在体溶液中,这导致 DEP、磺胺甲恶唑、苯酚、金四环素和苯甲酸等有机化合物的快速降解,阴离子  $\text{Cl}^-$  和  $\text{NO}_3^-$  对 DEP 降解的影响有限,而  $\text{HCO}_3^-$  由于反应 pH 的增加而抑制了 DEP 的降解(图 4(a))。Zhang 等人[51]研究了非晶态  $\text{FeOOH}$  活化过氧单硫酸盐(PMS)降解磺胺甲恶唑(SMX)。非晶态  $\text{FeOOH}$  在分解 PMS 和降解 SMX 方面表现出比晶态  $\alpha\text{-FeOOH}$  和  $\beta\text{-FeOOH}$  更好的性能。淬灭实验和 EPR 测试表明,非晶态  $\text{FeOOH}$  活化 PMS 的机制主要是表面结合自由基( $\cdot\text{OH}$  和  $\text{SO}_4^{\cdot-}$ )。基本上,表面结合的  $\cdot\text{OH}$  自由基是该体系中主要的活性氧化物,主要是通过非晶态  $\text{FeOOH}$ -PMS 配合物的分解产生的。Zhu 等人[52]合成的石墨烯纳米片支撑的空心硫化钴纳米晶体( $\text{Co}_3\text{S}_4@\text{GN}$ ,  $\text{CoS}@\text{GN}$ ),  $\text{CoS}@\text{GN}$ /PMS 对 BPA 的降解效率在 8 min 内达到 100%,动力学常数( $0.62 \text{ min}^{-1}$ )比大多数报道的多相催化剂高 1~2 个数量级。淬灭试验和 EPR 检测揭示了石墨烯在表面结合  $\text{SO}_4^{\cdot-}$  生成中的关键作用(图 4(b))。

识别表面结合自由基机理常用的方法: 1) 加入表面清除剂 KI [53]; 2) 加入对固体材料表面具有亲和力的苯酚[54]; 3) 测试加入 F 前后的 EPR 信号变化,根据文献调研, F 的加入可以促进表面结合自由基的释放, EPR 信号会增加[55]。



**Figure 4.** Schematic diagram of surface binding free radical mechanism: (a) reduced Fe-containing montmorillonite clay (R-NAu-2) activated PMS to degrade diethyl phthalate [50], (b)  $\text{CoS}@\text{GN}$  activated PMS to degrade BPA in situ [52]

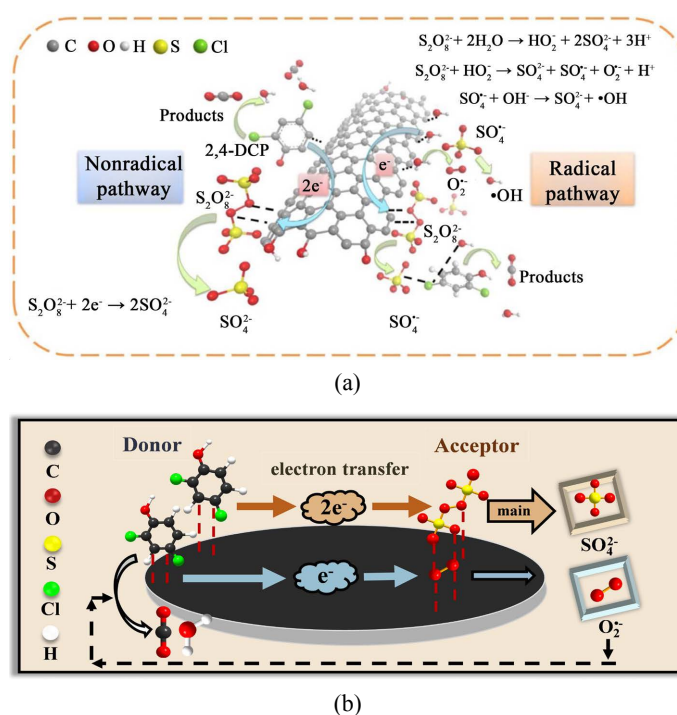
**图 4.** 表面结合自由基机理示意图: (a) 还原含铁蒙脱石粘土(R-NAu-2)活化 PMS 降解邻苯二甲酸二乙酯[50], (b)  $\text{CoS}@\text{GN}$  活化 PMS 原位降解 BPA [52]

### 2.4. 电子转移

过硫酸盐非自由基电子转移机制通常发生在导电性能好的金属和非金属异相催化剂中,在介导的电子转移过程中,催化剂作为电子桥(或导体),促进电荷从共吸附有机物(电子给体)向过硫酸盐(电子受体)

