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The Role of Iron in Advanced Oxidation Technologies: A Review of Applications in Wastewater Remediation

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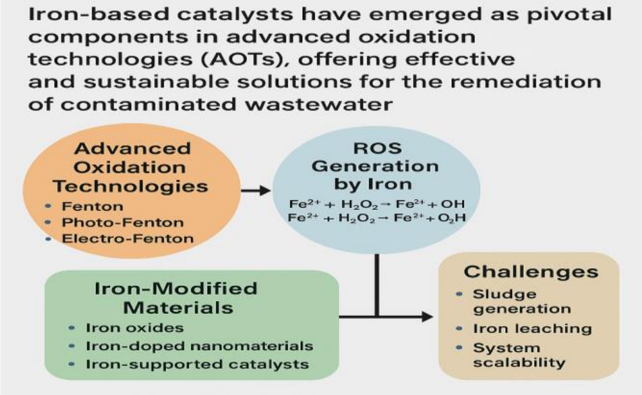
ABSTRACT

Iron-based catalysts have emerged as pivotal components in advanced oxidation technologies (AOTs), offering effective and sustainable solutions for the remediation of contaminated wastewater. This review provides a comprehensive overview of the multifaceted role of iron in various AOTs, including Fenton, photo-Fenton, electro-Fenton, and heterogeneous catalytic processes. Emphasis is placed on the mechanisms of reactive oxygen species (ROS) generation facilitated by iron, the influence of operational parameters, and the impact of iron speciation and redox cycling. Additionally, the review discusses recent advances in iron-modified materials, such as iron oxides, iron-doped nanomaterials, and iron-supported catalysts, highlighting their enhanced catalytic performance and reusability. Challenges related to sludge generation, iron leaching, and system scalability are critically analyzed, alongside proposed strategies for optimization and integration into existing wastewater treatment frameworks. By synthesizing current research and technological developments, this article underscores the central role of iron in advancing efficient, cost-effective, and environmentally friendly wastewater remediation methods.



INTRODUCTION

The rapid industrialization and urbanization over the past century have significantly increased the demand for clean water, leading to the generation of large volumes of wastewater from municipal, industrial, and agricultural sources (Khanam et al., 2022). This wastewater often contains persistent organic pollutants (POPs), heavy metals, pharmaceuticals, dyes, and endocrine-disrupting compounds, many of which are resistant to conventional treatment technologies (Akhtar et al., 2021). As environmental regulations become increasingly stringent and the necessity for sustainable water management grows, the development of effective, economical, and environmentally friendly technologies for wastewater treatment has become a global priority (Shehata et al., 2023). Among the various innovative treatment strategies, Advanced Oxidation Processes (AOPs) have emerged as a powerful and promising class of techniques capable of degrading a wide range of organic contaminants into less harmful or fully mineralized products (Giwa et al., 2021). AOPs are characterized by the in-situ generation of highly reactive oxidative species, primarily hydroxyl radicals (•OH), which are non-selective and potent oxidants (Cheng et al., 2016). These radicals can break down complex and stable organic molecules that are otherwise difficult to treat through biological or physical-chemical methods. The effectiveness of AOPs depends significantly on the catalyst employed, the type of oxidant, operational conditions, and the nature of the target contaminants (Salimi et al., 2017). Iron-based catalysts have gained particular attention in AOPs due to their abundance, low toxicity, environmental compatibility, and versatile redox chemistry (Luo et al., 2021). Iron plays a pivotal role in several AOPs, especially in Fenton and Fenton-like reactions, where Fe^{2+} activates hydrogen peroxide (H_2O_2) to generate hydroxyl radicals (Rehman et al., 2023). The classical homogeneous Fenton process, first introduced in the 1890s, has been widely studied and applied in the degradation of recalcitrant pollutants (Ribeiro et al., 2021). However, the homogeneous nature of this process presents limitations such as narrow operational pH range (typically acidic conditions around pH 2.5–3.5), high sludge production, and the requirement for continuous iron addition (Yu et al., 2016).

