Hans Journal of Chemical Engineering and Technology 化学工程与技术, 2026, 16(5), 347-358
Published Online September 2026 in Hans. https://www.hanspub.org/journal/hjcet
https://doi.org/10.12677/hjcet.2026.165034

过渡金属磷化物活化过一硫酸盐降解水中有机污染物的研究进展

杨　铭，宋正鑫，葛忠超，李丽华*

辽宁科技大学化学工程学院，辽宁　鞍山

收稿日期：2026年6月18日；录用日期：2026年9月8日；发布日期：2026年9月15日

摘　要

过一硫酸盐(PMS)活化技术因可原位生成$SO_4^{\cdot-}$、•OH、$O_2^{\cdot-}$、$^1O_2$及高价金属氧物种，已成为难降解有机污染物去除的重要高级氧化路径。传统均相金属离子、金属氧化物和碳材料虽然能够活化PMS，但常受限于金属残留、低价金属再生缓慢、pH适应性不足、界面电子转移效率有限和实际水体干扰。过渡金属磷化物(TMPs)近年来进入PMS催化领域，核心原因在于其类金属性导电性、M-P键诱导的$M^{\delta+}/P^{\delta-}$协同位点、以及还原性P物种对金属价态循环的促进作用。现有研究已从早期CoP、Fe_xP和Ni_2P单金属磷化物，发展到Co_2P/C、CoP/NC、Fe_2P/biocarbon、CoP/CoO_x、$CoFe_2P_x$、FeNiP、$NiFeP_x$、FeP/NiP_2异质界面、固定化FeCoP@NF、光热耦合Co-Ni_2P和磷空位调控体系。总体上，TMPs/PMS体系在抗生素、染料和酚类污染物去除中表现出较高反应速率、宽pH适用范围和一定循环稳定性。然而，机理判定仍存在自由基猝灭过度依赖、$^1O_2$来源不清、电子转移路径与高价金属氧物种难以区分等问题。未来研究应从结构可控合成、原位谱学和同位素追踪、固定化反应器、实际废水基质及毒性削减评价几个方向推进，使TMPs从高效模型催化剂走向可验证的水处理材料。

关键词

过渡金属磷化物，过一硫酸盐，高级氧化，自由基，非自由基

Recent Advances in Transition Metal Phosphides for Peroxymonosulfate Activation toward the Degradation of Organic Pollutants in Water

Ming Yang, Zhengxin Song, Zhongchao Ge, Lihua Li*

Department of Environmental Engineering, University of Science and Technology Liaoning, Anshan Liaoning

*通讯作者。

文章引用: 杨铭, 宋正鑫, 葛忠超, 李丽华. 过渡金属磷化物活化过一硫酸盐降解水中有机污染物的研究进展[J]. 化学工程与技术, 2026, 16(5): 347-358. DOI: 10.12677/hjcet.2026.165034

Received: June 18, 2026; accepted: September 8, 2026; published: September 15, 2026

Abstract

Peroxymonosulfate (PMS) activation has become an important advanced oxidation pathway for the removal of refractory organic pollutants because it can generate $SO_4^{\bullet-}$, •OH, $O_2^{\bullet-}$, $^1O_2$, and high-valent metal-oxo species *in situ*. Although conventional homogeneous metal ions, metal oxides, and carbon materials can activate PMS, they are often limited by metal residues, slow regeneration of low-valent metal species, insufficient pH adaptability, restricted interfacial electron-transfer efficiency, and interference from real water matrices. Transition metal phosphides (TMPs) have recently attracted increasing attention in PMS catalysis, mainly because of their metallic-like conductivity, $M^{\delta+}/P^{\delta-}$ synergistic sites induced by M-P bonds, and the ability of reductive phosphorus species to promote metal valence cycling. Existing studies have evolved from early monometallic phosphides, such as CoP, Fe_xP, and Ni_2P, to Co_2P/C, CoP/NC, Fe_2P/biocarbon, CoP/CoO_x, $CoFe_2P_x$, FeNiP, $NiFeP_x$, FeP/NiP_2 heterointerfaces, immobilized FeCoP@NF, photothermal-coupled Co-Ni_2P, and phosphorus-vacancy-regulated systems. Overall, TMPs/PMS systems exhibit high reaction rates, broad pH applicability, and certain cycling stability in the degradation of antibiotics, dyes, and phenolic pollutants. However, mechanistic identification still suffers from excessive reliance on radical quenching tests, unclear sources of $^1O_2$, and difficulty in distinguishing electron-transfer pathways from high-valent metal-oxo species. Future studies should focus on controllable structural synthesis, in situ spectroscopy and isotope tracing, immobilized reactors, real wastewater matrices, and toxicity reduction assessment, so that TMPs can move from efficient model catalysts toward verifiable water-treatment materials.

Keywords

Transition-Metal Phosphides, Peroxymonosulfate, Advanced Oxidation, Radical Pathway, Non-Radical Pathway

1. 引言

抗生素、染料、酚类、内分泌干扰物和药物中间体等有机污染物在常规生化、混凝和吸附工艺中去除不充分，推动了硫酸根自由基高级氧化过程(SR-AOPs)的发展。PMS 作为一种不对称过氧硫酸盐，O-O 键键能较低，既可直接氧化部分富电子污染物，也可在催化剂、热、光、电、碱或超声作用下转化为$SO_4^{\bullet-}$、•OH、$O_2^{\bullet-}$、$^1O_2$和高价金属氧物种[1]-[9]。与羟基自由基高级氧化相比，SR-AOPs 通常具有更宽 pH 适用范围和更强选择性，因此在抗生素、染料和含氮杂环污染物处理中受到关注。

均相 Co^{2+}、Fe^{2+}、Cu^{+}等金属离子可以快速启动 PMS，但金属残留、二次污染和催化剂回收困难限制了应用[10]。异相氧化物、尖晶石、碳材料和单原子材料提升了可回收性，却常面临低价金属再生慢、表面电子转移不足和活性位点衰减的问题[1] [11]-[14]。在这一背景下，过渡金属磷化物(TMPs)被引入 PMS 活化体系。与相应氧化物或氢氧化物相比，许多 TMPs 具有更高电导率、更强界面电子传输能力和更丰富的 $M^{\delta+}/P^{\delta-}$协同位点；$P^{\delta-}$或还原性 P 物种还可促进金属高价态向低价态回转，从而降低 PMS 活化的电子转移阻力[15]。

本文围绕 TMPs 活化 PMS 降解水中有机污染物的研究进展展开，重点综述单金属磷化物、碳限域磷化物、双金属/异质界面磷化物、缺陷调控磷化物及固定化体系的构效关系，并讨论自由基与非自由基路径、应用瓶颈和未来研究方向。