的转移[56]。Tang 等人[57]采用六孔有序介孔碳(CMK-3)活化过硫酸盐(PS)降解 2,4-二氯苯酚(2,4-DCP), 20 min 内去除率达 90%, 其较高的催化效率可能是由于 CMK-3 的大吸附容量加速了电子转移。研究发现, 活化剂的比表面积(SSA)、缺陷位点和官能团与其催化效率和钝化程度密切相关。与其他纳米碳相比, CMK-3 具有有序的介孔结构, SSA 大, 缺陷度高, 具有更好的可重用性(图 5(a))。Yang 等人[58]制备的石墨多壁碳纳米管(MWCNTs)被可控地解压缩成边缘丰富的石墨烯纳米带, 富集的碳边显著提高了催化性能, 并可作为杂原子(N, S)掺杂的承载位点, 促进碳催化。样品(NS-2)在 20 分钟内完全去除 BPA, 速率常数为  $0.182 \text{ min}^{-1}$ 。通过自由基筛选试验、原位拉曼和电化学表征, 阐明了解压缩的多壁碳纳米管遵循非自由基电子转移途径。揭示的机理强调了在边缘富集碳催化剂中必要的石墨度和电导率对于更好的催化性能的重要性。Yu 等人[59]制备了虾壳分级多孔生物炭(PSS-bio), 并将其用于过硫酸盐活化去除 2,4-二氯苯酚。热解温度对碳的结构和性质调控起着重要作用, 其中  $800^\circ\text{C}$  下制备的 PSS-bio (PSS-800)具有最快的吸附能力和最优的催化活性, 降解率是  $400^\circ\text{C}$  下制备的 PSS-bio (PSS-400)的 29 倍。进一步的分析表明, 层次孔和碳结构是影响生物炭 AOP 的两个关键因素。有趣的是, PSS-400 中原本以自由基为主的途径也在 PSS-800 中转变为非自由基的途径(直接双电子转移途径), 其效率会受到 pH 值、腐殖酸和阴离子的干扰, 无论其浓度低至 5 mm 还是高至 500 mm, 显示了其在处理高盐度水和富有机水方面的应用潜力(图 5(b))。

电子转移机理通常使用电化学手段来鉴定[56]。1) 线性扫描伏安法(LSV)监测体系电流变化[60]; 2) 时间安培(CP)揭示有机物到过硫酸盐的电子转移方向[61]; 3) 开路电压(OPC)反应电势变化[62]; 4) 电化学阻抗(EIS)估计催化剂的电导率; 5) Tafel 斜率评价催化剂电化学动力学和确定相应限速步骤的重要参数[63]; 6) 循环伏安法(CV)用来识别电化学可逆性和半波电势[27]。



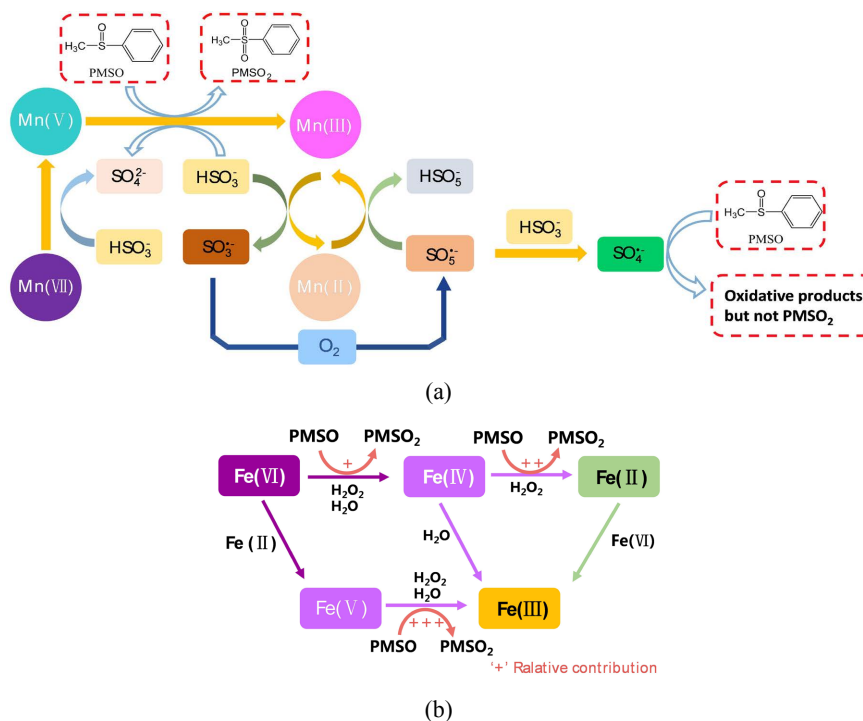
**Figure 5.** Electron transfer mechanism diagram: (a) activation of ordered mesoporous carbon by persulfate [57]; (b) PSS-800 activates PDS to degrade 2,4-DCP [59]

