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Transition Metal Oxides as Efficient Activators of Peroxymonosulfate: A Comprehensive Review on Dye Degradation Mechanisms and Applications

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Abstract**—** Synthetic dyes originating from textile, printing, pharmaceutical, and associated industries are increasingly detected in aquatic environments, where their high chemical stability and toxicity hinder effective removal by traditional wastewater treatment methods and raise concerns for ecosystem and human safety. Advanced oxidation processes relying on sulfate radicals, with PMS as the oxidant, provide an efficient pathway for removing chemically resistant dyes. Transition metal oxides stand out among PMS activators because their flexible redox chemistry, durable lattice frameworks, surface defect sites, and tunable catalytic characteristics collectively enhance PMS activation. This review provides a comprehensive and critical assessment of PMS activation by TMOs, including Co-, Mn-, Fe-, Ni-, and Cu-based oxides, with a specific focus on dye degradation applications. Fundamental mechanisms governing PMS activation on oxide surfaces are systematically discussed, highlighting the roles of metal redox cycling, oxygen vacancies, lattice oxygen participation, and surface-mediated electron transfer. Both radical pathways ($SO_4^{\bullet-}$ and •OH) and nonradical pathways ($^1O_2$, surface-bound reactive oxygen species, and direct electron transfer) are elucidated, emphasizing how catalyst structure, morphology, defect density, and reaction conditions dictate reactive oxygen species selectivity. Comparative degradation behaviors of major dye classes, including cationic, anionic azo, xanthene, and complex conjugated dyes, are critically analyzed to establish structure-reactivity relationships. Furthermore, the advantages, limitations, and stability challenges of TMO-based PMS systems under realistic water matrices are evaluated. Finally, future research directions are outlined, focusing on defect engineering, selective nonradical oxidation, advanced characterization, computational modeling, and pilot-scale validation. This review offers a unified mechanistic framework and design guidelines for developing efficient, stable, and sustainable TMO-based PMS activation systems for advanced wastewater treatment.

Keywords**—** TMO, PMS, waste water treatment, AOP, radicals

I. INTRODUCTION

The rapid expansion of textile, printing, leather, pharmaceutical, and food industries has led to an unprecedented rise in the discharge of synthetic dyes into aquatic environments. More than 100,000 dyes and pigments are produced globally, and an estimated 7×10^8 kg of dyestuffs enter wastewater streams annually [1]. Even at very low concentrations, dyes impart intense coloration, reducing light penetration, impairing photosynthesis, and causing ecological imbalance in aquatic systems. Methylene blue, crystal violet, rhodamine B, and azo dyes are among the most commonly detected contaminants; many exhibit mutagenic, carcinogenic, and cytotoxic properties, raising serious concerns for ecological integrity and human well-being [1–3]. Because these dyes are chemically stable, highly visible, and resistant to natural degradation, their removal from wastewater remains a global challenge. Despite their widespread use, adsorption, coagulation-flocculation, membrane-based, and biological treatment methods face inherent challenges, including secondary sludge generation, substantial operational costs, limited biodegradation capability, and incomplete conversion of recalcitrant dyes into benign end products [1,2]. Although adsorption using silica gel, eggshell powders, lignocellulosic biomass, and various agricultural wastes is considered economically attractive, such methods do not eliminate dyes but instead immobilize them on solid surfaces [1,2]. Biological techniques often fail due to dye toxicity toward microbial communities and slow degradation kinetics [1]. Consequently, the development of treatment strategies that can achieve complete oxidation, mineralization, and effective detoxification of dye contaminants is critically important.

Advanced oxidation processes are widely regarded as effective strategies for the removal of persistent organic dyes, as they rely on the in-situ generation of highly reactive oxygen

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species such as hydroxyl radicals (•OH), sulfate radicals ($SO_4•^-$), and singlet oxygen ($^1O_2$)-that possess strong oxidative capability. Among AOPs, photocatalysis has been extensively studied for dye degradation using semiconductors such as ZnO, TiO_2, and NiO-based nanocomposites. Several studies demonstrate that nanostructured photocatalysts promote visible-light-driven degradation by enhancing electron–hole separation and increasing surface reactivity [3–5]. For example, NiO-doped MWCNT/PVP nanocomposites exhibit superior visible-light absorption and enhanced degradation of methylene blue due to synergistic interactions between NiO nanoparticles and conductive carbon nanotube frameworks (Mechanism has shown in Figure 1) [5]. In a similar manner, carbon nanotubes decorated with ZnO/NiO exhibit enhanced photocatalytic performance under both ultraviolet and visible irradiation, which can be attributed to heterojunction-induced charge separation and improved charge transport pathways [4].

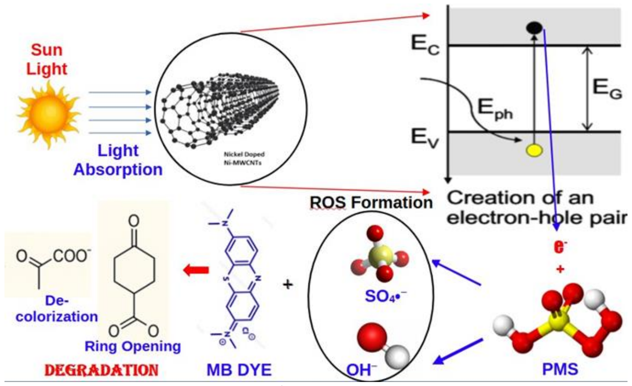

Figure 1. Schematic illustration of the proposed photocatalytic degradation pathway of methylene blue (MB) over Ni-doped MWCNTs under solar irradiation, involving PMS activation and the generation of reactive oxygen species.