2. TMPs 活化 PMS 的结构基础

2.1. M-P 键、表面重构与真实活性界面

在金属富集的 TMPs 中，M-P 键兼具共价和金属性特征，常形成相对缺电子的 $M^{\delta+}$位点和富电子的 $P^{\delta-}$位点。前者有利于 PMS 吸附和 O-O 键极化，后者可作为电子缓冲中心促进 Co、Fe 或 Ni 价态循环[15] [16]。但仅用反应前的 $M^{\delta+}/P^{\delta-}$电荷分布解释活性仍不充分。水相氧化条件下，TMP 表面往往发生羟基化、氧化或磷流失，原始磷化物、原位形成的 M-O(H)层和残余 M-P 界面可能共同构成工作态活性相。

因此，将反应前 XPS 中的 $M^{\delta+}/P^{\delta-}$直接等同于反应中活性位点存在风险。更可靠的构效关系应比较反应前后及原位条件下的晶相、表面配位和金属价态，并使用氧化物、磷化物、物理混合物和受控表面氧化样品作为对照。表面重构并非必然失活：适量 NiO_x 或 CoO_x 可与导电磷化物形成高效界面[17]-[19]；但过度氧化、$FePO_x$ 沉积或 P 流失也会遮蔽 M-P 位点并增加电子传输阻力。

2.2. Co、Fe 和 Ni 磷化物的多维比较

现有文献呈现出有条件的趋势：Co-P 通常活化较快，但需关注浸出和资源压力；Fe-P 在原料与环境负担方面较有优势，却更依赖低价态再生和表面状态；Ni-P 的表现则常由氧化层、掺杂和异质界面决定[10] [15]-[19]。三类金属体系的综合比较及代表性文献见表 1。

Table 1. Comprehensive comparison of Co, Fe and Ni-based phosphides for PMS activation
表 1. Co、Fe 和 Ni 基磷化物用于 PMS 活化的综合比较

金属体系	本征/表观活性及原因	稳定性与失活倾向	原料与成本压力	金属环境风险	适宜的设计方向	代表文献
Co-P	通常表现出最快 PMS 活化；Co(II)/Co(III)循环、表面重构及 Co-P 极化共同促进 O-O 键活化。	表面易形成 CoO_x/CoOOH；高活性位点也可能伴随 Co 浸出，碳限域只能降低而不能消除风险。	三者中供应和成本压力最高。	较高；应报告溶出、累计释放和处理后残留。	低 Co 负载、强限域、Fe/Ni 协同、整体式载体和真实水体长期验证。	[20]-[26]
Fe-P	单独活性多为中等；Fe(II)/Fe(III)循环、有 Fe/PMS 体系表明高价铁氧物种可能参与，以 Fe 位点循环、P 位点供电子和界面电子转移为主。	可能形成 FeO_x/$FePO_x$ 钝化层；磁分离有利于回收，但不能替代结构稳定性评价。	原料可得性最好，通常具有最低成本压力。	相对较低，但纳米颗粒、磷释放和铁泥仍需控制。	碳限域、缺陷调控、双金属耦合、低温绿色磷化和固定化。	[27]-[31]
Ni-P	单金属体系通常弱于 Co；活性常来自 Ni_2P/表面 NiO_x 协同、Ni(II)/Ni(III)循环及掺杂诱导的电子调控。	表面氧化既可能构成活性壳层，也可能过度钝化；性能对晶相和表面历史敏感。	低于 Co、高于 Fe，且存在资源波动。	中等至较高；应与 Co 同样进行浸出和生态风险评价。	Fe/Co 掺杂、异质界面、光热辅助及可控表面氧化层。	[32]-[35]

比较 Co、Fe 和 Ni 基磷化物时，应避免将不同研究中的表观速率直接等同于金属本征活性。由于污染物种类、PMS 剂量、催化剂投加量、pH 和水体基质差异较大，现有结论更适合作为非同平台趋势参考。后续研究应在统一反应条件下比较单位活性金属、单位表面积和单位 PMS 消耗对应的反应效率，并同步评价金属浸出、表面钝化和长期稳定性。

3. 材料体系、界面结构与反应路径的耦合

3.1. Co 基磷化物：高活性与高风险并存

CoP 是最早用于 PMS 活化的 TMP 代表，CoP、Co_2P 和 CoP_2 均可促进染料、卡马西平和抗生素转化[20] [21] [36]。Co-P 的高表观活性通常归因于 Co 位点对 PMS 的强吸附、Co(II)/Co(III)快速循环和 P 位点的电子补偿。与均相 Co(II)/PMS 相似，$SO_4^{\bullet-}$ 和•OH 在许多 Co-P 体系中贡献显著[20] [37] [38]；但近期研究提示，高价 Co 氧物种、表面结合 PMS 和 $^1O_2$ 也可能参与，且不同探针得到的路径比例并不一致[39]-[48]。

碳限域和晶相耦合可改变 Co 基体系的路径选择。CoP_2@NPC、Co_2P/biochar、CoP/g-C_3N_4 和 CoP/NC 兼具污染物富集、电子传输和金属限域作用[13] [22]-[25] [36] [49] [50]；CoP/CoO_x 和 CoP@Co_2P 则通过相邻界面调控 PMS 还原或氧化方向[18] [19]。然而，碳材料本身可以通过缺陷、共轭电子或含氮位点活化 PMS [39] [45] [46] [51]，因此负载后活性提高不能自动证明 Co-P/碳协同，即有必要设置去金属碳、等比物理混合物和位点毒化对照。

3.2. Fe 基磷化物：低资源压力与慢循环之间的权衡

Fe_xP、Fe_2P 和 FeP/C 将铁的低成本、相对较低环境风险和潜在磁分离能力引入 PMS 体系[11] [12] [27]-[31]。P 位点可促进 Fe(III)向 Fe(II)回转，碳限域则有助于电子传输和颗粒分散。与 Co-P 相比，Fe-P 常表现出较低的初始速率，但在生物质磷源、废酸洗液和低成本载体路线中具有更明确的工程吸引力[11] [27]-[29] [31]。

Fe-P 体系中自由基路径和界面电子转移已有较多报道。高价铁氧物种在铁配合物、铁卟啉、零价铁及其他 Fe/PMS 体系中已有研究提示，但这些证据主要来自非磷化物体系，只能作为 Fe-P 体系可能存在类似路径的类比依据，尚不能直接证明 Fe-P 催化界面中形成 Fe(IV) = O。后续仍需结合 TMP 工作态下的原位或准原位谱学、同位素氧转移和选择性产物证据进行确认[40] [52]-[54]。

3.3. Ni 基磷化物：表面氧化层决定的界面催化

表面氧化 Ni_2P 显示 Ni_2P/NiO_x 界面可以形成双活性区域：磷化物内核提供电子传输，表面 Ni(II)/Ni(III)物种参与 PMS 活化[17]。这一结果改变了“表面氧化必然导致失活”的简单判断，但也说明 Ni-P 活性对制备后暴露历史、氧化层厚度和晶相高度敏感。若不同研究未统一预处理和表征条件，所谓 Ni_2P 本征活性很难直接比较。