To overcome these limitations, extensive research has been directed toward the development of heterogeneous iron-based systems including zero-valent iron (ZVI), iron oxides (e.g., magnetite, hematite), iron-containing clays and zeolites, and iron-doped nanomaterials (Lama et al., 2022). These materials not only expand the effective pH range but also facilitate catalyst recovery and reusability, thereby making the process more sustainable and cost-effective (Xia et al., 20217). Furthermore, iron has been utilized in combination with various oxidants, such as peroxymonosulfate (PMS), peroxydisulfate (PDS), and ozone (O_3), in both homogeneous and heterogeneous systems, broadening the application of iron in different AOP configurations (Xiao et al., 2020). Recent advancements in material science and nanotechnology have further enhanced the catalytic efficiency of iron-based systems (Theofanidis et al., 2018). Techniques such as surface modification, doping with other metals, and coupling with carbonaceous materials (e.g., biochar, graphene oxide) have led to the development of novel hybrid materials with improved redox activity, stability, and selectivity (Georgakilas et al., 2016). Additionally, the integration of iron-based AOPs with other treatment methods such as biological processes, membrane filtration, and adsorption has demonstrated synergistic effects in achieving higher degradation efficiencies and better overall performance in complex wastewater matrices (Lin et al., 2022). Despite the significant progress, several challenges remain in optimizing iron-based AOPs for large-scale and long-term applications. Issues such as catalyst deactivation, iron leaching, energy consumption, and cost-effectiveness need to be carefully addressed (Satyam et al., 2025). Moreover, understanding the mechanisms of pollutant degradation, the influence of co-existing substances, and the fate of transformation products is crucial for the safe and efficient application of these technologies (Yang et al., 2024).

This review aims to provide a comprehensive overview of the role of iron in advanced oxidation technologies, with a specific focus on its applications in wastewater remediation. It discusses the fundamental principles of iron-mediated AOPs, highlights recent advances in material design and process integration, and critically evaluates the performance of different iron-based systems. Additionally, the review outlines the current limitations and offers perspectives on future research directions to enhance the practical viability of iron-catalyzed AOPs in real-world water treatment scenarios.

FUNDAMENTAL MECHANISMS OF IRON IN AOPS

Iron plays a central and multifaceted role in the activation of oxidants within Advanced Oxidation Processes (AOPs), acting as a catalyst in both homogeneous and heterogeneous systems (Zhao et al., 2021). The core mechanism of iron-mediated AOPs revolves around its ability to participate in redox reactions, particularly its capacity to alternate between the Fe(II) and Fe(III) oxidation states (Wang et al., 2022). This redox cycling facilitates the generation of reactive oxygen species (ROS), most notably hydroxyl radicals (•OH), which possess one of the highest known oxidation potentials (2.8 V) (Dong et al., 2022). These radicals are capable of non-selectively oxidizing a wide range of organic pollutants, breaking them down into less toxic compounds or fully mineralizing them into carbon dioxide and water (Nidheesh et al., 2022). The classic example of iron's role in AOPs is exemplified by the Fenton reaction, which involves the reaction of ferrous iron (Fe^{2+}) with hydrogen peroxide (H_2O_2) to produce hydroxyl radicals and ferric iron (Fe^{3+}), as shown in the simplified reaction:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^-$$