Electrochemical AOPs such as electro-Fenton and sono-electro-Fenton systems also demonstrate excellent degradation efficiencies for azo dyes and phenolic pollutants by generating •OH radicals in situ from Fenton-like reactions. Three-dimensional electrode architectures using iron foam, carbon fibers, and copper foams improve mass transfer, increase active sites, and enhance hydroxyl radical production, leading to rapid oxidation of methyl orange and phenol under optimized conditions [6,7]. Hybrid advanced oxidation processes are increasingly viewed as next-generation wastewater treatment strategies because of their high treatment efficiency, reduced formation of secondary pollutants, and the possibility of energy recovery when integrated into systems such as photocatalytic fuel cells [8].

In recent studies, sulfate radical ‑ driven advanced oxidation processes employing peroxymonosulfate have gained increasing attention. Upon activation, PMS can produce $SO_4•^-$ (E° ≈ 3.1 V) and •OH (E° ≈ 2.8 V), offering high redox potential, broad pH applicability, and strong degradation ability against a wide range of organic contaminants. Peroxymonosulfate can be activated through multiple pathways, including ultraviolet light exposure, thermal stimulation, carbon-based materials, electrochemical techniques, and catalysis by transition metals such as Co, Fe, Mn, Ni, and Cu. Transition metal catalysts particularly cobalt are among the most effective activators because PMS readily forms metal oxygen intermediates that promote radical generation. Recent studies on Co-N doped carbon nanotubes reveal that PMS activation may proceed via both radical and nonradical pathways (e.g., singlet oxygen formation and electron-transfer mechanisms), signifying the complexity and tunability of PMS-based AOPs [9].

Despite significant progress in PMS activation, transition metal oxides (TMOs) such as Co_3O_4, MnO_2, Fe_2O_3, CuO, NiO, $MnFe_2O_4$, and $CoFe_2O_4$ have emerged as a distinct and highly efficient class of PMS activators. Their catalytic potential arises from several unique attributes:

1. Abundant surface oxygen vacancies and defect sites, which promote PMS adsorption, peroxide bond cleavage, and rapid generation of reactive oxygen species (ROS).
2. Redox-active metal centers (e.g., Co^{2+}/Co^{3+}, Mn^{3+}/Mn^{4+}, Fe^{2+}/Fe^{3+}) that facilitate continuous electron transfer during PMS activation and stabilize key reaction intermediates.
3. Capability to generate both radical and nonradical oxidants, including $SO_4•^-$, •OH, $^1O_2$, and surface-bound reactive oxygen species through lattice oxygen participation and defect-mediated activation.
4. High stability and low energy requirements, enabling efficient PMS activation under ambient or visible-light-assisted conditions.
5. Tunability of catalytic activity through morphology, crystal facets, doping, and heterojunction engineering, which regulate electron mobility, defect concentration, and PMS interaction pathways.

While transition metal oxides are well-established catalysts in heterogeneous oxidation, their role in PMS-driven dye degradation has not been comprehensively synthesized in the literature. Existing AOP reviews primarily focus on carbon-based catalysts, doped metal–nitrogen materials, or electrochemical systems, with limited mechanistic emphasis on PMS activation specifically by TMOs. However, emerging studies indicate that TMOs may outperform many conventional catalysts by offering superior redox flexibility, defect-driven ROS generation, controllable selectivity between radical and nonradical pathways, and enhanced operational stability.

A systematic review of PMS activation by transition metal oxides is particularly relevant at present, given the expanding role of PMS-based advanced oxidation processes in dye removal and the demand for economically viable wastewater treatment technologies. Such a review can consolidate mechanistic understanding, clarify structure–activity relationships, and highlight opportunities for rational catalyst design.

Accordingly, this review presents a detailed and critical evaluation of transition metal oxides as effective catalysts for peroxymonosulfate activation in dye degradation applications. The review examines the fundamental chemistry governing PMS activation on oxide surfaces and elucidates both radical and nonradical pathways involved in pollutant oxidation. Particular emphasis is placed on understanding how metal oxidation states, defect concentration, pH, morphology, and reaction conditions collectively influence activation kinetics and ROS selectivity. Additionally, the review compares catalytic performance across different dyes to identify structure–reactivity correlations and oxide-specific advantages. The review further examines the benefits, existing limitations, and future research directions of transition metal oxide–based PMS systems for wastewater remediation. By integrating mechanistic insights with catalytic performance evaluation, this work provides a unified framework for understanding how transition metal oxides enable efficient, tunable, and sustainable PMS-driven dye degradation.

II. FUNDAMENTALS OF PEROXYMONOSULFATE ACTIVATION BY TRANSITION METAL OXIDES

A wide range of transition metal oxides, including Co_3O_4, Fe_2O_3, MnO_2, NiO, CuO, $MnFe_2O_4$, and $CoFe_2O_4$, have been widely reported as effective heterogeneous catalysts for peroxymonosulfate activation in advanced oxidation processes. Their catalytic functions originate from a combination of redox-active metal centers, surface oxygen vacancies, lattice oxygen participation, and structural tunability, all of which contribute to efficient ROS generation and dye degradation. This section outlines the fundamental chemistry underlying PMS activation by TMOs, highlighting the roles of metal centers, oxide structures, and operational parameters.

i) Chemistry of PMS and Its Interaction with Metal Oxide Surfaces

PMS (HSO_5^-) is a versatile oxidant containing a peroxide bond (-O-O-), which can be cleaved via electron transfer. When PMS interacts with TMO surfaces, several parallel processes can occur:

1. Adsorption of PMS onto Lewis acidic metal sites or oxygen vacancy sites
2. Electron transfer from the metal center or surface oxygen sites to PMS
3. O-O bond dissociation leading to reactive oxygen species formation

The generalized activation reaction involves:

$$M^{n+}\text{-O(surface)} + HSO_5^- \rightarrow M^{n+1}\text{-O(surface)} + SO_4^{\bullet -} + OH^-$$

Transition metal oxides facilitate PMS activation by offering both metal redox cycling and defect-driven electron transfer, creating multiple pathways for ROS production.

ii) Role of Redox-Active Metal Centers in PMS Activation

A key feature of transition metal oxides lies in the capacity of their metal centers to reversibly adopt multiple oxidation states [10]:

- Co^{2+}/Co^{3+} in Co_3O_4
- Fe^{2+}/Fe^{3+} in Fe_2O_3 and spinel ferrites
- Mn^{3+}/Mn^{4+} in MnO_2
- Cu^+/Cu^{2+} in CuO

These redox transitions enable catalytic cycles that drive PMS activation. For instance:

- Co_3O_4 exposes both Co^{2+} (tetrahedral sites) and Co^{3+} (octahedral sites), leading to rapid PMS activation and $SO_4^{\bullet -}$ production.
- Mn-based oxides promote PMS activation via Mn^{3+}/Mn^{4+} cycling and can generate both $SO_4^{\bullet -}$ and $^1O_2$ depending on surface conditions.

The flexibility of these redox couples is crucial for sustaining continuous ROS production without catalyst deactivation.

iii) Role of Oxygen Vacancies and Surface Defects

Unlike transition metal halides, metal oxides possess oxygen vacancies (V_0) and defect sites that strongly influence PMS activation [11].

Key functions of oxygen vacancies:

1. Enhance PMS adsorption through strong binding to defect sites.

2. Serve as electron donors, enabling PMS reduction and generating ROS.
3. Activate lattice oxygen, facilitating nonradical pathways.
4. Stabilize transient catalytic intermediates, improving turnover frequency.

Oxygen-deficient structures, such as defect-rich Co_3O_4, MnO_2 nanosheets, and NiO nanoparticles, often show dramatically higher PMS activation efficiency due to these defect-related processes.

iv) Radical Pathways in TMO-Activated PMS Systems

TMOs can generate a variety of free radicals during PMS activation:

(a) Sulfate Radicals ($SO_4^{\bullet -}$)

Formed via electron transfer between PMS and metal centers [10]:

$$M^{n+} + HSO_5^- \rightarrow M^{n+1} + SO_4^{\bullet -}$$

$SO_4^{\bullet -}$ selectively oxidizes electron-rich moieties in dyes and often initiates ring-opening and chromophore destruction.

(b) Hydroxyl Radicals (•OH)

Produced through secondary hydrolysis of $SO_4^{\bullet -}$ or direct formation at oxide surfaces:

$$SO_4^{\bullet -} + H_2O \rightarrow \bullet OH + HSO_4^-$$

•OH contributes to deeper oxidation and mineralization of dye molecules.

(c) Surface-Bound Radicals

TMOs can generate surface-bound $SO_4^{\bullet -}$ or •OH species that exhibit:

- higher selectivity,
- slower diffusion,
- stronger adsorption-driven oxidation.

This “surface radical” pathway is particularly important in ferrites and spinel oxides.

v) Nonradical Pathways: Defect-Driven and Lattice Oxygen Mechanisms

Although radical pathways are common, TMOs are also known to induce significant nonradical oxidation, including [12]:

(a) Singlet Oxygen ($^1O_2$)

$^1O_2$ can be generated through:

- PMS activation at oxygen vacancy sites,
- energy transfer from surface-bound PMS intermediates,
- transformation of superoxide intermediates.

MnO_2, Co_3O_4, and CuO frequently exhibit $^1O_2$-mediated dye degradation, which is especially effective in complex wastewater systems.

(b) Surface-Mediated Electron Transfer (SMET)

In this pathway:

- PMS adsorbs on metal oxide surfaces,
- electron transfer occurs without releasing free radicals,
- dyes are oxidized through direct interaction with adsorbed PMS.

This mechanism is enhanced by oxygen vacancies, which act as electron reservoirs. SMET pathways are highly resistant to radical scavengers (e.g., bicarbonate, chloride) and reduce by-product formation.

(c) Lattice Oxygen Participation (LOM)

In some TMOs, especially Co_3O_4 and MnO_2:

- lattice oxygen can directly participate in oxidation reactions,
- PMS triggers oxygen migration from the oxide lattice,
- reactive oxygen species are created without external electron donors.

LOM contributes to nonradical degradation and enhances selectivity toward specific dye structures.

vi) Influence of Metal Oxide Type on PMS Activation

Each oxide exhibits distinct catalytic behavior [13,14]:

- Co_3O_4: highest activity, dual redox centers, abundant defects.
- MnO_2: strong $^1O_2$ formation, tunable crystal phases (α, β, δ).
- Fe_2O_3 / Fe_3O_4: efficient for radical-dominated pathways, magnetic recovery.
- NiO: defect-rich surfaces favor nonradical pathways.
- CuO: electron-transfer-dominated PMS activation.