Ni 基体系更常通过 Fe-Ni 双金属、Co 掺杂或光热耦合获得较高性能[32]-[35]。$NiFeP_x$ 和 FeP/NiP_2 可利用双金属循环和界面电荷再分配扩展 pH 适用范围；Co-Ni_2P 则借助近红外升温和电子调控提高速率。但外场增强应扣除单纯温升贡献，并报告单位处理水量的能耗。Ni 释放也不能因其活性低于 Co 而被忽略。

3.4. 碳限域与绿色磷源：载体并非惰性

磷富集微生物、植酸、菌丝球和含磷生物质可同时提供磷源与碳骨架，形成 Co_2P/C、FeP/C、Fe_2P/biocarbon 和空心 CoP/C [11] [12] [22]-[25] [29] [31] [49] [50]。这些路线减少颗粒团聚并可能降低传统磷化剂的安全压力，但绿色前驱体并不必然意味着低环境负荷，磷化温度、保护气消耗、产物收率、酸洗过程和废液处置仍会影响其全流程环境效益。

在机理上，碳载体可通过缺陷位、石墨化 π 电子、N/P 杂原子和表面官能团吸附 PMS 或介导电子转移[39] [45] [46] [51]。因此，碳限域 TMPs 出现 $^1O_2$ 或电子转移路径时，不能把全部贡献归于 M-P 键。合理的解耦方案包括对比相同碳骨架的去金属样品、测定金属溶出后的均相贡献、进行污染物吸附－解吸平衡和使用电化学/开路电位验证电子转移。

3.5. 双金属、异质界面与晶相耦合

$CoFe_2P_x$、FeNiP、$NiFeP_x$ 和 FeP/NiP_2 通过双金属价态循环和 M-P-M 桥联降低单一金属再生瓶颈[26] [32] [34] [35]。CoP/CoO_x 和 $CoP@Co_2P$ 则分别代表磷化物/氧化物界面与同元素多晶相界面[18] [19]。这些结构的共同逻辑是把 PMS 吸附、污染物富集和电子传输分配到相邻但功能不同的位点，从而改变自由基与非自由基路径的相对比例。

异质界面效应的判定需要同时排除比表面积、粒径、金属溶出和物理混合效应的干扰。若等组成物理混合物明显弱于紧密界面样品，且界面密度、功函数变化、原位价态演化和理论吸附能能够指向同一趋势，界面电子调控的解释才较为可靠。

3.6. 缺陷工程：路径选择与证据强度

P 空位可改变局部电荷密度、PMS 吸附构型和水分子亲和性。Hong 等通过(从头算分子动力学) AIMD、原位 Raman 和 $^{18}O/^{16}O$ 示踪提出水氧可参与 $^1O_2$ 形成[55]，其证据链明显强于仅依赖猝灭剂的研究。该结果说明缺陷可能同时控制反应位点和氧来源，而非只增加“活性位点数量”。

但缺陷浓度增加通常伴随比表面积、晶粒尺寸、表面氧化和金属浸出的同步变化。可靠的缺陷构效关系需要连续梯度样品、缺陷定量和归一化活性，并排除 PMS 自分解、溶出金属和载体缺陷的贡献。尤其是 $^1O_2$ 归属，应在 $H_2{}^{18}O$、$^{18}O_2$ 和标记 PMS 之间进行氧来源闭合，而不能只依赖 D_2O 促进或 TEMP-EPR 增强。

3.7. 固定化与外场耦合

FeCoP@NF 和 CoP@NC/NF 将粉体转化为整体式催化界面，降低离心过滤需求并为流通式运行提供基础[56] [57]。固定化同时引入新的评价问题：面积归一化活性、载体腐蚀、Ni 泡沫释放、边界层传质和压降。若只以单位催化剂质量比较粉体与整体材料，会低估几何面积和传质差异。

近红外光热或可见光辅助可提高界面温度或光生载流子参与程度，但应与等温暗反应、空载体和无 PMS 对照分开[33] [58] [59]。外场耦合只有在单位污染负荷能耗、PMS 利用率和反应器尺度上保持优势时才具有工程意义，而非仅表现为更高的实验室 k_obs。

4. 活性物种证据标准与争议判定

4.1. $^1O_2$ 可能生成路径与证据矩阵

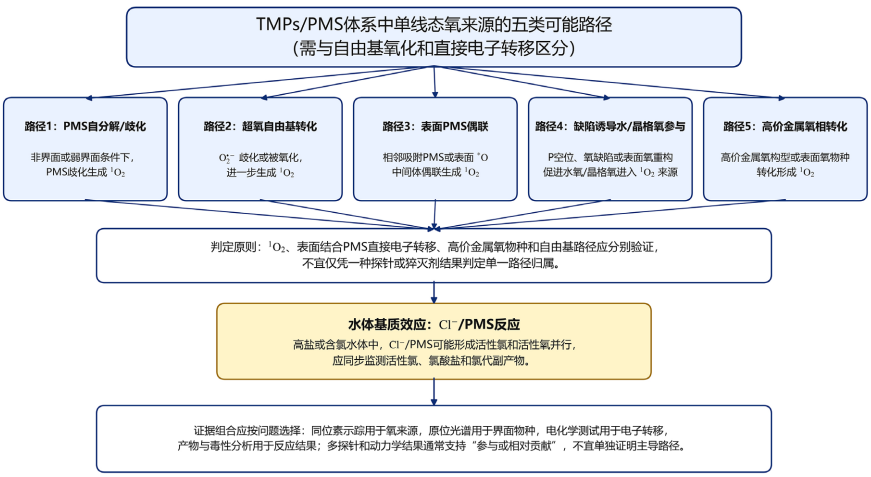

Figure 1. Possible pathways of $^1O_2$ generation and evidence assessment in the TMPs/PMS system
图 1. TMPs/PMS 体系中 $^1O_2$ 可能生成路径及证据判定

TMPs/PMS 研究提出了多种 $^1O_2$ 来源，包括 PMS 自分解、$O_2^{\bullet-}$ 二次转化、表面 PMS 偶联、水参与缺陷路径、Cl^-/PMS 反应和高价金属氧二次转化[7]-[9] [39] [45]-[48] [51] [55] [59]-[63]。不同路径的示意归纳见图 1，具体证据判定与限制见表 2。

TEMP-EPR、糠醇猝灭和 D_2O 效应可用于筛查 $^1O_2$，但三者都会受到其他氧化剂、吸附或溶剂性质影响。可进一步查看是否同时具有氧同位素、原位界面表征以及与底物选择性和动力学一致的化学证据[7]-[9] [39] [47] [48] [51] [59]-[63]。

Table 2. Possible pathways for the generation of $^1O_2$ in the TMPs/PMS system, Cl^--mediated substrate reactions, and evidence limitations
表 2. TMPs/PMS 体系中 $^1O_2$ 可能生成路径、Cl^-介导的基质反应及证据限制

