

SINGLE-ATOM IRON CATALYSTS FOR PERSULFATE ACTIVATION AND SELECTIVE DESTRUCTION OF PERSISTENT ORGANIC CONTAMINANTS IN WASTEWATER

Sher Muhammad Ghoto^{*1}, Abdul Rehman Jatoi², Habibullah Abbasi³

^{*1}Assistant Professor, PhD in Environmental Engineering, Department of Mechanical Engineering Quaid-e-Awam University of Engineering Science and Technology Nawabshah. Sindh Pakistan

²Professor, Mechanical Engineering Department Quaid-e-Awam University of Engineering, Science and Technology Nawabshah Sindh.

³Assistant Professor, Center for Environmental Sciences University of Sindh Jamshoro.

¹ghotosher@quest.edu.pk, ²arjatoi@quest.edu.pk, ³habibullah.abbasi@usindh.edu.pk

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Corresponding Author: *

Dr. Sher Muhammad Ghoto

Abstract

The unrelenting contamination of global water resources with recalcitrant organic pollutants such as pharmaceuticals, endocrine-disrupting chemicals (EDCs), and other industrial micropollutants presents formidable ecological and public health threats beyond the purview of conventional wastewater treatment technologies. Recently developed advanced oxidation processes (AOPs) utilizing persulfate (PMS) activation represent a promising route forward. However, traditional approaches using homogenous/heterogeneous catalysts face limitations including metal sludge formation, constrained operating pH window, and limited atom utilization efficiency. Single-atom iron catalysts (SA-Fe) incorporating Fe active sites coordinated to N-rich carbon matrix (Fe-N-C) have proven remarkably effective at enabling near complete PMS utilization via novel reaction mechanisms favoring selective, non-radical pathways involving high-valent Fe-oxo species ($\text{Fe}^{\text{IV}}=\text{O}$) and singlet O_2 ($^1\text{O}_2$). This perspective reviews the synthesis methodologies, design principles, and microenvironment coordination engineering of state-of-the-art SA-Fe catalysts. Emphasis is placed on their mechanistic deployment through advanced spectroscopic investigations in persulfate activation processes, alongside evaluation of system-level performance advantages in varied conditions spanning diverse pH regimes (3.0-11.0), real-world contaminant mixtures, and challenging aqueous media comprising background inorganic anions and natural organic matter (NOM). Representative pollutant fate trajectories of model sulfonamide antibiotic (sulfamethoxazole), tetracycline antibiotic and bisphenol A are discussed in detail regarding kinetic behaviors, mineralization routes, and detoxification efficiencies achieved via SA-Fe/PMS protocols. Critical barriers impeding further development including scalable synthesis strategies, operando characterization techniques, and reactor integration schemes are addressed along with prospective research

1. Introduction

Contamination of global aquatic environments by persistent organic pollutants (POPs), such as pharmaceuticals, personal care products, endocrine disrupting chemicals (EDC's), synthetic dyes and industrially-derived micro-pollutants, poses an imminent ecological and public health risk. Antibiotics such as sulfamethoxazole (SMX) and tetracycline (TC), along with industrial additives like bisphenol A (BPA), continue to be discharged into municipal and industrial wastewater streams (Giroux et al., 2024).

However, the persistence of these recalcitrant organic molecules, attributed to their complex aromatic rings and strong chemical bonds, makes most biological wastewater treatment facilities ineffective against them. These contaminants accumulate within receiving surface water bodies, inducing ecological toxicity, disturbing aquatic fauna and propagating antibiotic resistance genes (Kleber et al., 2011).

As an alternative mitigation strategy, extensive research has focused on developing efficient Advanced Oxidation Processes (AOP's). Of particular interest is persulfate-based advanced oxidation process (PS-AOP), due to its effectiveness compared to traditional hydroxyl radical-based Fenton system. Persulfates encompass a group that consists of symmetric peroxy disulphate ($\text{S}^{2-}_2 \text{O}_8^{2-}$, PDS) and asymmetric peroxymonosulfate (HSO_5^- , PMS); they function as stable sources of reactive species (Dewil et al., 2017). During catalytic activation, persulfates decompose into sulfate radicals ($\text{SO}_4^{\bullet-}$) having very good redox potentials (2.5–3.1 V vs SHE), long-half life (30–40 μs), and great selectivity towards electron rich organic structures. It should also be noted that besides the radical pathway (which leads to generation of $\text{SO}_4^{\bullet-}$), "•" OH, $\text{O}_2^{\bullet-}$ there are other routes of activating PMS, such as nonradical path that gives rise to production of singlet oxygen ($^1\text{O}_2$) or some high valent metal oxo-species or initiates

some kind of direct interfacial electron transfer reactions (Tang et al., 2018)

Even though homogeneous metal ions catalysts ($[\text{Fe}]^{2+}$, $[\text{Co}]^{2+}$, $[\text{Cu}]^{2+}$) demonstrate excellent activity in persulfate activation, their application at larger scales faces significant challenges arising from secondary metal sludge formation, narrow optimal operation pH window (usually pH 2.0–3.0) and complicated recovery procedure (Peng et al., 2016a,b). On the contrary, heterogeneous catalysts, such as bulk metal oxides ($[\text{Fe}]_3[\text{O}]_4$, $[\text{MnO}]_2$, $[\text{Co}]_3[\text{O}]_4$), spinel ferrite ($[\text{MeFe}]_2[\text{O}]_4$), or metal nanoparticles offer the benefit of easily recovering the used catalyst, however many of the traditional types of heterogeneous catalysts show poor atomic utilization efficiencies (<5%) (Saien, & Jafari, 2022) as well as surface active site aggregation, sluggish interfacial electron transport kinetics and pronounced leaching out of potentially harmful metals when operating under acidic/alkaline environments (Yang et al., 2013).