Structural modifications doping, forming heterojunctions, making nanostructures further improve activity.

vii) Effect of pH and Reaction Conditions

pH significantly influences PMS activation by TMOs[15,16]:

- Acidic pH (3-5): enhances $SO_4^{\bullet -}$ formation via rapid metal redox cycling.
- Neutral pH: favors $^1O_2$ and SMET pathways, especially in vacancy-rich oxides.
- Alkaline pH: slows radical production but promotes electron-transfer pathways.

Additional factors include:

- PMS concentration
- oxide dosage
- temperature
- ionic strength

- dye molecular structure

These parameters dictate whether radical or nonradical pathways dominate.

III. RADICAL AND NONRADICAL DEGRADATION PATHWAYS IN TRANSITION METAL OXIDE–ACTIVATED PMS SYSTEMS

Peroxymonosulfate activation by transition metal oxides proceeds via both radical and nonradical routes, which are regulated by the redox behavior of the metal centers, the concentration of oxygen vacancies, and the structural features of the oxide lattice. Unlike transition metal halides, which rely heavily on ligand-assisted reactivity, metal oxides activate PMS primarily through metal-centered electron transfer and defect-mediated catalysis. Understanding the balance between these pathways is essential for optimizing dye degradation efficiency and catalyst design [17–24].

i) Radical Pathways

a) Sulfate Radical Formation ($SO_4\bullet^-$)

Sulfate radicals ($SO_4\bullet^-$) are the primary oxidants produced in PMS activation:

$$M^{n+} + HSO_5^- \rightarrow M^{n+1} + SO_4\bullet^- + OH^-$$

TMOs with redox-active metal centers—such as Co_3O_4 (Co^{2+}/Co^{3+}), Fe_2O_3 (Fe^{2+}/Fe^{3+}), and MnO_2 (Mn^{3+}/Mn^{4+})—exhibit fast PMS activation cycles due to their ability to shuttle electrons efficiently. $SO_4\bullet^-$ is highly selective toward electron-rich dye molecules, attacking azo bonds, aromatic systems, and heteroatoms. In Co_3O_4/PMS systems, the high density of Co^{2+} sites enables rapid PMS activation, resulting in abundant $SO_4\bullet^-$ generation and accelerated decolorization.

b) Hydroxyl Radical Formation (•OH)

Hydroxyl radicals are produced either by hydrolysis of $SO_4\bullet^-$ or by direct surface-mediated activation:

$$SO_4\bullet^- + H_2O \rightarrow \bullet OH + HSO_4^-$$

•OH is highly reactive and nonselective, often responsible for deeper oxidation and mineralization of dye molecules. Fe-based oxides (Fe_2O_3, Fe_3O_4) favor pathways that generate •OH, reflecting their similarity to Fenton-type reactions. Under neutral to alkaline pH, this •OH generation becomes predominant due to the accelerated conversion of $SO_4\bullet^-$.

c) Surface-Bound Radicals

Metal oxides frequently generate surface-bound $SO_4\bullet^-$ and •OH, which differ from free radicals in solution. These surface radicals exhibit:

- slower diffusion,
- higher selectivity for adsorbed dye molecules,
- reduced scavenging by background ions.

Ferrite oxides (e.g., $CoFe_2O_4$, $MnFe_2O_4$) and defect-rich NiO often show strong contributions from surface-bound radicals, making them ideal for targeted dye oxidation with minimal secondary reactions.

ii) Nonradical Pathways

While radical species dominate in many PMS-AOP systems, TMOs are unique in their ability to also promote nonradical oxidation, especially via oxygen vacancies and lattice oxygen. These pathways provide superior selectivity, resistance to radical scavengers, and improved catalyst longevity.

a) Singlet Oxygen Pathway ($^1O_2$)

Singlet oxygen is an important nonradical ROS generated in many TMO/PMS systems. Its formation pathways include:

- PMS activation at oxygen vacancy sites,
- recombination of peroxo intermediates on the oxide surface,
- energy transfer involving lattice oxygen.

MnO_2, Co_3O_4, and CuO are particularly known for generating $^1O_2$ under PMS activation. $^1O_2$ selectively oxidizes aromatic rings and electron-rich groups, making it an effective oxidant for dyes such as RhB, MB, and reactive azo dyes while avoiding excessive mineralization.

b) Surface-Mediated Electron Transfer (SMET)

In SMET pathways:

- PMS adsorbs onto the oxide surface,
- electrons transfer directly from the oxide to PMS,
- dye molecules are oxidized without forming free radicals.

This mechanism is enhanced by:

- high oxygen vacancy concentrations,
- conductive oxide structures,
- well-defined nanostructures such as nanosheets or spinels.

SMET pathways are especially beneficial in wastewater containing high levels of bicarbonate, chloride, or natural organic matter-conditions that deactivate radicals but do not affect PMS-surface electron transfer.

c) Lattice Oxygen Mechanism (LOM)

Certain TMOs, particularly Co_3O_4 and MnO_2, can activate PMS via lattice oxygen participation:

1. PMS extracts electron density from the oxide surface.
2. Lattice oxygen becomes activated and participates in oxidizing the dye.
3. Oxygen vacancies are formed and subsequently replenished by dissolved oxygen or PMS itself.