$^1O_2$ 路径	化学图景	支持证据	不足与干扰
PMS 自分解/歧化	碱性或高 PMS 条件下，不同质子化/解离 PMS 物种反应并释放 $^1O_2$。	无催化剂空白、pH 依赖、PMS 物料衡算和氧同位素来源分析。	仅观察 TEMP-EPR 信号、糠醇损失或 D_2O 促进不足；催化剂可改变局部 pH，探针也可能直接与 PMS 或自由基反应。
$O_2^{\bullet-}$ 二次转化	表面还原氧或 PMS 产生 $O_2^{\bullet-}$，随后歧化或氧化形成 $^1O_2$。	$^{18}O_2$ 示踪、$O_2^{\bullet-}$ 定量、时间分辨关联；SOD 控制需设置 PMS 稳定性空白。	对苯醌会改变吸附和电子转移；SOD 可能受 PMS 或 ROS 影响；DMPO 加合物也可能转化。
表面 PMS 偶联/吸附中间体	相邻吸附 PMS、*O 或*OO 中间体在界面偶联，形成吸附态 $^1O_2$。	原位 Raman/FTIR、同位素标记、位点阻断、吸附构型计算和反应能垒一致。	DFT 预测叠加单一 EPR 信号不足；表面结合 PMS 也可直接氧化污染物，产生类似非自由基选择性。
缺陷诱导水/晶格氧参与	P 空位、氧缺陷或表面氧重构促进水氧或晶格氧进入 $^1O_2$。	$H_2{}^{18}O/{}^{18}O_2$/标记 PMS 对比、缺陷梯度样品、原位 Raman 和 AIMD 相互印证。	缺陷样品活性提高、D_2O 促进或 TEMP-EPR 增强不能单独证明氧来源；缺陷变化常伴随比表面积、金属浸出和表面氧化同步变化。
高价金属氧/表面氧重构	M(IV/V) = O 或表面氧物种可能经氧转移、表面重构或二次反应参与 $^1O_2$ 生成。	原位 XAS/Raman、选择性底物、同位素氧转移及产物证据共同支持。	仅依据 PMSO 氧化或非 TMP 体系高价金属氧文献不足；高价金属氧、自由基和表面结合 PMS 可能产生相似探针响应。
基质诱导的 Cl^-/PMS 反应	高 Cl^-水体中，Cl^-/PMS 反应可能诱导 $^1O_2$ 和活性氯并行。	Cl^-浓度梯度、活性氯、氯酸盐和氯代副产物同步监测。	仅以 Cl^-条件下去除率升高说明 $^1O_2$ 增强不足；活性氯和直接氯化可能主导污染物转化，不能视为材料本征路径。

4.2. 不同非自由基路径的区分与判定

高价 Co/Fe 氧物种常由 PMSO 氧化、选择性底物、弱 EPR 信号和理论计算推断，但 PMSO 本身也可能受到 Co(III)、自由基或表面结合 PMS 的影响[40] [41]。介导电子转移、表面结合 PMS 和 $^1O_2$ 均可能表现出抗阴离子干扰、偏好富电子底物以及醇类猝灭不敏感等特征，需结合开路电位、电流响应、吸附依赖、位点阻断和表面中间体谱学进行区分[39] [45]-[48]。

5. 典型 TMPs/PMS 体系的结构－活性－路径关系

代表性 TMPs/PMS 体系的结构特征、目标污染物与主要活性路径对比见表 3。

结合表 1 的横向比较及表 3 中代表性体系可以概括出一种非同平台趋势：Co 基磷化物通常具有较高表观活性，但需重点关注金属浸出和长期稳定性；Fe 基体系在资源成本和环境风险方面更具优势，但常需要碳限域、缺陷调控或双金属耦合提高电子转移效率；Ni 基体系的性能则更依赖表面氧化层、掺杂和异质界面调控。由于不同研究的污染物、剂量和水质条件并不统一，上述趋势不能替代同平台定量比较。

Table 3. Comparative analysis of structural characteristics, target pollutants, and primary reactive species and reaction pathways in representative TMPs/PMS systems
表 3. 代表性 TMPs/PMS 体系的结构特征、目标污染物和主要活性路径对比

材料体系	目标污染物	关键性能或设计特点	主要活性物种与机制判断	文献
CoP	Orange II	早期单金属 CoP/PMS 异相体系	$SO_4^{\bullet-}$、•OH 主导	[20]
CoP/NC	SMX，高盐废水	N 掺杂碳限域 CoP，抗盐度干扰	自由基和非自由基路径并存	[24]
$CoFe_2P_x$	磺胺氯哒嗪	由 $CoFe_2O_4$ 衍生，降低 Co 浸出	改变反应路径，非自由基贡献增强	[26]
Fe_xP	磺胺类抗生素	磁性铁磷化物，便于回收	Fe 位点循环与 P 调控电子结构	[27]
Fe_2P/biocarbon	左氧氟沙星	生物质磷源衍生 Fe_2P/碳	$SO_4^{\bullet-}$、•OH、$^1O_2$ 共同参与	[31]
$NiFeP_x$	甲硝唑	LDH 衍生非晶磷化物，pH 3~11 适用	Ni/Fe 价态循环及高价金属氧参与	[32]
FeNiP	盐酸四环素	双金属磷化物，宽 pH 适应	$SO_4^{\bullet-}$、•OH、$O_2^{\bullet-}$、$^1O_2$ 协同	[34]
FeP/NiP_2	SMX	MOF 衍生紧密异质界面，抗阴离子干扰	界面电子转移促进 Fe 循环	[35]
CoP_2@NPC	酚类/抗生素模型污染物	N、P 共掺杂碳限域 CoP_2，DFT 解释 PMS 吸附	自由基和 $^1O_2$ 协同	[36]
Co_2P/biochar	磺胺类抗生素	酵母生物质诱导 Co_2P/生物炭	生物炭富集与 Co_2P 活化协同	[49]
P 空位调控磷化物	多种模型污染物	AIMD、原位 Raman 和同位素示踪揭示氧来源	P 空位吸引 H_2O 参与 $^1O_2$ 生成	[55]
FeCoP@NF	染料废水	泡沫镍固定化，便于整体回收	双金属循环与载体传质协同	[56]

6. 从模型降解到实际水处理：性能评价与应用挑战

6.1. 水体基质效应不是单一阴离子抑制实验

HCO_3^- 和天然有机质通常竞争 $SO_4^{\bullet-}$/•OH 或覆盖表面位点，磷酸盐可能络合金属并改变表面电荷，Cl^- 则具有双重作用：既可能消耗自由基，也可能形成活性氯、促进特定污染物转化甚至参与 $^1O_2$ 生成[1] [62] [64]-[67]。因此，Cl^-条件下去除加快不能被简单解释为抗盐性，更不能替代氯酸盐、活性氯和氯代副产物监测。

天然有机质不只是竞争剂，也可能被 PMS 部分氧化并改变后续光化学和消毒副产物形成潜力[64]-[67]。真实水体实验应报告 DOC、碱度、主要离子、浊度和背景吸光度，采用多组分矩阵而非逐个离子测试。若材料依赖自由基路径，基质猝灭往往更明显；非自由基体系可能保持母体污染物去除，但其选择性也可能导致矿化不足。