**图 5.** 电子转移机理图: (a) 过硫酸盐活化有序介孔碳[57]; (b) PSS-800 活化 PDS 降解 2,4-DCP [59]

## 2.5. 高价金属

文献通常报道的高价金属为 Fe、Co、Cu、Mn 等, 通过直接或间接利用具有较强氧化还原能力的高价金属来降解有机污染物。Jiang 等人[64]报道了单原子 Fe(III)和氮掺杂碳(Fe-N-C)可以有效地激活 PDS, 选择性地去除一些有机污染物, 遵循非自由基途径。单原子 Fe(III)与吡啶 N 原子配位是催化分解 PDS 的活性位点。然而, PDS 分解不产生自由基或活性氧。配位的 Fe(III)很可能通过 PDS 的双电子抽离转化为 Fe(V), Fe(V)可能是去除有机污染物的中间氧化剂。Yi 等人[65]揭示了 Co(IV)介导的氧化降解芳香烃污染物的机理。以  $\text{Co}_3\text{O}_4/\text{PMS}$  为基础的分级反应器对芳香性有机污染物的降解效率达到 90%。电子对磁共振表征、自由基猝灭和探针氧化实验证实, Co(IV)是  $\text{Co}_3\text{O}_4/\text{PMS}$  分级反应器中的主要反应物质。进一步的清除实验验证了 Co(IV)在去除芳香族污染物中起着最关键的作用。Co(IV)的主要来源是固定化的  $\text{Co}_3\text{O}_4/\text{PMS}$ , 而不是  $\text{Co}^{x+}$ 离子在  $\text{Co}_3\text{O}_4/\text{PMS}$  分级反应器中的浸出。Chen 等人[66]首次报道了 Cu(II)配合物在配位涉及合适的配体时可能是 PDS 的有效激活剂。以头孢氨苄(CFX)为代表, 研究表明 Cu(II)与 CFX 配合物能有效激活 PDS, 诱导 CFX 快速降解。PDS/Cu(II)对 CFX 的转化产物与典型的自由基氧化过程(如 PDS/Ag(I))有很大的不同, 但与 Cu(III)对 CFX 的氧化产物非常相似。与 CFX 络合后 Cu(II)的电子密度增大, 有利于 Cu(II)向 PDS 的电子转移, 生成自由基和 Cu(III)。产生的 Cu(III), 而不是自由基, 在 CFX 的整体降解中起主要作用, 并在催化循环中再生 Cu(II)。当与 Cu(II)配合时, 这种新的激活过程可以发生在广泛的污染物(头孢菌素、青霉素和四环素抗生素)和配体上, 并且发现含 N 的官能团(如胺)可以形成有效的 Cu(II)配合物来激活 PDS。

高价金属通常用二苯甲基亚砷(PMSO)来鉴定(图 6), 文献报道高价金属 Mn、Co、Fe 可以将 PMSO 转化成甲基苯基砷(PMSO<sub>2</sub>) [67] [68] [69]。



**Figure 6.** Schematic diagram of identification of high-priced metals through PMSO: (a) high-priced Mn [67], (b) high-priced Fe [70]

**图 6.** 高价金属通过 PMSO 识别的示意图: (a) 高价态 Mn [67], (b) 高价态 Fe [70]

### 3. 结语与展望

目前, 过硫酸盐体系中的非自由基氧化引起了人们极大的兴趣, 深入了解将极大地促进其在催化氧化和废水处理中的应用。本文主要总结了不同非自由基途径降解有机污染物的研究进展、研究成果以及非自由基机理的识别方法。过硫酸盐体系中的非自由基途径具有中等的氧化还原电位, 这使其能够适应不同的 pH, 并抵抗无机离子和背景有机物的干扰。因此, 非自由基氧化过程在去除自然水体中的有机污染物方面具有广阔的前景。研究者在这一方面也做出了大量努力, 提出可能的反应途径和作用机理。然而, 非自由基途径大多集中在催化剂的表面, 作用位点和氧化能力有限, 造成对有机污染物氧化不完全, 矿化能力弱。因此, 自由基与非自由基的结合体系对于有机污染物的完全分解具有重要意义, 未来在此基础上结合多种氧化技术来提升对有机污染物的氧化效率是非常重要的。

### 参考文献

- [1] Richmond, E.K., Rosi, E.J., Walters, D.M., Fick, J., Hamilton, S.K., Brodin, T., Sundelin, A. and Grace, M.R. (2018) A Diverse Suite of Pharmaceuticals Contaminates Stream and Riparian Food Webs. *Nature Communication*, **9**, Article No. 4491. <https://doi.org/10.1038/s41467-018-06822-w>
- [2] Xiang, Y., Wu, H.H., Li, L., Ren, M., Qie, H.T. and Lin, A.J. (2021) A Review of Distribution and Risk of Pharmaceuticals and Personal Care Products in the Aquatic Environment in China. *Ecotoxicology and Environmental Safety* **213**, Article ID: 112044. <https://doi.org/10.1016/j.ecoenv.2021.112044>
- [3] UshaVipinachandran, V., Rajendran, S., Badagoppam Haroon, K.H., Ashokan, I., Mondal, A. and Bhunia, S.K. (2020) Detoxification of Endocrine Disruptors in Water Using Visible-Light-Active Nanostructures: A Review. *ACS Applied Nano Materials*, **3**, 11659-11687. <https://doi.org/10.1021/acsanm.0c02974>