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The LOM pathway can significantly enhance nonradical degradation efficiency, making it an attractive mechanism for stable and selective oxidation in real wastewater environments.

iii) Interplay Between Radical and Nonradical Pathways

The dominant pathway-radical or nonradical-depends on several key factors:

Factor	Radical-Dominated Conditions	Nonradical-Dominated Conditions
pH	Acidic	Near-neutral
PMS concentration	High	Moderate
Oxygen vacancy concentration	Low–moderate	High
Dye adsorption strength	Adjusts radical access	Promotes SMET
Oxide type	Fe_2O_3, Co_3O_4	MnO_2, NiO, Co_3O_4 (defect-rich)

Many TMOs operate via dual mechanisms, where radicals initiate dye decolorization while nonradical pathways complete degradation or handle intermediate species.

iv) Key Mechanistic Insights

1. Transition metal oxides provide both metal-centered and defect-driven PMS activation, unlike halide systems, which rely mainly on ionic ligand effects.
2. Oxygen vacancies play a decisive role in enabling nonradical pathways, particularly $^1O_2$ and SMET.
3. The balance between $SO_4^{\bullet}$, •OH, $^1O_2$, and surface oxygen species can be tuned via doping, morphology control, and pH adjustment.
4. Nonradical mechanisms enhance catalyst stability, making TMOs promising for practical wastewater treatment.

IV. INFLUENCE OF METAL OXIDE TYPE, MORPHOLOGY, DEFECT STRUCTURE, AND REACTION CONDITIONS ON PMS ACTIVATION

The efficiency of PMS activation over transition metal oxides is determined by a combination of inherent material characteristics, such as metal valence states, crystal framework, oxygen-vacancy density, and morphology and operational parameters including solution pH, PMS concentration, temperature, and coexisting inorganic ions. Understanding how these factors interact is crucial for designing oxide catalysts capable of delivering optimal dye degradation performance. This section systematically examines these influences, integrating mechanistic insights and experimental findings from the literature [25–33].

i) Influence of the Metal Center and Oxide Composition

a) Co-Based Oxides (Co_3O_4, CoO)

Cobalt oxides are among the most active PMS activators owing to their dual-valence Co^{2+}/Co^{3+} redox couples and abundant surface-active sites. Co_3O_4 exposes both tetrahedral Co^{2+} and octahedral Co^{3+} sites, enabling fast PMS adsorption and efficient generation of $SO_4^{\bullet -}$ and $^1O_2$. Oxygen-deficient Co_3O_4 nanostructures further enhance activity by increasing electron density around Co^{2+} and stabilizing PMS-bound intermediates.

b) Mn-Based Oxides (MnO_2, Mn_2O_3, Mn_3O_4)

Mn oxides possess multiple oxidation states ($Mn^{2+}/Mn^{3+}/Mn^{4+}$), promoting PMS activation through both radical and nonradical pathways. Their strong affinity for generating $^1O_2$ is well-documented, particularly in δ-MnO_2 nanosheets with high vacancy densities. MnO_2 also exhibits strong adsorption toward aromatic dyes, facilitating electron transfer at the oxide–dye interface.

c) Fe-Based Oxides (Fe_2O_3, Fe_3O_4)

Iron oxides activate PMS primarily through Fe^{2+}/Fe^{3+} cycles analogous to heterogeneous Fenton processes [6] (Figure 2). Fe_3O_4 offers the added advantage of magnetic recovery and can generate both $SO_4^{\bullet -}$ and •OH efficiently. Defect engineering in hematite (α-Fe_2O_3) enhances PMS activation by increasing Fe^{2+} availability on the surface.

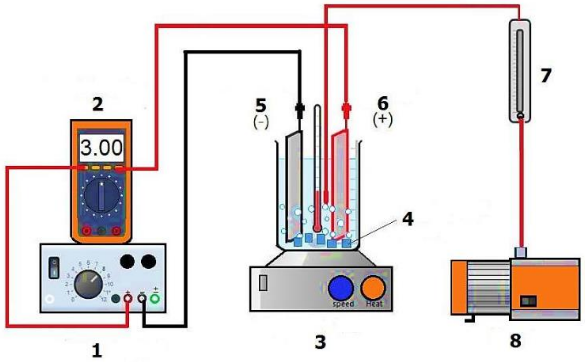

Figure 2. Schematic illustration of the electro-Fenton setup, comprising: 1) power source, 2) multimeter, 3) magnetic stirrer, 4) iron particles, 5) cathode, 6) anode, 7) flow meter and 8) pump [6].

d) NiO-Based Catalysts

NiO often favors nonradical PMS activation mechanisms such as surface-mediated electron transfer (SMET), especially when enriched with surface defects. NiO nanoparticles exhibit good structural stability and tunable reactivity via doping with Co or Fe.

e) CuO-Based Catalysts

CuO activates PMS primarily through electron-transfer pathways, generating $O_2\bullet^-$ and promoting $^1O_2$-mediated oxidation. Cu^+/Cu^{2+} cycles support continuous PMS activation and allow selective oxidation of aromatic dye structures.

ii) Influence of Crystal Structure and Phase

Crystal phase strongly affects catalytic properties by modifying the coordination environment of active metal centers:

- **Spinel structures (Co_3O_4, $MnFe_2O_4$)** show high activity because of synergistic interactions among tetrahedral and octahedral metal sites.
- **Layered δ-MnO_2** phase demonstrates enhanced catalytic performance relative to the α- and β-polymorphs, primarily due to its larger surface area and higher density of defect sites.
- **Mixed metal oxides (ferrites)** offer enhanced stability and tunable band structures, improving PMS activation efficiency.

These structural differences influence adsorption energy, electron mobility, and defect formation.

iii) Role of Morphology and Nanostructure

Nanostructured TMOs such as nanosheets, nanorods, hollow spheres, and porous frameworks exhibit significantly enhanced PMS activation due to:

1. Increased surface area for PMS adsorption
2. High density of defect sites (oxygen vacancies, edges)
3. Improved charge transfer rates
4. Short diffusion paths for reactants and intermediates

For example:

- Co_3O_4 nanoneedles outperform bulk Co_3O_4 because of their sharp tip geometry and higher defect density.
- MnO_2 nanosheets exhibit superior $^1O_2$ generation due to exposed edge sites.
- Hierarchical Fe_3O_4 microspheres enable magnetic recovery while maintaining high PMS activation efficiency.