真实废水验证至少应包含目标污染物、TOC/COD、PMS 残余、主要中间体和毒性变化。Fe(II)/PMS 与膜耦合、$LaCoO_3$/PMS 和固定床研究说明反应器及水基质可显著改变实验室结论[66]-[69]，TMPs 也需要在相似边界条件下验证。

6.2. 长期稳定性与失活机制

TMPs 的失活可由四类过程共同造成：金属和 P 溶出导致活性相损失；表面氧化或磷酸盐沉积导致钝化；有机中间体和 NOM 覆盖位点；颗粒团聚、载体腐蚀或孔道堵塞引起传质下降。不同失活机制需要不同再生方法，仅凭反应后 XRD 主峰不变无法排除表面重构。

常见 4~5 次批次循环主要检验短期可重复使用性，不能代表连续稳定性。应报告累计处理水量、每周期金属/P 释放、单位面积或单位金属活性、PMS 无效分解比例和失活速率。对于泡沫镍和膜载体，还应监测载体元素释放、压降和机械完整性[56] [68] [69]。

失活诊断应把性能衰减与材料变化对应：若清水冲洗即可恢复，主要问题可能是可逆吸附；若还原处理恢复，可能涉及高价态积累；若需要再磷化，则说明活性相已发生不可逆 P 损失。将这些情况统称为“稳定”会掩盖材料寿命和二次废物差异。

6.3. 工程评价与应用边界

工程评价应把再生、固定化、连续流和风险成本合并考虑。再生实验需区分清洗、化学还原和再磷化，并同步报告活性恢复、质量损失、金属/P 释放和再生废液；固定床、泡沫金属和催化膜则应报告空床接触时间、通量、压降、床层高度、PMS 停留时间和面积归一化活性。母体污染物去除不能等同于矿化和风险降低，建议同时报告 TOC 或 COD、关键中间体、残余 PMS、处理前后毒性及单位污染负荷药耗。

7. 未来研究方向

未来研究应围绕三个方面展开：第一，在同一载体、粒径和表面氧化程度下开展同平台比较，统一 PMS/污染物摩尔比、水基质和归一化指标；第二，结合 $H_2{}^{18}O$、$^{18}O_2$ 和标记 PMS，以及原位 XAS/Raman/FTIR、EPR 和选择性产物分析，建立位点－氧源－活性物种之间的证据链；第三，将真实废水、连续运行、金属/P 累计释放、通量/压降、再生废液和全流程药耗纳入早期评价，避免只以实验室 k_obs 判断材料应用价值。

8. 结论

TMPs/PMS 领域已经从证明磷化物能够活化 PMS，发展到利用金属种类、晶相、表面氧化、碳限域、异质界面和缺陷调控反应路径。横向比较表明，Co-P 的高活性与高环境/供应风险并存，Fe-P 在成本和风险方面占优但面临慢循环与钝化，Ni-P 则高度依赖表面和界面工程。因研究条件差异显著，任何简单的 Co > Fe > Ni 活性排序都只能作为趋势，不能替代同平台评价。

更关键的是，$^1O_2$、高价金属氧和电子转移的归属仍存在方法学争议。后续研究的重点不宜停留在材料配方扩展和 ROS 类型罗列上，而应转向可验证的位点－物种－通量关系构建，并以真实水体、长期稳定、再生、毒性和全流程成本验证应用边界。只有同时解决机理可信度和工程可行性，TMPs 才能从高活性粉体走向稳定、可回收和可连续运行的水处理催化界面。

参考文献

[1] Lee, J., von Gunten, U. and Kim, J. (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

[2] Wang, J. and Wang, S. (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

[3] Anipsitakis, G.P. and Dionysiou, D.D. (2004) Radical Generation by the Interaction of Transition Metals with Common Oxidants. *Environmental Science & Technology*, **38**, 3705-3712. https://doi.org/10.1021/es035121o

[4] 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

[5] Oh, W., Dong, Z. and Lim, T. (2016) Generation of Sulfate Radical through Heterogeneous Catalysis for Organic Contaminants Removal: Current Development, Challenges and Prospects. *Applied Catalysis B*: *Environmental*, **194**, 169-201. https://doi.org/10.1016/j.apcatb.2016.04.003

[6] Wacławek, 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

[7] Yan, Y., Wei, Z., Duan, X., Long, M., Spinney, R., Dionysiou, D.D., *et al*. (2023) Merits and Limitations of Radical vs. Nonradical Pathways in Persulfate-Based Advanced Oxidation Processes. *Environmental Science & Technology*, **57**, 12153-12179. https://doi.org/10.1021/acs.est.3c05153

[8] Cheng, X., Guo, H., Zhang, Y., 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

[9] Wang, L., Xiao, K. and Zhao, H. (2023) The Debatable Role of Singlet Oxygen in Persulfate-Based Advanced Oxidation Processes. *Water Research*, **235**, Article ID: 119925. https://doi.org/10.1016/j.watres.2023.119925

[10] Zhao, W., Shen, Q., Nan, T., Zhou, M., Xia, Y., Hu, G., *et al.* (2023) Cobalt-based Catalysts for Heterogeneous Peroxymonosulfate (PMS) Activation in Degradation of Organic Contaminants: Recent Advances and Perspectives. *Journal of Alloys and Compounds*, **958**, 170370. https://doi.org/10.1016/j.jallcom.2023.170370

[11] Dai, L., Xie, Y., Zhang, Y. and Wang, Y. (2023) Fe_2p/n-doped Biocarbon Composite Derived from Mycelial Pellet for Bisphenol AF Removal through Peroxymonosulfate Activation. *Journal of Environmental Chemical Engineering*, **11**, 109130. https://doi.org/10.1016/j.jece.2022.109130

[12] Lan, J., Zhang, Q., Yang, G., Liu, Z. and Peng, F. (2023) Removal of Tetracycline Hydrochloride by N,P Co-Doped Carbon Encapsulated Fe_2p Activating PMS: A Non-Radical Pathway Dominated by Singlet Oxygen. *Journal of Environmental Chemical Engineering*, **11**, 110481. https://doi.org/10.1016/j.jece.2023.110481

[13] Dong, C., Zheng, Z., Wang, Z., He, J., Ye, Z., Gong, X., *et al.* (2021) N-doped Graphitic C_3N_4 Nanosheets Decorated with Cop Nanoparticles: A Highly Efficient Activator in Singlet Oxygen Dominated Visible-Light-Driven Peroxymonosulfate Activation for Degradation of Pharmaceuticals and Personal Care Products. *Journal of Hazardous Materials*, **416**, 125891. https://doi.org/10.1016/j.jhazmat.2021.125891

[14] Hou, L., Zang, J., Liu, S., You, P. and Fan, G. (2025) Nitrogen-mediated Engineering Cobalt Phosphide Sites for Enhanced Peroxymonosulfate Activation Towards Organic Wastewater Purification. *Environmental Research*, **277**, 121551. https://doi.org/10.1016/j.envres.2025.121551