- [4] Rout, P.R., Zhang, T.C., Bhunia, P. and Surampalli, R.Y. (2021) Treatment Technologies for Emerging Contaminants in Wastewater Treatment Plants: A Review. *Science of the Total Environment*, **753**, Article ID: 141990. <https://doi.org/10.1016/j.scitotenv.2020.141990>
- [5] Patel, M., Kumar, R., Kishor, K., Mlsna, T., Pittman, C.U., Jr. and Mohan, D. (2019) Pharmaceuticals of Emerging Concern in Aquatic Systems: Chemistry, Occurrence, Effects, and Removal Methods. *Chemical Reviews*, **119**, 3510-3673. <https://doi.org/10.1021/acs.chemrev.8b00299>
- [6] He, M.J., Wan, Z.H., Tsang, D.C.W., Sun, Y.Q., Khan, E., Hou, D.Y. and Graham, N.J.D. (2021) Performance Indicators for a Holistic Evaluation of Catalyst-Based Degradation—A Case Study of Selected Pharmaceuticals and Personal Care Products (PPCPs). *Journal of Hazardous Materials*, **402**, Article ID: 123460. <https://doi.org/10.1016/j.jhazmat.2020.123460>
- [7] Su, C., Cui, Y., Liu, D., Zhang, H. and Baninla, Y. (2020) Endocrine Disrupting Compounds, Pharmaceuticals and Personal Care Products in the Aquatic Environment of China: Which Chemicals are the Prioritized Ones? *Science of the Total Environment*, **720**, Article ID: 137652. <https://doi.org/10.1016/j.scitotenv.2020.137652>
- [8] Zhou, Z., Liu, X., Sun, K., Lin, C.Y., Ma, J., He, M.C. and Ouyang, W. (2019) Persulfate-Based Advanced Oxidation Processes (AOPs) for Organic-Contaminated Soil Remediation: A Review. *Chemical Engineering Journal*, **372**, 836-851. <https://doi.org/10.1016/j.cej.2019.04.213>
- [9] Li, Z.P., Yu, X.P., Yu, F.R. and Huang, X. (2021) Occurrence, Sources and Fate of Pharmaceuticals and Personal Care Products and Artificial Sweeteners in Groundwater. *Environmental Science and Pollution Research*, **28**, 20903-20920. <https://doi.org/10.1007/s11356-021-12721-3>
- [10] Ghanbari, F. and Moradi, M. (2017) Application of Peroxymonosulfate and Its Activation Methods for Degradation of Environmental Organic Pollutants: Review. *Chemical Engineering Journal*, **310**, 41-62. <https://doi.org/10.1016/j.cej.2016.10.064>
- [11] Waclawek, S., Lutze, H.V., Grübel, K., Padil, V.V.T., Černík, M. and Dionysiou, D.D. (2017) Chemistry of Persulfates in Water and Wastewater Treatment: A Review. *Chemical Engineering Journal*, **330**, 44-62. <https://doi.org/10.1016/j.cej.2017.07.132>
- [12] Chen, X., Oh, W.D. and Lim, T.T. (2018) Graphene- and CNTs-Based Carbocatalysts in Persulfates Activation: Material Design and Catalytic Mechanisms. *Chemical Engineering Journal*, **354**, 941-976. <https://doi.org/10.1016/j.cej.2018.08.049>
- [13] Wang, J.L. and Wang, S.Z. (2018) Activation of Persulfate (PS) and Peroxymonosulfate (PMS) and Application for the Degradation of Emerging Contaminants. *Chemical Engineering Journal*, **334**, 1502-1517.