The advent of single-atom catalysts (SACs), particularly those based on nitrogen-doped carbon ("M-N-C") supports, has ushered in a transformative era for heterogeneous environmental catalysis, with SACs demonstrating remarkable atomic utilization efficiencies close to 100% (Shang et al., 2021).

Within these catalytic materials, the intrinsic catalytic activities of individual SACs depend on the degree of isolation among the active site metals, wherein isolated single atoms (~0.1 nm) possess superior catalytic abilities compared to atomic clusters (~1 nm), which outperform nanoparticle structures (>5 nm). Iron-based single-atom catalysts (SA-Fe) have emerged as particularly intriguing candidates in this context, thanks to their earth abundance, inherent environmental benignity, and low intrinsic toxicities. The rich redox chemistry associated with the multiple oxidation states ($[\text{Fe}]^{\text{II}}/[\text{Fe}]^{\text{III}}/[\text{Fe}]^{\text{IV}}$) further broadens the utility window of such catalysts. When

appropriately positioned into nitrogenated carbon lattice environments (e.g., "Fe-N-C"), isolated Fe centers exhibit unique d-orbital electron configurations that modulate their ability to activate different types of oxidants (persulfates and peroxymonosulfates) through reduced activation energy barriers. More importantly, SA-Fe materials favorably alter the chemical pathway of target contaminant degradation to become more selective towards non-radical processes dominated by the formation of high valency iron-oxo species (e.g., $[\text{Fe}^{\text{IV}}=\text{O}]$) and the evolution of other reactive molecular species such as singlet oxygen ($^1\text{O}_2$) under specific reaction conditions (Yan et al., 2025). Thus, such materials offer exceptional specificity in degrading recalcitrant organics while minimizing detrimental effects caused by the presence of interfering background ions (such as Cl^- , NO_3^- etc.) and biologically relevant OM constituents commonly encountered in complex water matrices (Yang et al., 2021).

This review aims at providing an overarching perspective on applying SA-Iron Catalysts toward persulfate activation technologies for achieving effective and selective removal of persistent organic pollutants from contaminated waters. The discussion covers various facets including methods for fabricating SA-Fe catalysts, strategies for fine-tuning local coordination environments around iron centers, application of state-of-the-art spectroscopic tools to obtain deeper insights about surface chemistry phenomena occurring during oxidative transformation events, comparative analyses between radical vs. non-radical oxidation schemes, detailed kinetic studies regarding fate conversions undergone by targeted organic micropollutants during treatment protocols, identification of factors contributing towards interference issues experienced under realistic operation conditions, evaluation of long-term performance stability & recyclability characteristics exhibited by selected SA-Fe formulations when put forward for large scale applications along with determination of crucial parameter settings needed to ensure maximum effectiveness of these cutting edge materials for

actual implementation purposes (Zhou et al., 2024).

2. Synthesis and Microenvironment Engineering of Single-Atom Iron Catalysts

2.1 Synthetic Methodologies and Structural Fabrication

The main difficulty in producing stable single-atom iron catalysts is counteracting the strong thermodynamic tendency that causes individual iron atoms to gather together and form inactive clusters or metallic nanoparticles when undergoing high-temperature thermal treatment. In order to achieve rigid spatial separation of the atoms, researchers use methods involving physical confinement, chemical coordination, and template-assisted pyrolysis (Singh et al., 2021). As a result, the development of heterogeneous iron catalysts has moved from bulk oxides and supported nanoparticles which have a limited number of active surface sites to very fine atomic clusters, and finally to isolated single-atom sites at which each iron atom takes part directly in the catalytic process (Ding et al., 2024).

The pyrolytic conversion of Metal-Organic Frameworks (MOFs) is a main method of synthesis. Zeolitic imidazolate frameworks, for example ZIF-8, act as sacrificial structural templates in which $[\text{Fe}^{2+}]$ or $[\text{Fe}^{3+}]$ ions replace a portion of the zinc atoms at the nodes in the porous framework (Huang et al., 2023). When the material is pyrolysed at high temperatures (800-1000 °C) in an inert nitrogen or argon atmosphere, the zinc, which has a low boiling point (bp ~907 °C), volatilises and leaves behind uniform spatial vacancies, while the organic linkers break down to form a highly porous, nitrogen-doped carbon matrix ("N-C"). The nitrogen atoms that remain in the carbon structure bind and hold the isolated iron atoms through strong covalent "Fe-N" coordination bonds, thus thermally stabilising the single metal sites and preventing them from sintering (Septien et al., 2012).

Cascade anchoring strategies and polymer or covalent organic framework (COF) template methods have also been used to prepare porous

"Fe-SACs". By using Schiff base or ketoenamine COFs as structural backbones, surface defect cavities can be generated through chemical etching treatments with agents such as NaBH_4 or NaBH_3CN . The resulting coordination sites bind the iron ions strongly before carbonization, leading to the production of catalytic materials with a high surface area that contain a large number of single-atom iron centres which are uniformly distributed (Feng et al., 2026).

2.2 Primary Coordination Sphere Engineering (Fe-N_x Configurations)

The catalytic activity of a single iron atom is determined by its local coordination environment, more precisely by the coordination number, the type of ligand, and the spatial symmetry of the atoms surrounding it. In carbon matrices of the standard type, the iron centres bond with nitrogen atoms to give rise to planar, square-planar $[\text{Fe-N}]_4$ complexes. Changes in the structure of this first coordination shell, whether from symmetric planar $[\text{Fe-N}]_4$ arrangements to unsaturated $[\text{Fe-N}]_3$ or $[\text{Fe-N}]_2$ geometries, have a major effect on the catalytic results (Pan et al., 2019).