[15] Yu, H., Ji, J., Yan, Q. and Xing, M. (2022) Transition Metal Phosphides for Heterogeneous Fenton-Like Oxidation of Contaminants in Water. *Chemical Engineering Journal*, **449**, Article ID: 137856. https://doi.org/10.1016/j.cej.2022.137856

[16] Liu, Y., McCue, A.J. and Li, D. (2021) Metal Phosphides and Sulfides in Heterogeneous Catalysis: Electronic and Geometric Effects. *ACS Catalysis*, **11**, 9102-9127. https://doi.org/10.1021/acscatal.1c01718

[17] Wan, X., Qian, D., Ai, L. and Jiang, J. (2020) Highly Efficient Peroxymonosulfate Activation by Surface Oxidized Nickel Phosphide with Dual Active Sites. *Industrial & Engineering Chemistry Research*, **59**, 22040-22048. https://doi.org/10.1021/acs.iecr.0c04797

[18] Liu, Y., Zou, H., Ma, H., Ko, J., Sun, W., Andrew Lin, K., *et al*. (2022) Highly Efficient Activation of Peroxymonosulfate by MOF-Derived CoP/CoO_x Heterostructured Nanoparticles for the Degradation of Tetracycline. *Chemical Engineering Journal*, **430**, Article ID: 132816. https://doi.org/10.1016/j.cej.2021.132816

[19] Xu, D., Yang, T., Dong, Y., Wang, Q., Zhu, J., Zhang, G., Lv, L., Xia, Y., Ren, Z. and Wang, P. (2023) Activation of Peroxymonosulfate by CoP@Co_2P Heterostructures via Radical and Non-Radical Pathways for Antibiotics Degradation. *Ceramics International*, **49**, 16999-17007. https://doi.org/10.1016/j.ceramint.2023.02.062

[20] Luo, R., Liu, C., Li, J., Wang, J., Hu, X., Sun, X., *et al*. (2017) Nanostructured CoP: An Efficient Catalyst for Degradation of Organic Pollutants by Activating Peroxymonosulfate. *Journal of Hazardous Materials*, **329**, 92-101. https://doi.org/10.1016/j.jhazmat.2017.01.032

[21] Chen, Y., Kang, J., Li, Z., Zhu, M. and Yin, R. (2023) Activation of Peroxymonosulfate by Co_2P via Interfacial Radical Pathway for the Degradation and Mineralization of Carbamazepine. *Surfaces and Interfaces*, **40**, Article ID: 103045. https://doi.org/10.1016/j.surfin.2023.103045

[22] Tong, W., Xie, Y., Luo, H., Niu, J., Ran, W., Hu, W., *et al*. (2019) Phosphorus-Rich Microorganism-Enabled Synthesis of Cobalt Phosphide/Carbon Composite for Bisphenol a Degradation through Activation of Peroxymonosulfate. *Chemical Engineering Journal*, **378**, Article ID: 122187. https://doi.org/10.1016/j.cej.2019.122187

[23] Tong, W., Xie, Y., Hu, W., Peng, Y., Liu, W., Li, Y., *et al*. (2020) A Bifunctional CoP/N-Doped Porous Carbon Composite Derived from a Single Source Precursor for Bisphenol a Removal. *RSC Advances*, **10**, 9976-9984. https://doi.org/10.1039/d0ra00998a

[24] Fu, X., Lin, Y., Yang, C., Wu, S., Wang, Y. and Li, X. (2022) Peroxymonosulfate Activation via CoP Nanoparticles Confined in Nitrogen-Doped Porous Carbon for Enhanced Degradation of Sulfamethoxazole in Wastewater with High Salinity. *Journal of Environmental Chemical Engineering*, **10**, Article ID: 107734. https://doi.org/10.1016/j.jece.2022.107734

[25] Khan, M.A.N., Klu, P.K., Xiao, C., Qi, J., Noor, T., Sheikh, Z., *et al*. (2024) Hollow CoP/Carbon as an Efficient Catalyst for the Peroxymonosulfate Activation Derived from Phytic Acid Assisted Metal-Organic Framework. *Chemosphere*, **355**,

Article ID: 141775. https://doi.org/10.1016/j.chemosphere.2024.141775

[26] Gao, D., Lu, Y., Chen, Y., Bao, M. and Xu, N. (2022) Novel $CoFe_2P_x$ Derived from $CoFe_2O_4$ for Efficient Peroxymonosulfate Activation: Switching the Reaction Route and Suppressing Metal Leaching. *Applied Catalysis B*: *Environmental*, **309**, Article ID: 121234. https://doi.org/10.1016/j.apcatb.2022.121234

[27] Cai, W., Zhou, Z., Tan, X., Wang, W., Lv, W., Chen, H., *et al*. (2020) Magnetic Iron Phosphide Particles Mediated Peroxymonosulfate Activation for Highly Efficient Elimination of Sulfonamide Antibiotics. *Chemical Engineering Journal*, **397**, Article ID: 125279. https://doi.org/10.1016/j.cej.2020.125279

[28] Wu, M., Wang, Y., Lu, B., Xiao, B., Chen, R. and Liu, H. (2021) Efficient Activation of Peroxymonosulfate and Degradation of Orange G in Iron Phosphide Prepared by Pickling Waste Liquor. *Chemosphere*, **269**, Article ID: 129398. https://doi.org/10.1016/j.chemosphere.2020.129398

[29] Wang, X., He, Z., Xie, Y., Zhang, Y. and Wang, Y. (2023) An FeP/Carbon Composite Derived from a Phytic Acid-Fe^{3+} Complex for Sulfathiazole Degradation through Peroxymonosulfate Activation. *Chemosphere*, **313**, Article ID: 137562. https://doi.org/10.1016/j.chemosphere.2022.137562

[30] Zheng, N., He, X., Hu, R., Guo, W. and Hu, Z. (2022) Co-Activation of Persulfate by Cation and Anion from FeP for Advanced Oxidation Processes. *Applied Catalysis B*: *Environmental*, **298**, Article ID: 120505. https://doi.org/10.1016/j.apcatb.2021.120505

[31] He, Z., Zheng, W., Li, M., Liu, W., Zhang, Y. and Wang, Y. (2022) Fe_2P/Biocarbon Composite Derived from a Phosphorus-Containing Biomass for Levofloxacin Removal through Peroxymonosulfate Activation. *Chemical Engineering Journal*, **427**, Article ID: 130928. https://doi.org/10.1016/j.cej.2021.130928

[32] Sun, X., Xi, H., Dang, Y. and Yun, S. (2025) Layered Double Hydroxide-Derived Amorphous Ni-Fe Phosphides for Efficient Activation of Peroxymonosulfate to Degrade Metronidazole. *Journal of Environmental Chemical Engineering*, **13**, Article ID: 116300. https://doi.org/10.1016/j.jece.2025.116300