- <https://doi.org/10.1016/j.cej.2017.11.059>
- [14] Lee, J., Von Gunten, U. and Kim, J.H. (2020) Persulfate-Based Advanced Oxidation: Critical Assessment of Opportunities and Roadblocks. *Environmental Science & Technology*, **54**, 3064-3081. <https://doi.org/10.1021/acs.est.9b07082>
- [15] Wang, L.H., Xu, H.D., Jiang, N., Wang, Z.M., Jiang, J. and Zhang, T. (2020) Trace Cupric Species Triggered Decomposition of Peroxymonosulfate and Degradation of Organic Pollutants: Cu(III) Being the Primary and Selective Intermediate Oxidant. *Environmental Science & Technology*, **54**, 4686-4694. <https://doi.org/10.1021/acs.est.0c00284>
- [16] Gao, Y., Wang, Q., Ji, G.Z. and Li, A.M. (2022) Degradation of Antibiotic Pollutants by Persulfate Activated with Various Carbon Materials. *Chemical Engineering Journal*, **429**, Article ID: 132387. <https://doi.org/10.1016/j.cej.2021.132387>
- [17] Ding, Y.B., Wang, X.R., Fu, L.B., Peng, X.Q., Pan, C., Mao, Q.H., Wang, C.J. and Yan, J.C. (2021) Nonradicals Induced Degradation of Organic Pollutants by Peroxydisulfate (PDS) and Peroxymonosulfate (PMS): Recent Advances and Perspective. *Science of the Total Environment*, **765**, Article ID: 142794. <https://doi.org/10.1016/j.scitotenv.2020.142794>
- [18] Zhou, X.Q., Zhao, Q.D., Wang, J., Chen, Z.L. and Chen, Z.Q. (2021) Nonradical Oxidation Processes in PMS-Based Heterogeneous Catalytic System: Generation, Identification, Oxidation Characteristics, Challenges Response and Application Prospects. *Chemical Engineering Journal*, **410**, Article ID: 128312. <https://doi.org/10.1016/j.cej.2020.128312>
- [19] Yu, J.F., Tang, L., Pang, Y., Liang, X.M., Lu, Y., Feng, H.P., Wang, J.J., Deng, L.F., Zou, J.J., Zhu, X. and Tang, J.L. (2022) Non-Radical Oxidation in Environmental Catalysis: Recognition, Identification, and Perspectives. *Chemical Engineering Journal*, **433**, Article ID: 134385. <https://doi.org/10.1016/j.cej.2021.134385>
- [20] Duan, X.G., Sun, H.Q., Shao, Z.P. and Wang, S.B. (2018) Nonradical Reactions in Environmental Remediation Processes: Uncertainty and Challenges. *Applied Catalysis B: Environmental*, **224**, 973-982. <https://doi.org/10.1016/j.apcatb.2017.11.051>
- [21] Xue, Y., Wang, Z.H., Naidu, R., Bush, R., Yang, F., Liu, J.S. and Huang, M.H. (2022) Role of Halide Ions on Organic Pollutants Degradation by Peroxygens-Based Advanced Oxidation Processes: A Critical Review. *Chemical Engineering Journal*, **433**, Article ID: 134546. <https://doi.org/10.1016/j.cej.2022.134546>
- [22] Peng, W.Y., Dong, Y.X., Fu, Y., Wang, L.L., Li, Q.C., Liu, Y.J., Fan, Q.Y. and Wang, Z.H. (2021) Non-Radical Reactions in Persulfate-Based Homogeneous Degradation Processes: A Review. *Chemical Engineering Journal*, **421**, Article ID: 127818. <https://doi.org/10.1016/j.cej.2020.127818>
- [23] Ge, L., Shao, B.B., Liang, Q.H., Huang, D.L., Liu, Z.F., He, Q.Y., Wu, T., Luo, S.H., Pan, Y., Zhao, C.H., Huang, J.H. and Hu, Y.M. (2022) Layered Double Hydroxidebased Materials Applied in Persulfate Based Advanced Oxidation Processes: Property, Mechanism, Application and Perspectives. *Journal of Hazardous Materials*, **424**, Article ID: 127612. <https://doi.org/10.1016/j.jhazmat.2021.127612>
- [24] Zhang, T., Ding, Y.B. and Tang, H.Q. (2015) Generation of Singlet Oxygen over Bi(V)/Bi(III) Composite and Its Use for Oxidative Degradation of Organic Pollutants. *Chemical Engineering Journal*, **264**, 681-689. <https://doi.org/10.1016/j.cej.2014.12.014>
- [25] Jawad, A., Zhan, K., Wang, H.B., Shahzad, A., Zeng, Z.H., Wang, J., Zhou, X.Q., Ullah, H., Chen, Z.L. and Chen, Z.Q. (2020) Tuning of Persulfate Activation from a Free Radical to a Nonradical Pathway through the Incorporation of Non-Redox Magnesium Oxide. *Environmental Science & Technology*, **54**, 2476-2488. <https://doi.org/10.1021/acs.est.9b04696>
- [26] Lee, H., Kim, H.I., Weon, S., Choi, W., Hwang, Y.S., Seo, J., Lee, C. and Kim, J.H. (2016) Activation of Persulfates by Graphitized Nanodiamonds for Removal of Organic Compounds. *Environmental Science & Technology*, **50**, 10134-10142. <https://doi.org/10.1021/acs.est.6b02079>
- [27] Ren, W., Xiong, L.L., Yuan, X.H., Yu, Z.W., Zhang, H., Duan, X.G. and Wang, S.B. (2019) Activation of Peroxydisulfate on Carbon Nanotubes: Electron-Transfer Mechanism. *Environmental Science & Technology*, **53**, 14595-14603. <https://doi.org/10.1021/acs.est.9b05475>
- [28] Bu, Y.G., Li, H.C., Yu, W.J., Pan, Y.F., Li, L.J., Wang, Y.F., Pu, L.T., Ding, J., Gao, G.D. and Pan, B.C. (2021) Peroxydisulfate Activation and Singlet Oxygen Generation by Oxygen Vacancy for Degradation of Contaminants. *Environmental Science & Technology*, **55**, 2110-2120. <https://doi.org/10.1021/acs.est.0c07274>
- [29] Yao, Y.Y., Wang, C.H., Yan, X., Zhang, H., Xiao, C.M., Qi, J.W., Zhu, Z.G., Zhou, Y.J., Sun, X.Y., Duan, X.G. and Li, J.S. (2022) Rational Regulation of Co-N-C Coordination for High-Efficiency Generation of  $^1\text{O}_2$  Toward Nearly 100% Selective Degradation of Organic Pollutants. *Environmental Science & Technology*, **56**, 8833-8843. <https://doi.org/10.1021/acs.est.2c00706>
- [30] Li, H., Liu, Y., Jiang, F., Bai, X., Li, H.J., Lang, D., Wang, L. and Pan, B. (2022) Persulfate Adsorption and Activation by Carbon Structure Defects Provided New Insights into Ofloxacin Degradation by Biochar. *Science of the Total En-*