Morphology engineering therefore plays a central role in optimizing catalytic activity.

iv) Influence of Oxygen Vacancies and Surface Defects

Oxygen vacancies (V_0) are critically important in PMS activation by TMOs, influencing both radical and nonradical pathways.

Key functions of oxygen vacancies:

- Enhance PMS adsorption and activation
- Facilitate electron transfer from the oxide to PMS
- Promote formation of $^1O_2$ and surface-bound ROS
- Support lattice oxygen participation (LOM)
- Stabilize transition states and reaction intermediates

Vacancy-rich Co_3O_4, δ-MnO_2, and NiO have shown markedly enhanced catalytic performance compared to vacancy-poor analogues.

v) Effect of pH

pH is one of the most influential external parameters:

Acidic pH (3–5):

- Enhances $SO_4\bullet^-$ production
- Promotes metal-centered redox cycling
- Increases surface protonation, improving PMS adsorption

Neutral pH (6–8):

- Shifts mechanism toward $^1O_2$ and SMET pathways
- Reduces $SO_4\bullet^-$ lifetime but increases stability
- Ideal for real wastewater treatment

Alkaline pH (> 8):

- Suppresses radical formation
- Encourages electron-transfer mechanisms
- May cause oxide dissolution in some systems (e.g., Co-based oxides)

Thus, the optimal pH depends on the desired oxidation pathway and target dye.

vi) Effect of PMS Concentration

While increasing PMS concentration generally enhances ROS generation, excessively high levels can:

- Lead to self-scavenging of radicals
- Generate unnecessary oxidant waste
- Shift mechanisms toward nonradical pathways

Therefore, catalytic systems require PMS optimization to balance radical and nonradical oxidation.

vii) Influence of Co-existing Ions and Natural Organic Matter

Chloride and bicarbonate ions:

Can scavenge radicals ($SO_4\bullet^-$, •OH) but do not significantly affect $^1O_2$ and SMET pathways.

Natural organic matter (NOM):

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Competes with dyes for adsorption sites, reducing radical-driven oxidation but having limited effect on nonradical pathways.

Metal ions (Ca^{2+}, Mg^{2+}):

May promote aggregation, reducing catalytic activity.

These findings highlight the robustness of nonradical systems in complex matrices.

V. COMPARATIVE DEGRADATION EFFICIENCIES OF DIFFERENT DYES USING TRANSITION METAL OXIDE–ACTIVATED PMS SYSTEMS

The performance of transition metal oxides in peroxymonosulfate activation is influenced by multiple factors, including the molecular structure of the target dye, the prevailing oxidation mechanism (radical or nonradical), and the physicochemical characteristics of the catalyst. Accordingly, this section evaluates the degradation behavior of commonly studied dyes-such as methylene blue (MB), rhodamine B (RhB), methyl orange (MO), crystal violet (CV), and representative reactive azo dyes-in TMO/PMS systems, with emphasis on the mechanistic factors that control dye-dependent degradation kinetics [13,34–42].

i) Degradation of Cationic Dyes (Methylene Blue, Crystal Violet)

Cationic dyes are positively charged and readily adsorb onto negatively charged oxide surfaces, making them highly responsive to TMO/PMS treatment.

Methylene Blue (MB)

Co_3O_4/PMS and MnO_2/PMS systems often achieve rapid MB removal due to strong electrostatic adsorption and efficient ROS generation. For instance:

- Co_3O_4 nanorods activated PMS to degrade >95% MB within 10–15 minutes through combined $SO_4^{\bullet-}$ and $^1O_2$ oxidation pathways.
- Vacancy-rich MnO_2 nanosheets achieved complete MB decolorization primarily through $^1O_2$-dominated pathways.

The strong π-conjugated structure of MB facilitates ring-opening reactions initiated by $SO_4^{\bullet-}$, while $^1O_2$ contributes to stepwise N-demethylation.

Crystal Violet (CV)

Crystal violet degradation is typically slower than MB due to steric hindrance and multi-branched aromatic rings. However:

- Co_3O_4/PMS systems demonstrate high efficiency (>90% removal in 20–30 min) via surface-bound $SO_4^{\bullet-}$ and lattice oxygen-mediated oxidation.
- CuO/PMS systems exhibit selective oxidation of dimethyl-amino functional groups through SMET and $^1O_2$ pathways.

Thus, cationic dyes generally respond well to TMO/PMS activation, with reaction rates influenced by molecular size and electron density.

ii)Degradation of Anionic Azo Dyes (Methyl Orange, Orange II, Reactive Black 5)

Azo dyes contain one or more -N=N- groups that serve as chromophoric sites highly susceptible to attack by $SO_4^{\bullet-}$ and $Cl_2^{\bullet-}$ (if present). However, their anionic nature reduces electrostatic attraction to many oxides.

Methyl Orange (MO)

- Fe_3O_4/PMS systems efficiently degrade MO (>90% in 30 min) using $SO_4^{\bullet-}$ and •OH, aided by strong adsorption through Fe-O-S interactions.
- Co_3O_4/PMS systems show faster azo bond cleavage due to Co^{2+}-centered electron transfer.
- MnO_2/PMS systems exhibit moderate degradation rates because $^1O_2$ interacts selectively with electron-rich groups but less efficiently with azo bonds.