The way in which the $[\text{Fe-N}]_4$ group is structured depends very much on whether the nitrogen atoms involved in coordination are in pyridinic, pyrrolic, or graphitic form. Both density functional theory (DFT) calculations and experimental results show that $[\text{Fe-pyridinic N}]_4$ sites result in an asymmetric distribution of charge: the central iron atom becomes electron-rich while the carbon atoms adjacent to the pyridinic nitrogen become electron-poor (Tylus et al., 2024). This charge polarization leads to an active site with two functions: the electron-rich iron atom promotes the adsorption of persulfate and "O-O" bond cleavage, and the neighbouring electron-poor carbon atoms act as binding sites for organic pollutants or are involved in further activation steps (Ahmed et al., 2025).

On the other hand, $[\text{Fe-pyrrolic N}]_4$ coordination environments change the position of the d-band of the iron atom, thereby affecting the

adsorption energy of peroxymonosulfate ($[\text{HSO}]_5^-$). The donation of electrons by pyrrolic nitrogen results in a shift of electron density at the iron centre, which favours non-radical pathways of PMS decomposition rather than radical cleavage. Coordination states that are lower in number, such as the unsaturated planar $[\text{Fe-N}]_3$ centres, increase the coordinative unsaturation of the iron, improve the binding of the reactants, and speed up the electron-transfer kinetics during oxidation (Liu et al., 2026).

2.3 Secondary Coordination Shell Modulation and Axial Ligand Tuning

When the main coordination sphere is altered there is usually a compromise between catalytic activity and structural stability. Replacing a heteroatom directly in the first coordination shell may lead to a disruption of the $[\text{Fe-N}]_4$ planar symmetry and could thus cause demetallation during multiple oxidation cycles. In order to overcome this limitation, methods involving the engineering of the secondary coordination shell and the adjustment of axial ligands have been devised (Wu, & Zelenay, 2024). In models based on axial coordination for example, the "4+1" method an extra axial nitrogen ligand binds at right angles to the plane of the $[\text{Fe-N}]_4$ square, resulting in an asymmetric $[\text{Fe-N}]_5$ species which is five-coordinate. This axial ligand changes the crystal field splitting energy of the d-orbitals of the iron ($d_{xz}, d_{yz}, d_{xy}, d_{z^2}, d_{x^2-y^2}$). It has the effect of stabilising the high-spin electronic states in the iron atom, lowers the orbital splitting energy, and promotes hybridisation between the d orbitals of the single iron centre and those of the peroxymonosulfate molecule (Fan et al., 2026).

Secondary shell modulation can also be achieved by incorporating electronegative heteroatoms, such as oxygen or sulfur, into the carbon matrix that surrounds the primary $[\text{Fe-N}]_4$ motif without bonding directly to the iron atom. For instance, secondary-shell oxygen doping ($[\text{Fe-N}]_4$ $[\text{-C}]_6$ "O"₂) makes use of long-range d-p interactions to reduce the electron density at

the iron centre, thereby lowering the energy of the σ^* anti-bonding orbital of the bound intermediates (Qi & Guan, 2026). As a result, electrophilic attack by high-valent iron-oxo species is facilitated and carbon vacancies are created which stabilise the metal centre against chemical leaching, thus successfully overcoming the compromise between activity and stability (Yang et al., 2026).

2.4 Dual-Site Interactions and Hybrid Atomic Ensembles

By combining separate single atoms with nearby metal nanoclusters or with other single-metal sites, synergistic dual-site catalytic systems are obtained. In catalysts which contain both isolated Fe single atoms and ultrafine iron atomic clusters, for example 'FeUAC@FeSA-NC' or 'FeMn-NC', the different metal arrangements carry out complementary catalytic functions (Luo et al., 2024).

The isolated $[\text{Fe-N}]_4$ sites mainly promote non-radical pathways, such as the formation of high-valent iron-oxo ($[\text{Fe}]^{\text{IV}}=\text{O}$) or the production of singlet oxygen ($[(^1\text{O})]_2$). The metallic nanoclusters adjacent to these sites or the other single-metal centres (for example, Mn or Co) function as electron reservoirs. They speed up interfacial charge transfer, reduce the thermodynamic barrier for "O-O" bond cleavage, and provide an additional radical generation pathway ($[\text{SO}]_4 \cdot / \cdot \text{OH}$). This combination of radical and non-radical mechanisms increases the range of organic pollutants that can be degraded in complex wastewater (Lv et al., 2026).

2.5 Spectroscopic Characterization Techniques

Confirming the atomic dispersion and local coordination geometry of single-atom iron

catalysts requires advanced characterization techniques:

- **High-Angle Annular Dark-Field Scanning Transmission Electron Microscopy (HAADF-STEM):** Enables direct visualization of atomic dispersion, where single iron atoms appear as bright, isolated spots on the less dense carbon matrix (Leng, 2013).

- **X-ray Absorption Fine Structure (XAFS) Spectroscopy:**

- **X-ray Absorption Near-Edge Structure (XANES):** Determines the average oxidation state of iron (typically between Fe^{II} and Fe^{III}) by measuring the absorption edge position relative to standard Fe foil, FeO, and Fe_2O_3 references (Wilke et al., 2004).

- **Extended X-ray Absorption Fine Structure (EXAFS):** Fourier-transformed EXAFS spectra in R -space display a prominent peak corresponding to the Fe-N coordination shell at $\sim 1.4 - 1.6$ Å while showing no detectable Fe-Fe metallic scattering peak at ~ 2.2 Å (Cheng et al., 2025).

- **Wavelet-Transform EXAFS (WT-EXAFS):** Provides simultaneous radial distance and k -space resolution, confirming the absence of metal clusters or crystalline nanoparticles (Xia et al., 2018).

- **^{57}Fe Mössbauer Spectroscopy:** Resolves local electronic and magnetic configurations, distinguishing specific iron oxidation and spin states (such as low-spin vs. high-spin $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ in doublet signals like D1, D2, or D3) (Gütlich, 2012).