- vironment*, **806**, Article ID: 150968. <https://doi.org/10.1016/j.scitotenv.2021.150968>
- [31] Liu, Z., Pan, S.Y., Xu, F., Wang, Z.W., Zhao, C., Xu, X., Gao, B.Y. and Li, Q. (2022) Revealing the Fundamental Role of MoO<sub>2</sub> in Promoting Efficient and Stable Activation of Persulfate by Iron Carbon Based Catalysts: Efficient Fe<sup>2+</sup>/Fe<sup>3+</sup> Cycling to Generate Reactive Species. *Water Research*, **225**, Article ID: 119142. <https://doi.org/10.1016/j.watres.2022.119142>
  - [32] Pirsaeheb, M., Hossaini, H., Asadi, A., Mansouri, B., Jafari, Z. and Motlagh, R.J. (2023) Facile Fabrication of WO<sub>3</sub>-CuO/RGO as a Catalyst for Enhanced Catalytic Oxidation of Pesticide and Organic Dye by Activation of Persulfate under Visible Light. *Surfaces and Interfaces*, **36**, Article ID: 102609. <https://doi.org/10.1016/j.surf.2022.102609>
  - [33] Zhu, S.S., Jin, C., Duan, X.G., Wang, S.B. and Ho, S.H. (2020) Nonradical Oxidation in Persulfate Activation by Graphene-Like Nanosheets (GNS): Differentiating the Contributions of Singlet Oxygen (<sup>1</sup>O<sub>2</sub>) and Sorption-Dependent Electron Transfer. *Chemical Engineering Journal*, **393**, Article ID: 124725. <https://doi.org/10.1016/j.cej.2020.124725>
  - [34] Zhang, L.H., Xiao, C., Li, Z.M., Guo, J.B., Du, G.G., Cheng, X. and Jia, Y.P. (2023) Degradation of Methyl Orange Using Persulfate Activated by Magnetic CuS/Fe<sub>3</sub>O<sub>4</sub> Catalyst: Catalytic Performance and Mechanisms. *Applied Surface Science*, **618**, Article ID: 156595. <https://doi.org/10.1016/j.apsusc.2023.156595>
  - [35] Jiang, M.D., Lu, J.H., Ji, Y.F. and Kong, D.Y. (2017) Bicarbonate-Activated Persulfate Oxidation of Acetaminophen. *Water Research*, **116**, 324-331. <https://doi.org/10.1016/j.watres.2017.03.043>
  - [36] Haag, W.R. and Hoigne, J. (1986) Singlet Oxygen in Surface Waters. 3. Photochemical Formation and Steady-State Concentrations in Various Types of Waters. *Environmental Science & Technology*, **20**, 341-348. <https://doi.org/10.1021/es00146a005>
  - [37] Cheng, X., Guo, H.G., Zhang, Y.L., Wu, X. and Liu, Y. (2017) Non-Photochemical Production of Singlet Oxygen via Activation of Persulfate by Carbon Nanotubes. *Water Research*, **113**, 80-88. <https://doi.org/10.1016/j.watres.2017.02.016>
  - [38] Chen, H.X., Xu, Y., Zhu, K.M. and Zhang, H. (2021) Understanding Oxygen-Deficient La<sub>2</sub>CuO<sub>4</sub>-Delta Perovskite Activated Peroxymonosulfate for Bisphenol A Degradation: The Role of Localized Electron within Oxygen Vacancy. *Applied Catalysis B: Environmental*, **284**, Article ID: 119732. <https://doi.org/10.1016/j.apcatb.2020.119732>
  - [39] Li, Y., Ma, S.L., Xu, S.J., Fu, H.C., Li, Z.Q., Li, K., Sheng, K., Du, J.G., Lu, X., Li, X.H. and Liu, S.L. (2020) Novel Magnetic Biochar as an Activator for Peroxymonosulfate to Degrade Bisphenol A: Emphasizing the Synergistic Effect between Graphitized Structure and CoFe<sub>2</sub>O<sub>4</sub>. *Chemical Engineering Journal*, **387**, Article ID: 124094. <https://doi.org/10.1016/j.cej.2020.124094>
  - [40] Sun, P., Liu, H., Feng, M.B., Guo, L., Zhai, Z.C., Fang, Y.S., Zhang, X.S. and Sharma, V.K. (2019) Nitrogen-Sulfur Co-Doped Industrial Graphene as an Efficient Peroxymonosulfate Activator: Singlet Oxygen-Dominated Catalytic Degradation of Organic Contaminants. *Applied Catalysis B: Environmental*, **251**, 335-345. <https://doi.org/10.1016/j.apcatb.2019.03.085>
  - [41] Yun, E.T., Lee, J.H., Kim, J., Park, H.D. and Lee, J. (2018) Identifying the Nonradical Mechanism in the Peroxymonosulfate Activation Process: Singlet Oxygenation versus Mediated Electron Transfer. *Environmental Science & Technology*, **52**, 7032-7042. <https://doi.org/10.1021/acs.est.8b00959>
  - [42] Zhang, T., Chen, Y., Wang, Y.R., Le Roux, J., Yang, Y. and Croue, J.P. (2014) Efficient Peroxydisulfate Activation Process Not Relying on Sulfate Radical Generation for Water Pollutant Degradation. *Environmental Science & Technology*, **48**, 5868-5875. <https://doi.org/10.1021/es501218f>
  - [43] Ren, W., Xiong, L.L., Nie, G., Zhang, H., Duan, X.G. and Wang, S.B. (2020) Insights into the Electron-Transfer Regime of Peroxydisulfate Activation on Carbon Nanotubes: The Role of Oxygen Functional Groups. *Environmental Science & Technology*, **54**, 1267-1275. <https://doi.org/10.1021/acs.est.9b06208>
  - [44] Guan, C.T., Jiang, J., Pang, S.Y., Luo, C.W., Ma, J., Zhou, Y. and Yang, Y. (2017) Oxidation Kinetics of Bromophenols by Nonradical Activation of Peroxydisulfate in the Presence of Carbon Nanotube and Formation of Brominated Polymeric Products. *Environmental Science & Technology*, **51**, 10718-10728. <https://doi.org/10.1021/acs.est.7b02271>
  - [45] Hu, P.D., Su, H.R., Chen, Z.Y., Yu, C.Y., Li, Q.L., Zhou, B.X., Alvarez, P.J.J. and Long, M. (2017) Selective Degradation of Organic Pollutants Using an Efficient Metal-Free Catalyst Derived from Carbonized Polypyrrole via Peroxymonosulfate Activation. *Environmental Science & Technology*, **51**, 11288-11296. <https://doi.org/10.1021/acs.est.7b03014>
  - [46] Miao, J., Zhu, Y., Lang, J.Y., Zhang, J.Z., Cheng, S.X., Zhou, B.X., Zhang, L.Z., Alvarez, P.J.J. and Long, M. (2021) Spin-State-Dependent Peroxymonosulfate Activation of Single-Atom M-N Moieties via a Radical-Free Pathway. *ACS Catalysis*, **11**, 9569-9577. <https://doi.org/10.1021/acscatal.1c02031>
  - [47] Ma, Y.H., Wang, D.L., Xu, Y., Lin, H. and Zhang, H. (2022) Nonradical Electron Transfer-Based Peroxydisulfate Activation by a Mn-Fe Bimetallic Oxide Derived from Spent Alkaline Battery for the Oxidation of Bisphenol A. *Journal of Hazardous Materials*, **436**, Article ID: 129172. <https://doi.org/10.1016/j.jhazmat.2022.129172>