Reactive Black 5 / Reactive Orange 16

These dyes contain multiple azo groups and sulfonate substituents:

- Fe_2O_3/PMS systems often require acidic conditions to achieve high efficiency due to limited adsorption at neutral pH.
- $CoFe_2O_4$/PMS systems combine magnetic recoverability with higher activity due to synergistic Fe-Co redox interactions.

iii) Degradation of Xanthene Dyes (Rhodamine B)

Rhodamine B (RhB) is a common representative of xanthene dyes, characterized by its conjugated ring structure and high photostability.

Key Observations:

- Co_3O_4/PMS achieves >90% RhB degradation in minutes due to rapid deethylation and ring cleavage via $SO_4^{\bullet-}$.
- MnO_2/PMS and CuO/PMS show strong nonradical pathways ($^1O_2$ and SMET), producing fewer intermediates and minimizing over-oxidation.
- NiO/PMS generally shows slower RhB degradation but high stability, making it suitable for repeated cycles.

RhB degradation typically begins with N-deethylation, followed by ring opening and mineralization.

iv) Degradation of Mixed Molecular Structure Dyes (e.g., Congo Red, Malachite Green)

Congo Red (CR)

CR contains two azo bonds and large aromatic moieties:

- Co_3O_4 and Fe_3O_4 activate PMS to cleave azo bonds rapidly, producing low-molecular-weight aromatic intermediates.
- MnO_2/PMS shows slower CR degradation due to limited radical generation and selective $^1O_2$ reactivity.

Malachite Green (MG)

MG degradation requires radical-driven pathways due to steric hindrance:

- Co_3O_4/PMS rapidly degrades MG via $SO_4^{\bullet-}$-assisted oxidation.
- CuO/PMS shows moderate performance, relying more on SMET pathways.

v) Mechanistic Comparison Across Dye Classes

Dye Class	Preferred Pathway	Most Effective Oxide Catalysts	Mechanistic Notes
Cationic dyes (MB, CV)	$SO_4^{\bullet-}$ + $^1O_2$	Co_3O_4, MnO_2, CuO	Strong adsorption accelerates oxidation
Anionic azo dyes (MO, RB5)	$SO_4^{\bullet-}$, •OH	Fe_3O_4, Co_3O_4, $CoFe_2O_4$	Azo bonds cleaved rapidly by $SO_4^{\bullet-}$
Xanthene dyes (RhB)	$SO_4^{\bullet-}$, $^1O_2$	Co_3O_4, MnO_2	Deethylation precedes mineralization
Large conjugated dyes (CR, MG)	$SO_4^{\bullet-}$ dominant	Co_3O_4, Fe_2O_3	Steric hindrance slows nonradical pathways

vi) Key Insights from Comparative Studies

1. Co_3O_4 remains the most universally effective catalyst across different dye structures due to dual-valence redox centers and strong PMS affinity.
2. MnO_2 excels in nonradical oxidation, offering high selectivity and stability but sometimes slower degradation.
3. Fe_2O_3 and Fe_3O_4 show strong performance for azo dyes, particularly under acidic conditions.
4. CuO favors electron-transfer pathways, making it ideal for dyes containing electron-donating substituents.

Dye structure dictates the dominant pathway—cationic dyes respond better to nonradical pathways, while azo dyes require radical-driven oxidation.

VI. ADVANTAGES, LIMITATIONS, AND FUTURE PROSPECTS OF TRANSITION METAL OXIDE–BASED PMS ACTIVATION

Transition metal oxides (TMOs) offer a promising platform for PMS activation in advanced oxidation processes due to their rich redox chemistry, structural tunability, and environmental compatibility. However, despite their rapid progress, significant challenges remain that must be addressed before large-scale deployment in wastewater treatment can be realized. This section summarizes the key advantages, limitations, and emerging research opportunities for TMO-driven PMS oxidation systems [43–45].

i) Advantages of TMO-Based PMS Activation

a) Abundant Redox-Active Sites

TMOs such as Co_3O_4, MnO_2, Fe_2O_3, Fe_3O_4, and CuO possess multiple accessible oxidation states (e.g., Co^{2+}/Co^{3+}, Mn^{3+}/Mn^{4+}, Fe^{2+}/Fe^{3+}), enabling efficient electron transfer in PMS activation cycles. This allows continuous ROS generation without external co-activators.

b) Tunable Radical and Nonradical Pathways

TMOs can activate PMS through a versatile combination of:

- $SO_4^{\bullet-}$ and •OH (radical pathways)
- $^1O_2$, lattice oxygen participation (LOM), and SMET (nonradical pathways)

This tunability allows tailoring the oxidation mechanism for specific dyes or wastewater compositions.

c) Structural Robustness and High Stability

Compared with metal halides or homogeneous metal salts, TMOs are:

- resistant to dissolution,
- chemically and thermally stable,
- reusable for many cycles without losing activity (Chen et al., 2020).

Magnetic ferrites (e.g., Fe_3O_4, $CoFe_2O_4$) enable easy recovery with external magnets, reducing secondary pollution.

d) Environmentally Friendly and Economically Viable

TMOs are generally low-cost, abundant, and have:

- minimal toxicity,
- long operational lifetimes,
- no need for supporting electrolytes or UV/visible light (although light can enhance activity).