[33] Wu, Y., Sen, T., Zhou, L., Lei, J., Wang, L., Zhang, J., *et al*. (2025) Utilizing the Enhanced Fenton-Like Catalytic Reactivity and Superior Photothermal Conversion Capacity of Cobalt Doped Nickel Phosphide for Efficient Peroxymonosulfate Activation and Antibiotics Degradation. *Journal of Environmental Chemical Engineering*, **13**, Article ID: 116797. https://doi.org/10.1016/j.jece.2025.116797

[34] Pan, X., Pu, J., Zhang, L., Gong, X., Luo, X. and Fan, L. (2024) Bimetallic Iron-Nickel Phosphide as Efficient Peroxymonosulfate Activator for Tetracycline Hydrochloride Degradation: Performance and Mechanism. *Environmental Research*, **249**, Article ID: 118362. https://doi.org/10.1016/j.envres.2024.118362

[35] Liu, X., Zhu, Y., He, M., Zhang, C., Zuo, G., Wang, Y., *et al*. (2025) MOFs-Derived Fe Ni Bimetallic Phosphide with Tightly Coupled Heterogeneous Interface for PMS Activation. *Chemical Engineering Journal*, **521**, Article ID: 166974. https://doi.org/10.1016/j.cej.2025.166974

[36] Fan, Y., Zhou, Y., Zhang, L., Feng, Y. and Shih, K. (2021) Highly Efficient Catalysts of Phytic Acid-Derivative Cobalt Phosphide Encapsulated in N,P-Codoped Carbon for Activation of Peroxymonosulfate in Norfloxacin Degradation. *Separation and Purification Technology*, **264**, 118367. https://doi.org/10.1016/j.seppur.2021.118367

[37] Anipsitakis, G.P. and Dionysiou, D.D. (2003) Degradation of Organic Contaminants in Water with Sulfate Radicals Generated by the Conjunction of Peroxymonosulfate with Cobalt. *Environmental Science & Technology*, **37**, 4790-4797. https://doi.org/10.1021/es0263792

[38] Chan, K.H. and Chu, W. (2009) Degradation of Atrazine by Cobalt-Mediated Activation of Peroxymonosulfate: Different Cobalt Counteranions in Homogenous Process and Cobalt Oxide Catalysts in Photolytic Heterogeneous Process. *Water Research*, **43**, 2513-2521. https://doi.org/10.1016/j.watres.2009.02.029

[39] Yun, E., Lee, J.H., Kim, J., Park, H. 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

[40] Yao, J., Wu, N., Tang, X., Wang, Z., Qu, R. and Huo, Z. (2022) Methyl Phenyl Sulfoxide (PMSO) as a Quenching Agent for High-Valent Metal-Oxo Species in Peroxymonosulfate Based Processes Should Be Reconsidered. *Chemical Engineering Journal Advances*, **12**, Article ID: 100378. https://doi.org/10.1016/j.ceja.2022.100378

[41] Cao, Y., Wang, Z., He, S., Shi, L., Guo, K. and Fang, J. (2024) Reinvestigation on High-Valent Cobalt for the Degradation of Micropollutants in the Co(II)/Peroxymonosulfate System: Roles of Co(III). *Environmental Science & Technology*, **58**, 3564-3575. https://doi.org/10.1021/acs.est.3c10062

[42] Jiang, J., Zhao, Z., Gao, J., Li, T., Li, M., Zhou, D., *et al*. (2022) Nitrogen Vacancy-Modulated Peroxymonosulfate Nonradical Activation for Organic Contaminant Removal via High-Valent Cobalt-OXO Species. *Environmental Science & Technology*, **56**, 5611-5619. https://doi.org/10.1021/acs.est.2c01913

[43] Liu, B., Guo, W., Wang, H., Zheng, S., Si, Q., Zhao, Q., *et al*. (2021) Peroxymonosulfate Activation by Cobalt(II) for Degradation of Organic Contaminants via High-Valent Cobalt-Oxo and Radical Species. *Journal of Hazardous*

Materials, **416**, 125679. https://doi.org/10.1016/j.jhazmat.2021.125679

[44] Wang, Y., Shen, H., Shi, Z., Xing, Q. and Pi, Y. (2023) Activation of Peroxymonosulfate by Sulfonated Cobalt (II) Phthalocyanine for the Degradation of Organic Pollutants: The Role of High-Valent Cobalt-Oxo Species. *Chemical Engineering Journal*, **455**, Article ID: 140671. https://doi.org/10.1016/j.cej.2022.140671

[45] Ren, W., Cheng, C., Shao, P., Luo, X., Zhang, H., Wang, S., *et al*. (2021) 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

[46] Zhu, S., Jin, C., Duan, X., Wang, S. and Ho, S. (2020) Nonradical Oxidation in Persulfate Activation by Graphene-Like Nanosheets (GNS): Differentiating the Contributions of Singlet Oxygen ($^1O_2$) and Sorption-Dependent Electron Transfer. *Chemical Engineering Journal*, **393**, Article ID: 124725. https://doi.org/10.1016/j.cej.2020.124725

[47] Zhou, X., Wei, X., Lu, W., Wang, H., Liu, J., Zhang, R., *et al*. (2024) Multi-Dimensional Induction and Analysis of Singlet Oxygen Oxidation in Persulfate-Based Catalytic Oxidation Systems. *Separation and Purification Technology*, **332**, Article ID: 125811. https://doi.org/10.1016/j.seppur.2023.125811

[48] Chen, J., Dong, L., Huang, S. and Xing, S. (2025) Underestimated Role of Surface-Bound Peroxymonosulfate and Overestimated Role of SO_4^- and $^1O_2$ in Peroxymonosulfate Activation with Metal Oxides. *The Journal of Physical Chemistry C*, **129**, 20573-20582. https://doi.org/10.1021/acs.jpcc.5c06135

[49] Peng, Y., Tong, W., Xie, Y., Hu, W., Li, Y., Zhang, Y., *et al.* (2021) Yeast Biomass-Induced Co2p/biochar Composite for Sulfonamide Antibiotics Degradation through Peroxymonosulfate Activation. *Environmental Pollution*, **268**, 115930. https://doi.org/10.1016/j.envpol.2020.115930

[50] He, Z., He, Y., Chang, F., Li, Z., Niu, J., Li, M., *et al.* (2022) Efficient Ph-Universal Degradation of Antibiotic Tetracycline via Co2p Decorated Neosinocalamus Affinis Biochar. *Chemosphere*, **286**, 131759. https://doi.org/10.1016/j.chemosphere.2021.131759

[51] Wang, H., Guo, W., Si, Q., Liu, B., Zhao, Q., Luo, H., *et al*. (2021) Non-Covalent Doping of Carbon Nitride with Biochar: Boosted Peroxymonosulfate Activation Performance and Unexpected Singlet Oxygen Evolution Mechanism. *Chemical Engineering Journal*, **418**, Article ID: 129504. https://doi.org/10.1016/j.cej.2021.129504