- [48] Zhang, T., Zhu, H.B. and Croue, J.P. (2013) Production of Sulfate Radical from Peroxymonosulfate Induced by a Magnetically Separable  $\text{CuFe}_2\text{O}_4$  Spinel in Water: Efficiency, Stability, and Mechanism. *Environmental Science & Technology*, **47**, 2784-2791. <https://doi.org/10.1021/es304721g>
- [49] Liang, H.Y., Zhang, Y.Q., Huang, S.B. and Hussain, I. (2013) Oxidative Degradation of *p*-Chloroaniline by Copper Oxidate Activated Persulfate. *Chemical Engineering Journal*, **218**, 384-391. <https://doi.org/10.1016/j.cej.2012.11.093>
- [50] Chen, N., Fang, G.D., Zhu, C.Y., Wu, S., Liu, G.X., Dionysiou, D.D., Wang, X.L., Gao, J. and Zhou, D.M. (2020) Surface-Bound Radical Control Rapid Organic Contaminant Degradation through Peroxymonosulfate Activation by Reduced Fe-Bearing Smectite Clays. *Journal of Hazardous Materials*, **389**, Article ID: 121819. <https://doi.org/10.1016/j.jhazmat.2019.121819>
- [51] Zhang, X., Gang, D.D., Lei, X.B., Wang, T.J., Lian, Q., Holmes, W.E., Fei, L., Zappi, M.E. and Yao, H. (2022) Surface-Bound Hydroxyl Radical-Dominated Degradation of Sulfamethoxazole in the Amorphous Feooh/Peroxymonosulfate System: The Key Role of Amorphous Structure Enhancing Electron Transfer. *Environmental Research*, **214**, Article ID: 113964. <https://doi.org/10.1016/j.envres.2022.113964>
- [52] Zhu, C.Q., Liu, F.Q., Ling, C., Jiang, H., Wu, H.D. and Li, A.M. (2019) Growth of Graphene-Supported Hollow Cobalt Sulfide Nanocrystals via Mof-Templated Ligand Exchange as Surface-Bound Radical Sinks for Highly Efficient Bisphenol a Degradation. *Applied Catalysis B: Environmental*, **242**, 238-248. <https://doi.org/10.1016/j.apcatb.2018.09.088>
- [53] He, Y.Z., Wang, Z.W., Wang, H., Almatrafi, E., Qin, H., Huang, D.L., Zhu, Y., Zhou, C.Y., Tian, Q.Y., Xu, P. and Zeng, G.M. (2022) Confinement of ZIF-Derived Copper-Cobalt-Zinc Oxides in Carbon Framework for Degradation of Organic Pollutants. *Journal of Hazardous Materials*, **440**, Article ID: 129811. <https://doi.org/10.1016/j.jhazmat.2022.129811>
- [54] Bai, Z.Y., Wang, S.X., Tian, J.Y., Gao, S.S., Zhang, R.J. and Liu, X.W. (2022) Aluminum-Based Layered Metal Oxides Activating Peroxymonosulfate for Bisphenol a Degradation via Surface-Bound Sulfate Radicals and Singlet Oxygen. *Journal of Hazardous Materials*, **424**, Article ID: 127515. <https://doi.org/10.1016/j.jhazmat.2021.127515>
- [55] Fang, G.D., Deng, Y.M., Huang, M., Dionysiou, D.D., Liu, C. and Zhou, D.M. (2018) A Mechanistic Understanding of Hydrogen Peroxide Decomposition by Vanadium Minerals for Diethyl Phthalate Degradation. *Environmental Science & Technology*, **52**, 2178-2185. <https://doi.org/10.1021/acs.est.7b05303>
- [56] Ren, W., Cheng, C., Shao, P.H., Luo, X.B., Zhang, H., Wang, S.B. and Duan, X.G. (2022) Origins of Electron-Transfer Regime in Persulfate-Based Nonradical Oxidation Processes. *Environmental Science & Technology*, **56**, 78-97. <https://doi.org/10.1021/acs.est.1c05374>
- [57] Tang, L., Liu, Y., Wang, J., Zeng, G.M., Deng, Y.C., Dong, H.R., Feng, H.P., Wang, J.J. and Peng, B. (2018) Enhanced Activation Process of Persulfate by Mesoporous Carbon for Degradation of Aqueous Organic Pollutants: Electron Transfer Mechanism. *Applied Catalysis B: Environmental*, **231**, 1-10. <https://doi.org/10.1016/j.apcatb.2018.02.059>
- [58] Yang, Q., Chen, Y., Duan, X.G., Zhou, S.K., Niu, Y., Sun, H.Q., Zhi, L.J. and Wang, S.B. (2020) Unzipping Carbon Nanotubes to Nanoribbons for Revealing the Mechanism of Nonradical Oxidation by Carbocatalysis. *Applied Catalysis B: Environmental*, **276**, Article ID: 119146. <https://doi.org/10.1016/j.apcatb.2020.119146>
- [59] Yu, J.F., Tang, L., Pang, Y., Zeng, G.M., Feng, H.P., Zou, J.J., Wang, J.J., Feng, C.Y., Zhu, X., Ouyang, X.L. and Tan, J.S. (2020) Hierarchical Porous Biochar from Shrimp Shell for Persulfate Activation: A Two-Electron Transfer Path and Key Impact Factors. *Applied Catalysis B: Environmental*, **260**, Article ID: 118160. <https://doi.org/10.1016/j.apcatb.2019.118160>
- [60] Lee, H.S., Lee, H.J., Jeong, J., Lee, J., Park, N.B. and Lee, C.H. (2015) Activation of Persulfates by Carbon Nanotubes: Oxidation of Organic Compounds by Nonradical Mechanism. *Chemical Engineering Journal*, **266**, 28-33. <https://doi.org/10.1016/j.cej.2014.12.065>
- [61] Ahn, Y.Y., Bae, H., Kim, H.I., Kim, S.H., Kim, J.H., Lee, S.G. and Lee, J. (2019) Surface-Loaded Metal Nanoparticles for Peroxymonosulfate Activation: Efficiency and Mechanism Reconnaissance. *Applied Catalysis B: Environmental*, **241**, 561-569. <https://doi.org/10.1016/j.apcatb.2018.09.056>
- [62] Guo, X., Zhang, H., Yao, Y.Y., Xiao, C.M., Yan, X., Chen, K., Qi, J.W., Zhou, Y.J., Zhu, Z.G., Sun, X.Y. and Li, J.S. (2023) Derivatives of Two-Dimensional Mxene-MOFs Heterostructure for Boosting Peroxymonosulfate Activation: Enhanced Performance and Synergistic Mechanism. *Applied Catalysis B: Environmental*, **323**, Article ID: 122136. <https://doi.org/10.1016/j.apcatb.2022.122136>
- [63] Ren, W., Nie, G., Zhou, P., Zhang, H., Duan, X.G. and Wang, S.B. (2020) The Intrinsic Nature of Persulfate Activation and N-Doping in Carbocatalysis. *Environmental Science & Technology*, **54**, 6438-6447. <https://doi.org/10.1021/acs.est.0c01161>
- [64] Jiang, N., Xu, H.D., Wang, L.H., Jiang, J. and Zhang, T. (2020) Nonradical Oxidation of Pollutants with Single-Atom-Fe(III)-Activated Persulfate: Fe(V) Being the Possible Intermediate Oxidant. *Environmental Science & Technology*, **54**, 14057-14065. <https://doi.org/10.1021/acs.est.0c04867>