Table 1 summarizes representative single-atom iron catalysts, detailing their microenvironment configurations, synthetic routes, and key structural properties.

Table 1. Microenvironment Configurations and Structural Parameters of Representative Single-Atom Iron Catalysts for Persulfate Activation

Catalyst System	Active Site Microenvironment	Synthesis Strategy	Primary Characterization Methods	Key Structural / Electronic Properties
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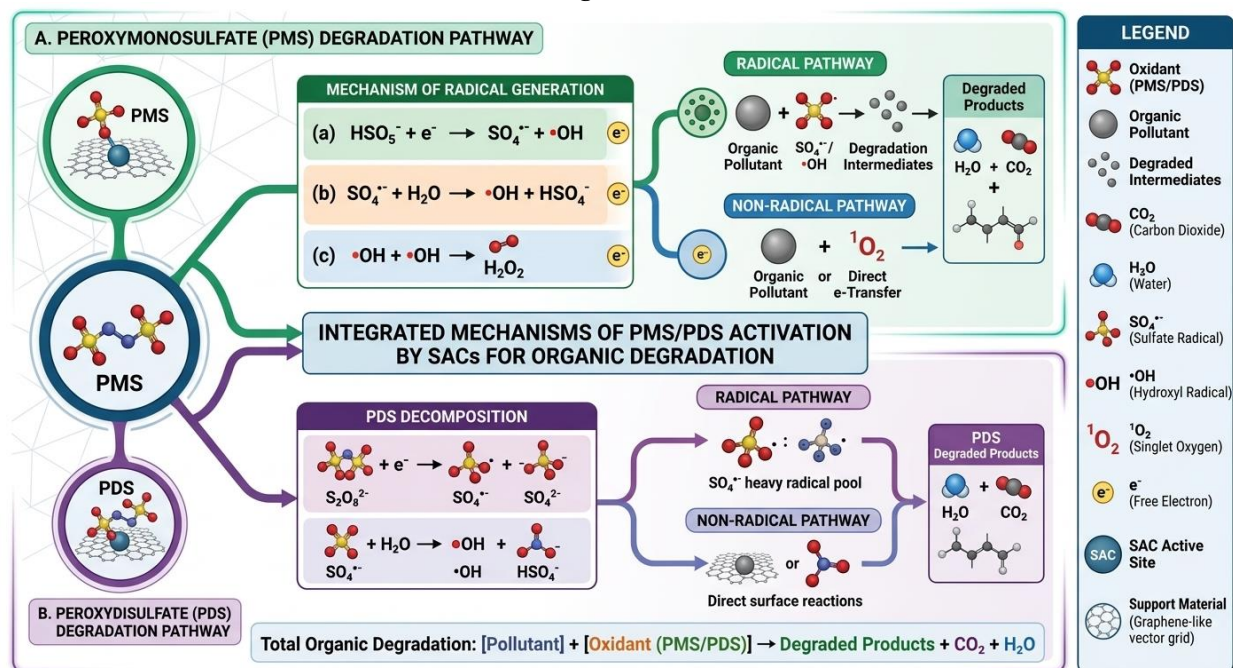
SA-Fe-NC	Pyridinic Fe-N ₄	Cascade anchoring & Pyrolysis	EXAFS, WT-EXAFS, XPS	Electron-rich Fe site coupled with electron-poor neighboring carbon sites
FeSA-N-C	Pyrrolic Fe-N ₄	ZIF-8 MOF derivative pyrolysis	HAADF-STEM, EXAFS, XANES	High adsorption energy for PMS, optimized orbital symmetry
SA-FeN ₅	Axially coordinated Fe-N ₅	"4+1" spatial fabrication strategy	EXAFS, ⁵⁷ Fe Mössbauer, XANES	High-spin state, reduced <i>d</i> -orbital splitting energy
Fe-N ₄ -C ₆ O ₂	Secondary-shell O-doped Fe-N ₄	Post-synthetic heteroatom insertion	XANES, EXAFS, ⁵⁷ Fe Mössbauer	Reduced σ^* anti-bonding orbital energy, enhanced anti-demetalation
FeUAC@FeSA-NC	Single Fe atom + ultrafine clusters	Biomass/polymer precursor carbonization	HAADF-STEM, WT-EXAFS, XPS	Synergistic charge transfer between clusters and isolated atomic sites
FeMn-NC	Dual-site single Fe + Fe nanoclusters	Mn-regulated pyrolytic assembly	HR-TEM, EXAFS, DFT modeling	Adjusted <i>d</i> -band center, dual radical and non-radical activation mechanisms

3. Mechanisms of Persulfate Activation and Reactive Species Generation

Single-atom iron catalysts for persulfate activation can produce reactive species via radical pathways,

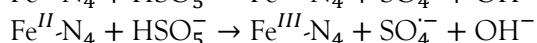
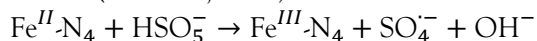
non-radical pathways, or hybrid mechanisms. Understanding these pathways is key to the design of catalysts for the removal of specific pollutants in complex water matrices (Guo et al., 2025).

Figure 1: Integrated Mechanisms and Pathways of Radical and Non-Radical Activation of Peroxymonosulfate (PMS) and Peroxydisulfate (PDS) by Single-Atom Catalysts for Organic Contaminant Degradation.