[52] Li, H., Shan, C., Li, W. and Pan, B. (2018) Peroxymonosulfate Activation by Iron(III)-Tetraamidomacrocyclic Ligand for Degradation of Organic Pollutants via High-Valent Iron-Oxo Complex. *Water Research*, **147**, 233-241. https://doi.org/10.1016/j.watres.2018.10.015

[53] Chen, S., Hu, J., Lu, L., Wu, L., Liang, Z., Tang, J., *et al*. (2022) Iron Porphyrin-TiO_2 Modulated Peroxymonosulfate Activation for Efficient Degradation of 2,4,6-Trichlorophenol with High-Valent Iron-Oxo Species. *Chemosphere*, **309**, Article ID: 136744. https://doi.org/10.1016/j.chemosphere.2022.136744

[54] Guo, S., Chen, M., Wei, Y., You, L., Cai, C., Wei, Q., *et al*. (2023) Designing Hierarchically Porous Zero-Valent Iron via 3D Printing to Degrade Organic Pollutants by Activating Peroxymonosulfate Using High-Valent Iron-Oxo Species. *Chemical Engineering Journal*, **476**, Article ID: 146523. https://doi.org/10.1016/j.cej.2023.146523

[55] Hong, Y., Fu, Y., Xiao, J., Zhang, R., Feng, H., Zhang, Q., *et al*. (2025) Unraveling the Vital Role of Oxygen at the Molecular Level by Regulating Surface Phosphorus Vacancies for High-Performance Catalytic Oxidation. *Journal of Colloid and Interface Science*, **699**, Article ID: 138117. https://doi.org/10.1016/j.jcis.2025.138117

[56] Pan, X., Zhu, R., Zhao, L., Ma, H., Qiu, Z., Gong, X., *et al*. (2024) Peroxymonosulfate Activation by Iron-Cobalt Bimetallic Phosphide Modified Nickel Foam for Efficient Dye Degradation. *Environmental Research*, **258**, Article ID: 119420. https://doi.org/10.1016/j.envres.2024.119420

[57] Sun, Q., Wang, X., Liu, Y., Zhang, Y., Xia, S. and Zhao, J. (2023) Visible-Light-Driven g-C_3N_4 Doped $CuFe_2O_4$ Floating Catalyst Enhanced Peroxymonosulfate Activation for Sulfamethazine Removal via Singlet Oxygen and High-Valent Metal-Oxo Species. *Chemical Engineering Journal*, **455**, Article ID: 140198. https://doi.org/10.1016/j.cej.2022.140198

[58] He, P., Gu, C., Tang, B., Zhou, Y., Gan, M. and Zhu, J. (2022) Expeditious Degradation of SMX by High-Valent Cobalt-Oxo Species Derived from Cobalt-Doped C_3N_5-Activated Peroxymonosulfate with the Assistance of Visible Light. *Separation and Purification Technology*, **301**, Article ID: 122009. https://doi.org/10.1016/j.seppur.2022.122009

[59] Dong, C., Yi, Q., He, J., Xing, M. and Zhang, J. (2023) Evolution of Singlet Oxygen in Peroxymonosulfate Activation: A Review. *EES Catalysis*, **1**, 103-116. https://doi.org/10.1039/d2ey00107a

[60] Yang, P., Li, S., Xiaofu, L., Xiaojing, A., Liu, D. and Huang, W. (2022) Singlet Oxygen-Dominated Activation of Peroxymonosulfate by CuO/MXene Nanocomposites for Efficient Decontamination of Carbamazepine under High Salinity Conditions: Performance and Singlet Oxygen Evolution Mechanism. *Separation and Purification Technology*, **285**, Article ID: 120288. https://doi.org/10.1016/j.seppur.2021.120288

[61] Tian, X., Gao, P., Nie, Y., Yang, C., Zhou, Z., Li, Y., *et al*. (2017) A Novel Singlet Oxygen Involved Peroxymonosulfate Activation Mechanism for Degradation of Ofloxacin and Phenol in Water. *Chemical Communications*, **53**, 6589-6592. https://doi.org/10.1039/c7cc02820b

[62] Wang, A., Zhu, B., Huang, C., Zhang, W., Wang, M., Li, X., *et al*. (2023) Generation Mechanism of Singlet Oxygen from the Interaction of Peroxymonosulfate and Chloride in Aqueous Systems. *Water Research*, **235**, Article ID: 119904. https://doi.org/10.1016/j.watres.2023.119904

[63] Li, Y., Yu, Y., Diao, Y., Li, Y., Xie, Z. and Chen, M. (2025) Non-Radical Activation of Peroxymonosulfate by Iron-Chitosan Carbonization Composites for Selective Bisphenol a Degradation: Focusing on Singlet Oxygen and Iron-Oxo Species. *Environmental Technology & Innovation*, **40**, Article ID: 104517. https://doi.org/10.1016/j.eti.2025.104517

[64] Hou, S., Ling, L., Dionysiou, D.D., Wang, Y., Huang, J., Guo, K., *et al*. (2018) Chlorate Formation Mechanism in the Presence of Sulfate Radical, Chloride, Bromide and Natural Organic Matter. *Environmental Science & Technology*, **52**, 6317-6325. https://doi.org/10.1021/acs.est.8b00576

[65] Jing, K., Kong, D. and Lu, J. (2020) Change of Disinfection Byproducts Formation Potential of Natural Organic Matter after Exposure to Persulphate and Bicarbonate. *Water Research*, **182**, Article ID: 115970. https://doi.org/10.1016/j.watres.2020.115970

[66] Bai, L., Liu, Z., Wang, H., Li, G. and Liang, H. (2021) Fe(II)-Activated Peroxymonosulfate Coupled with Nanofiltration Removes Natural Organic Matter and Sulfamethoxazole in Natural Surface Water: Performance and Mechanisms. *Separation and Purification Technology*, **274**, Article ID: 119088. https://doi.org/10.1016/j.seppur.2021.119088

[67] Yang, X., Wu, P., Chu, W. and Wei, G. (2021) Peroxymonosulfate/$LaCoO_3$ System for Tetracycline Degradation: Performance and Effects of Co-Existing Inorganic Anions and Natural Organic Matter. *Journal of Water Process Engineering*, **43**, Article ID: 102231. https://doi.org/10.1016/j.jwpe.2021.102231

[68] Hu, C. and Yan, Y. (2024) Sulfur-Doped Carbon Nanotube Membrane Catalyst for Efficient Activation of Peroxymonosulfate and Degradation of Phenol Continuously in a Fixed Bed Reactor. *Journal of Water Process Engineering*, **67**, Article ID: 106085. https://doi.org/10.1016/j.jwpe.2024.106085

[69] Xu, P., Wei, R., Wang, P., Shen, T., Zheng, T. and Zhang, G. (2024) A Nanoconfined $FeCo_2O_4$-Embedded Ceramic Membrane Regulates Electron Transfer in Peroxymonosulfate Activation to Selectively Generate Singlet Oxygen for Water Decontamination. *Environmental Science & Technology*, **58**, 17464-17474. https://doi.org/10.1021/acs.est.4c07566