Fe-, Mn-, and Ni-based oxides are especially attractive for scalable, sustainable wastewater treatment.

e) Morphology and Defect Engineering Enhance Performance

Innovations such as nanosheets, nanorods, hollow spheres, and doped oxides dramatically enhance PMS activation by:

- increasing oxygen vacancy concentration,
- exposing more surface-active sites,
- improving PMS adsorption and charge mobility.

ii) Limitations and Challenges

a) Potential Release of Metal Ions

Although TMOs are more stable than halides, partial dissolution of Co, Mn, or Cu may occur under acidic conditions, raising concerns about toxicity and secondary contamination.

This is especially relevant for cobalt-based systems.

b) Reduced Efficiency in Real Wastewater

Competing ions (Cl^-, HCO_3^-, SO_4^{2-}) and natural organic matter (NOM) can:

- scavenge $SO_4^{\bullet-}$ and •OH
- block adsorption sites
- shift the mechanism toward less efficient pathways

Although nonradical mechanisms are less sensitive to these ions, they may degrade dyes more slowly.

c) Difficulty in Controlling Reaction Selectivity

Radical pathways may lead to:

- non-selective oxidation,
- formation of undesired by-products,
- excessive mineralization consuming more PMS than necessary.

Balancing radical and nonradical contributions remains a challenge.

d) Oxygen Vacancies: Hard to Quantify and Control

While oxygen vacancies enhance performance, precisely tuning and characterizing them is nontrivial. Most synthesis methods lack reproducibility, and the stability of vacancies during long-term operation is insufficiently understood.

e) Catalyst Deactivation

Catalyst fouling may occur due to:

- adsorption of dye intermediates,
- blockage of active sites,
- structural changes under PMS exposure.

Repeated cycling may require regeneration steps.

iii) Future Prospects and Research Directions

a) Rational Design Through Defect and Interface Engineering

Future catalyst design should focus on:

- controlled oxygen vacancy creation,
- heterojunction engineering (Co_3O_4/MnO_2, Fe_2O_3/NiO),
- metal-oxygen-metal (M-O-M) bond optimization.

These strategies can enhance electron transfer, PMS activation, and ROS selectivity.

b) Development of Selective Nonradical Oxidation Systems

$^1O_2$- and SMET-driven processes offer:

- minimal by-products
- strong resistance to scavengers
- better performance in real wastewater

Designing catalysts that favor these pathways-such as vacancy-rich MnO_2 or NiO is a promising direction.

c) Real Wastewater Application and Pilot-Scale Studies

Most current studies use model dyes; however, full-scale validation requires:

- continuous-flow reactor studies,
- multi-contaminant wastewater,
- assessment of catalyst stability over long periods.

Integration into hybrid systems (electrochemical, photocatalytic) may further improve efficiency.

d) Sustainable and Green Catalyst Synthesis

Future efforts should prioritize:

- biomass-derived templates,
- green precipitation methods,
- solvent-free and low-energy synthesis,
- doping with earth-abundant metals.

These approaches can make TMO catalysts more environmentally and economically viable.

e) Advanced Characterization and Computational Modeling

To understand PMS activation mechanisms more clearly, progress is needed in:

- operando spectroscopy (XPS, EPR, XRD),
- in situ Raman/FTIR for intermediate identification,

- density functional theory (DFT) simulations to map activation pathways.

DFT-guided design will be central to next-generation PMS catalysts.

VII. CONCLUSION

Transition metal oxides (TMOs) have emerged as one of the most promising classes of catalysts for activating peroxymonosulfate (PMS) in advanced oxidation processes for dye degradation. Their success stems from a unique combination of features, including redox-active metal centers, abundant surface defects, tunable morphology, and strong structural stability. Together, these attributes enable TMOs to activate PMS through a rich diversity of oxidative pathways, encompassing both highly reactive radical species ($SO_4^{\bullet-}$, •OH) and selective nonradical species such as singlet oxygen ($^1O_2$) and surface-mediated electron transfer (SMET). This mechanistic versatility allows TMOs to be adapted for a wide range of dye molecules with varying charge, molecular structure, and electronic characteristics. Comparative studies demonstrate that Co-, Mn-, Fe-, Ni-, and Cu-based oxides each exhibit distinct reactivity patterns. Co_3O_4 remains one of the most potent catalysts due to efficient Co^{2+}/Co^{3+} cycling and high affinity toward PMS, whereas MnO_2 excels in nonradical oxidation pathways driven by abundant oxygen vacancies. Iron oxides offer cost-effective and environmentally benign alternatives with strong PMS activation, particularly for azo dyes. The catalytic performance of TMOs can be further enhanced through morphology engineering, defect generation, heteroatom doping, and formation of mixed-metal oxides or heterojunction composites.

Despite these advancements, several challenges impede large-scale application. Metal ion leaching, reduced activity in complex wastewater matrices, difficulty in controlling radical selectivity, and catalyst deactivation remain critical limitations. Moreover, the mechanistic roles of oxygen vacancies, lattice oxygen, and surface-bound intermediates are not yet fully understood and require deeper investigation through operando spectroscopy and computational modeling. Looking forward, the development of next-generation PMS catalysts will depend on rational design strategies that optimize defect structures, maximize nonradical oxidation efficiency, and ensure long-term stability under practical conditions. Integrating TMOs into hybrid processes electrochemical, photocatalytic, or membrane-assisted may provide synergistic performance gains. Real wastewater studies and pilot-scale demonstrations will be essential to translate laboratory findings into feasible treatment technologies.

Overall, TMOs present a highly versatile and sustainable platform for PMS-based dye degradation, offering a balance between catalytic efficiency, environmental safety, and operational robustness. Continued innovation in material design and mechanistic understanding will pave the way for their broader application in advanced wastewater treatment systems.

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