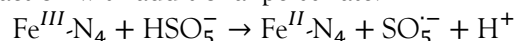


3.1 Radical Pathways ($\text{SO}_4^{\bullet-}$, $\bullet\text{OH}$, and $\text{O}_2^{\bullet-}$)

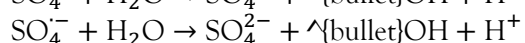
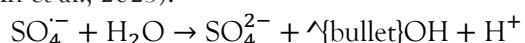
In standard radical-dominated activation, the process begins with a single-electron transfer from the transition metal center to the peroxide bond (O-O) of the persulfate molecule. For peroxymonosulfate (HSO_5^-), homolytic cleavage of the peroxide bond yields sulfate radicals and hydroxyl radicals according to the following reactions (Bai et al., 2025):



To maintain continuous catalysis, the oxidized iron site ($\text{Fe}^{\text{III}}\text{-N}_4$) is reduced back to $\text{Fe}^{\text{II}}\text{-N}_4$ via reaction with additional persulfate:



Sulfate radicals can further react with water molecules or hydroxyl ions in aqueous solution, generating secondary hydroxyl radicals, particularly under neutral to alkaline conditions (An et al., 2023):



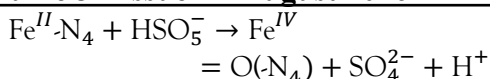
Superoxide radicals ($\text{O}_2^{\bullet-}$) can also form via nucleophilic attack on PMS by water molecules or through electron-transfer interactions at carbon support defect sites:



Although free radicals feature high redox potentials, their environmental efficacy is often limited by short half-lives, unselective oxidation behavior, and high susceptibility to scavenging by background wastewater component (Basaga, 1990).

3.2 Non-Radical Pathway I: High-Valent Iron-Oxo Species ($\text{Fe}^{\text{IV}}=\text{O}$)

A key advantage of single-atom iron catalysts is their ability to suppress free radical formation in favor of selective non-radical pathways, particularly those driven by high-valent iron-oxo species ($\text{Fe}^{\text{IV}}=\text{O}$). Instead of single-electron transfer leading to homolytic cleavage, the isolated Fe-N_4 site undergoes a two-electron oxidation upon interacting with peroxymonosulfate:

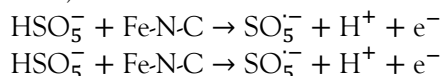


The formation of the $[\text{Fe}^{\text{IV}}=\text{O}]$ species is controlled by the particular coordination geometry of the single iron center (Chen et al., 2025). Axially coordinated configurations, such as $[\text{Fe-N}]_5$, lower the formation energy of the $[\text{Fe}^{\text{IV}}=\text{O}]$ by up to 42% compared to regular $[\text{Fe-N}]_4$ sites. The axial coordination promotes a high-spin electronic state, which enhances the delocalization of d-orbital electrons and thus facilitates the two-electron injection into the “O-O” bond of PMS. High-valent $[\text{Fe}^{\text{IV}}=\text{O}]$ species are strong electrophiles that can selectively attack organic pollutants by oxygen atom transfer or direct electron abstraction, without producing free radicals in the bulk solution (Huang et al., 2019).

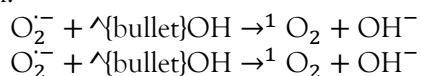
3.3 Non-Radical Pathway II: Singlet Oxygen ($^1\text{O}_2$) Generation

Singlet oxygen ($^1\text{O}_2$) represents another important non-radical reactive species generated during persulfate activation over single-atom iron catalysts. Its formation proceeds primarily through two chemical routes:

1. **Peroxymonosulfate Self-Recombination:** Interaction of PMS with electron-poor carbon centers adjacent to nitrogen or iron sites induces PMS oxidation, producing peroxymonosulfate radicals ($\text{SO}_5^{\cdot-}$), which then undergo self-recombination to yield singlet oxygen (Nidheesh et al., 2025):



2. **Superoxide Radical Transformation:** Superoxide radicals ($\text{O}_2^{\cdot-}$) generated at active sites can undergo subsequent oxidation by $\cdot\text{OH}$ or spontaneous dismutation to generate singlet oxygen:



Singlet oxygen selectively oxidizes electron-rich organic compounds such as phenols, sulfonamides, and olefins while remaining largely

unreactive toward common inorganic background ions (Garg & Waite, 2025).

3.4 Non-Radical Pathway III: Direct Surface Electron-Transfer Mechanisms

For some single-atom iron systems, a surface complex mediated direct electron-transfer mechanism is responsible for the activation of persulfate. In this non-radical pathway, the single-atom metal center and surrounding carbon matrix form a conductive bridge (Li et al., 2024). The persulfate molecule adsorbs on the isolated iron center (electron acceptor) and the target organic pollutant adsorbs on the nearby nitrogen doped carbon sites (electron donor). This double adsorption leads to a metastable ternary complex catalyst-oxidant-pollutant. Electrons are directly transferred from the organic contaminant to the bound persulfate molecule through the conductive catalyst substrate, degrading the pollutant without the need for intermediate free radical or oxo species formation (Duan et al., 2021).

3.5 Density Functional Theory (DFT) Insights into Activation Kinetics

Density functional theory (DFT) calculations give a detailed molecular picture of persulfate activation on single-atom iron catalysts. The adsorption of peroxymonosulfate on the isolated “Fe-N-C” sites is spontaneous with exothermic adsorption energy ($\Delta G < 0$) in the thermodynamic process (Hu et al., 2026). Then, the adsorbed PMS intermediate experiences the elongation and activation of the “O-O” bond, surmounting a low-energy transition barrier to yield a high-valent iron-oxo species ($[\text{Fe}^{\text{IV}}=\text{O}]$) and a sulfate byproduct, thereby completing a thermodynamically favorable non-radical cycle (Ma et al., 2024).

DFT analysis highlights several key mechanistic factors:

- **Binding Energy Optimization:** Isolated Fe-N₄ centers exhibit adsorption free energies (ΔG_{ads}) for PMS that are significantly more exothermic than those of pristine carbon supports or metallic iron surfaces (Huang et al., 2026).

• **O-O Bond Elongation:** Upon coordination to an isolated Fe center, the internal O-O bond length of PMS stretches from its unreacted distance (~ 1.32 Å) to over $1.45 - 1.48$ Å, weakening the peroxide link and lowering the energy barrier for cleavage (Tian et al., 2026).