- 
- [65] Yi, Q.Y., Li, X.S., Li, Y., Dai, R.B. and Wang, Z.W. (2022) Unraveling the Co(IV)-Mediated Oxidation Mechanism in a  $\text{Co}_3\text{O}_4$ /PMS-Based Hierarchical Reactor: Toward Efficient Catalytic Degradation of Aromatic Pollutants. *ACS ES&T Engineering*, **2**, 1836-1846. <https://doi.org/10.1021/acsestengg.2c00087>
- [66] Chen, J.B., Zhou, X.F., Sun, P.Z., Zhang, Y.L. and Huang, C.H. (2019) Complexation Enhances Cu(II)-Activated Peroxydisulfate: A Novel Activation Mechanism and Cu(III) Contribution. *Environmental Science & Technology*, **53**, 11774-11782. <https://doi.org/10.1021/acs.est.9b03873>
- [67] Gao, Y., Zhou, Y., Pang, S.Y., Jiang, J., Yang, Z.F., Shen, Y.M., Wang, Z., Wang, P.X. and Wang, L.H. (2019) New Insights into the Combination of Permanganate and Bisulfite as a Novel Advanced Oxidation Process: Importance of High Valent Manganese-Oxo Species and Sulfate Radical. *Environmental Science & Technology*, **53**, 3689-3696. <https://doi.org/10.1021/acs.est.8b05306>
- [68] Pan, L.H., Shi, W., Sen, T., Wang, L.Z. and Zhang, J.L. (2021) Visible Light-Driven Selective Organic Degradation by  $\text{FeTiO}_3$ /Persulfate System: The Formation and Effect of High Valent Fe(IV). *Applied Catalysis B: Environmental*, **280**, 119414. <https://doi.org/10.1016/j.apcatb.2020.119414>
- [69] Su, R.D., Li, N., Liu, Z., Song, X.Y., Liu, W., Gao, B.Y., Zhou, W.Z., Yue, Q.Y. and Li, Q. (2023) Revealing the Generation of High-Valent Cobalt Species and Chlorine Dioxide in the  $\text{Co}_3\text{O}_4$ -Activated Chlorite Process: Insight into the Proton Enhancement Effect. *Environmental Science & Technology*, **57**, 1882-1893. <https://doi.org/10.1021/acs.est.2c04903>
- [70] Zhu, J.H., Yu, F.L., Meng, J.R., Shao, B.B., Dong, H.Y., Chu, W.H., Cao, T.C., Wei, G.F., Wang, H.J. and Guan, X.H. (2020) Overlooked Role of Fe(IV) and Fe(V) in Organic Contaminant Oxidation by Fe(VI). *Environmental Science & Technology*, **54**, 9702-9710. <https://doi.org/10.1021/acs.est.0c03212>