• **Bader Charge Redistribution:** Substantial charge density transfers from the iron d -orbitals into the anti-bonding σ^* orbital of the peroxide group, destabilizing the O-O bond (Lgaz et al., 2025).

• **d -Band Center Modulation:** Modulating the secondary coordination sphere or introducing dual active sites shifts the metal d -band center closer to the Fermi level. This shift reduces anti-bonding orbital filling in reaction intermediates, lowering the energy barrier for high-valent iron-oxo species formation (Li et al., 2026).

4. Selective Destruction of Persistent Organic Contaminants

4.1 Target Contaminant Classes and Degradation Rates

Single-atom iron catalyst/persulfate systems demonstrate high catalytic activity across a wide array of recalcitrant organic contaminants found in wastewater. Primary pollutant categories include:

• **Pharmaceuticals and Antibiotics:** Sulfamethoxazole (SMX), tetracycline (TC), ciprofloxacin, and chloroquine phosphate.

• **Endocrine-Disrupting Phenolics:** Bisphenol A (BPA), 2,4-dichlorophenol, and substituted nitrophenols.

• **Industrial Synthetic Dyes:** Methylene blue (MB), acid orange 7 (AO7), and methyl orange (Wen et al., 2026).

In optimized “SA-Fe/PMS” systems, the pseudo-first-order degradation rate constants (k_{obs}) are orders of magnitude higher than those of conventional metal oxide catalysts or iron nanoparticles. For example, supported single Fe atom catalysts (4.8 wt% Fe) in low dosage completely remove 22 ppm bisphenol A in 40 seconds. Similarly, “Fe/NC-SAC” platforms reach

98.2% sulfamethoxazole degradation in 5' minutes' reaction time (Cline & Hanna, 1988).

4.2 Mechanisms of Selective Attack

The unique selectivity of single atom iron catalysts is attributed to the dominance of non-radical active species ($[\text{Fe}^{\text{IV}}=\text{O}]$ and $[(\text{O})_2]$) over non-selective free radicals ($^{\bullet}\text{OH}$ and $^{\bullet}\text{SO}$). Free radicals ($^{\bullet}\text{OH}$ $E^{\circ} = 1.8-2.7$ V; $^{\bullet}\text{SO}$ $E^{\circ} = 2.5-3.1$ V) react unselectively by fast hydrogen abstraction or non-specific addition. In real wastewater, this results in significant radical consumption by background matrix components, reducing target pollutant removal efficiency (Panjwani et al., 2026). Conversely, non-radical pathways mediated by $\text{Fe}^{\text{IV}}=\text{O}$ and $(\text{O})_2$ involve selective electrophilic attack. High-valent oxo species preferentially react with electron-dense functional moieties such as amine groups in sulfonamides, hydroxyl groups in phenolics, and double bonds in aromatic rings, with minimal reactivity toward the constituents of the background matrix (Ning et al., 2025).

4.3 Degradation Pathways, Mineralization, and Detoxification

Complete mineralization converts complex organic pollutants into harmless inorganic end-products (H_2O , CO_2 , SO_4^{2-} , NO_3^-). Degradation intermediate pathways are identified using Ultra-Performance Liquid Chromatography coupled with Mass Spectrometry (UPLC-MS/MS) alongside Fukui function quantum chemical calculations (Saravanan et al., 2019).

For example, during tetracycline (TC) and sulfamethoxazole (SMX) degradation via $\text{Fe}^{\text{IV}}=\text{O}$ attack:

1. **Electrophilic Hydroxylation:** High-valent oxo species transfer oxygen atoms to aromatic rings, forming hydroxylated intermediates.
2. **Ring Cleavage:** Continued oxidation cleaves C-N, C-C, and S-N bonds, breaking down ring structures.

3. **Dealkylation and Desulfonation:** Functional side chains are systematically removed, yielding low-molecular-weight carboxylic acids.

4. **Final Mineralization:** Small-chain dicarboxylic acids are oxidized into H_2O and CO_2 (Tang et al., 2026).

Standard biological assays, such as wheat germination tests and cellular toxicity assays, confirm that transformation products generated via non-radical pathways exhibit lower ecotoxicity than parent compounds, avoiding the formation of toxic degradation byproducts (Jitäreanu et al., 2019).

Table 2. Catalytic Performance and Degradation Characteristics of SA-Fe Catalysts in Wastewater Treatment

Catalyst / Oxidant System	Target Organic Contaminant	Removal Efficiency & Kinetic Rate (k _{obs})	Primary Active Species Involved	Operational pH Window	Matrix Tolerance & Stability Performance
SA-Fe-NC / PMS	Bisphenol A (BPA)	8.1-fold specific activity enhancement vs. NPs	Direct electron transfer & Surface complex	pH 3.0 – 9.0	High resistance to background wastewater ions
Fe/NC-SAC / PMS	Sulfamethoxazole (SMX)	98.2% degradation in 5 min	$Fe^{IV} = O$ and 1O_2	pH 3.0 – 11.1	Sustainable capacity across real water matrices
Fe-g-C ₃ N ₄ / PMS	Tetracycline (TC)	High efficiency (k_{obs} enhanced)	$Fe^{IV} = O$ and 1O_2	pH 3.0 – 10.0	Low metal leaching; active site retention
FeN ₅ -SAC / PMS	Phenol / Micropollutants	> 99% non-radical pathway selectivity	High-valent $Fe^{IV} = O$	Neutral to alkaline	Operational stability exceeding 240 hours
FeSAC@COF / PMS	Methylene Blue (MB)	$k_{obs} = 0.125 \text{ min}^{-1}$	1O_2 and $O_2^{\cdot-}$	pH 4.0 – 10.0	Stable catalytic recovery over 4 cycles
FeMn-NC / PMS	Tetracycline (TC)	97.1% removal ($k_{obs} = 0.1152 \text{ min}^{-1}$)	Synergistic $Fe^{IV} = O$ & $SO_4^{\cdot-}$	Broad pH range	Substantial ecotoxicity reduction post-treatment

5. Matrix Effects, Dynamic Stability, and Environmental Applicability

5.1 pH Adaptability

Conversely, conventional homogeneous Fenton chemistry requires stringent pH control (i.e., “pH” ≈ 2.8 – 3.5) since Fe^{2+} readily forms an insoluble ferric hydroxide sludge ([“Fe (OH)”] ₃) above these values, causing reactor deactivation. In marked contrast, SAI catalysts based on N-doped

carbon substrates function efficiently over a wide operational pH window (“pH” ≈ 3.0 – 11.0). The covalent binding of [“Fe-N”] ₄ active centers prevent metal hydroxide precipitation even at high alkalinity (Mansour et al., 2026).

Moreover, their nonradical reaction pathways, mediated primarily by [“Fe”] ^{IV}= “O” and [(¹ “O”)] ₂ species, exhibit no dependence on

proton availability for efficient contaminant mineralization. This ensures consistent degradation kinetics for various wastewater types, including those containing strong acid or base additives (Chang 2022).

5.2 Influence of Background Matrix Constituents

Real industrial effluents and municipal wastewater contain background inorganic anions (Cl^- , HCO_3^- , NO_3^- , H_2PO_4^-) and Natural Organic Matter (NOM, such as humic acid).

In radical-dominated processes, chloride ions (Cl^-) and bicarbonate ions (HCO_3^-) scavenge $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$, producing lower-reactivity secondary radicals ($\text{Cl}^\cdot$, $\text{Cl}_2^{\cdot-}$, $\text{CO}_3^{\cdot-}$) and reducing degradation performance. Similarly, humic acid consumes free radicals non-selectively, competing with target pollutants (Xie et al., 2021).

In contrast, non-radical single-atom iron processes ($\text{Fe}^{\text{IV}} = \text{O}$ and $^1\text{O}_2$) demonstrate high tolerance to background matrix components. High-valent oxo species do not react with Cl^- or HCO_3^- , preventing radical scavenging losses. This non-radical pathway enables consistent target pollutant removal even in complex water bodies, industrial effluents, and landfill leachates (Huang et al., 2026).

6. Challenges and Future Perspectives

Despite significant progress in single-atom iron catalysis for persulfate-based wastewater treatment, several key challenges remain for real-world implementation:

- **Scalable Synthesis and Manufacturing:** Laboratory synthesis methods for Fe-SACs such as multi-step MOF preparation, chemical etching,

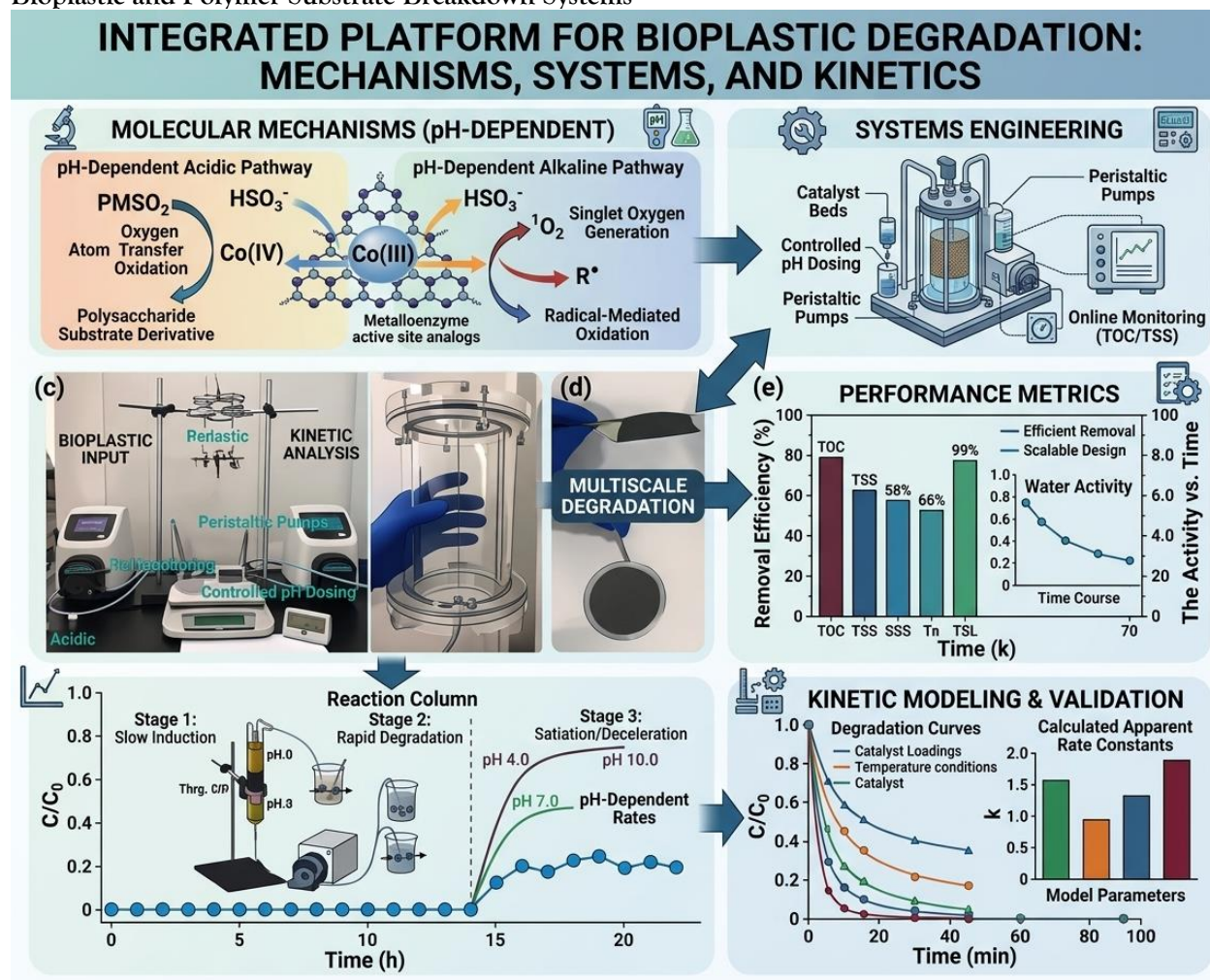
and high-temperature inert pyrolysis often involve complex steps and low yields. Developing high-yield, continuous manufacturing protocols (e.g., flash Joule heating, spray pyrolysis, or mechanochemical synthesis) is needed to lower production costs while maintaining precise control over atomic dispersion (Julien et al., 2017).

- **Operando Characterization of Dynamic Active Sites:** While static spectroscopy (EXAFS, XPS) establishes initial coordination structures, single-atom sites undergo dynamic structural transformations during persulfate activation. Applying advanced *in situ* and *operando* characterization techniques such as *in situ* Synchrotron X-ray Absorption Spectroscopy and ambient-pressure XPS is essential to track transient oxidation states ($\text{Fe}^{\text{II}} \leftrightarrow \text{Fe}^{\text{III}} \leftrightarrow \text{Fe}^{\text{IV}} = \text{O}$) and short-lived reactive intermediates under operational conditions (Yang et al., 2025).

- **Performance in Complex Real Effluents:** Real industrial wastewater contains complex mixtures of heavy metals, surfactants, and suspended solids. Future work must focus on improving catalyst resistance to surface fouling and evaluating long-term performance under continuous flow conditions (Lam et al., 2018).

- **Integration into Continuous-Flow Reactors:** Moving from batch experiments to industrial application requires incorporating single-atom iron catalysts into structured support architectures. Immobilizing Fe-SACs onto macroscopic substrates such as ceramic membranes, carbon fiber felt, or 3D-printed scaffolds can minimize pressure drops, eliminate catalyst recovery steps, and enable continuous water treatment (Daly et al., 2026).

Figure Title: Integrated Engineering, Multiscale Degradation Kinetics, and Performance Metrics of Bioplastic and Polymer Substrate Breakdown Systems



7. Conclusion

Single-atom iron catalysts have transformed persulfate-based advanced oxidation processes for wastewater treatment by providing hitherto unheard-of atomic utilization efficiency, outstanding catalytic activity, and extraordinary selectivity for the breakdown of ongoing organic pollutants. Robust Fe-N coordination bonds effectively stops metal aggregation, avoids leaching, and allows almost 100% metal atom participation in catalytic processes an essential benefit over traditional heterogeneous catalysts where only surface atoms help to drive reactivity by which isolated iron atoms are anchored within nitrogen-doped carbon matrices. Fe-SACs'

structural flexibility which results from main coordination sphere engineering (Fe-N_2 , Fe-N_3 , Fe-N_4 configurations), secondary shell modification via heteroatom doping, and axial ligand coordination (Fe-N_5 sites) gives strong levers for managing catalytic selectivity and activity. By methodically changing the electronic structure of iron centers, these microenvironment changes control d-band positions, spin states, and orbital hybridization to support certain persulfate activation mechanisms. The mechanistic change from radical-dominated processes to non-radical pathways, which are driven by high-valent iron-oxo species ($\text{Fe}^{\text{IV}}=\text{O}$) and singlet oxygen (${}^1\text{O}_2$), marks a major advancement in environmental catalysis.

This mechanistic change offers significant practical benefits as non-radical pathways show remarkable tolerance to background matrix components including chloride, bicarbonate, and natural organic matter that would normally catch free radicals, therefore guaranteeing consistent performance in complex actual wastewater matrices. The wide working pH range of 3.0 to 11.0 removes the strict acidic needs of conventional Fenton systems, therefore greatly increasing use over many different types of industrial and municipal wastewater streams. Extensive toxicity tests verify that $\text{Fe}^{\text{IV}}=\text{O}$ and $^1\text{O}_2$ species' selective electrophilic attack mechanisms enable quick pollutant degradation free of hazardous byproducts. These revolutionary developments notwithstanding, effective translation from laboratory-scale experiments to industrial use calls for solutions to still existent problems. Moving away from multi-step MOF pyrolysis and toward continuous manufacturing techniques like flash Joule heating and spray pyrolysis, scalable synthesis techniques able to create high-quality Fe-SACs at minimal cost must be developed. Tracking dynamic structural changes of single-atom sites during persulfate activation depends on sophisticated operando characterization methods, notably in situ synchrotron X-ray absorption spectroscopy and ambient-pressure XPS, therefore offering mechanistic insights that will inform next-generation catalyst design. Moreover, Fe-SACs must be included into continuous-flow reactor setups by immobilisation on macroscopic supports including 3D-printed scaffolds and ceramic membranes in order to have functional, scalable water treatment systems. Looking ahead, the convergence of computational catalysis (machine learning-guided design), advanced operando spectroscopy, and creative reactor engineering will help to speed up the creation of strong, cost-effective single-atom iron catalytic systems. The basic ideas explained for Fe-SACs in persulfate activation, especially the relationship between coordination microenvironment, electronic structure, and reaction selectivity, offer a portable platform for creating next-generation single-atom

catalysts for several environmental cleanup uses. From theoretical interest to technical reality, these catalysts offer great promise for tackling the increasing worldwide issue of persistent organic pollutant pollution in water sources, therefore promoting sustainable water security and environmental protection.

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