This primary reaction is followed by a series of secondary reactions that regenerate Fe^{2+} from Fe^{3+}, allowing the catalytic cycle to continue. However, this regeneration is often limited by the rate of reduction, and Fe^{3+} can also react with H_2O_2 to form less reactive species such as hydroperoxyl radicals (HO_2•), which have a lower oxidation potential (Deng et al., 2023). The overall efficiency of the Fenton process thus depends on the relative rates of Fe^{2+} oxidation and Fe^{3+} reduction, the availability of H_2O_2, and the operational pH (Li et al., 2020). Notably, the Fenton reaction is most efficient at acidic pH (typically around 2.8–3.5), where Fe^{2+} remains soluble and reactive (Li et al., 2019). In response to these pH constraints and issues like iron sludge formation, Fenton-like reactions have been explored, involving other iron species or modified systems (Yu et al., 2016). For instance, iron complexes or chelated iron (e.g., Fe-EDTA, Fe-citrate) are used to maintain solubility at near-neutral pH levels, enabling application under broader environmental conditions (Wang et al., 2020). In these systems, the mechanism still relies on iron redox cycling, but the presence of ligands alters the electron transfer kinetics and can influence the generation and stability of ROS (Huang et al., 2021). Beyond hydrogen peroxide, iron can also activate peroxymonosulfate (PMS) and persulfate

(PDS) in sulfate radical-based AOPs (SR-AOPs) (Giannakis et al., 2021). In these systems, Fe^{2+} reacts with PMS or PDS to produce sulfate radicals ($SO_4\bullet^-$), which are also powerful oxidants (oxidation potential of ~2.6 V) and often exhibit better selectivity and performance in high-salinity or high-organic-content wastewaters (Adly et al., 2025). These reactions follow similar redox principles:

$Fe^{2+} + HSO_5^- \rightarrow Fe^{3+} + SO_4^{\cdot-} + OH^-$

$Fe^{2+} + S_2O_8^{2-} \rightarrow Fe^{3+} + SO_4^{\cdot-} + SO_4^{2-}$

These sulfate radicals can subsequently react with water to generate hydroxyl radicals, or directly oxidize contaminants. Importantly, SR-AOPs are often more effective over a wider pH range compared to traditional Fenton processes, enhancing the applicability of iron-based catalysis in diverse wastewater conditions (Fan et al., 2023).

Heterogeneous iron catalysts add another dimension to the mechanisms of iron in AOPs. In these systems, iron is immobilized on solid supports such as clays, zeolites, activated carbon, or engineered nanomaterials like iron oxides (Fe_3O_4, Fe_2O_3), zero-valent iron (ZVI), or iron-doped catalysts (Tian et al., 2024). These materials facilitate surface-mediated redox reactions, where pollutants adsorb onto the catalyst surface and interact with oxidants activated by surface-bound iron species. The catalytic activity in heterogeneous systems often hinges on factors such as surface area, porosity, iron dispersion, crystallinity, and surface charge (Zhu et al., 2024). Additionally, these systems allow for better iron recovery, reduced sludge formation, and operation under neutral or slightly basic pH. In many heterogeneous systems, the generation of ROS occurs via the same fundamental principles, with Fe^{2+}/Fe^{3+} centers on the catalyst surface engaging in electron transfer with oxidants (Merchant et al., 2024). For example, in the presence of H_2O_2, surface Fe^{2+} species catalyze hydroxyl radical formation, while Fe^{3+} species may require reduction to reinitiate the catalytic cycle. The availability of reducing agents (e.g., organic matter, reducing functional groups) in the system can therefore influence the overall efficiency of the AOP (Choe et al., 2018). Surface defects, oxygen vacancies, and the interaction of iron with co-dopants or support materials can further enhance redox activity and broaden functional performance.

Another important aspect of iron-mediated AOPs is the generation of reactive oxygen species beyond hydroxyl and sulfate radicals, such as superoxide anion radicals ($O_2\bullet^-$), singlet oxygen ($^1O_2$), and high-valent iron-oxo species (Fe(IV)=O or Fe(V)=O), especially in photo-Fenton or electro-Fenton systems. These species are often generated under specific reaction conditions involving light irradiation or electrical input, where iron acts as a photo- or electro-catalyst. The formation of these species adds complexity and versatility to the degradation mechanisms, potentially offering synergistic or targeted degradation pathways for specific pollutants (Wang et al., 2022).

Table 1

Fundamental Mechanisms of Iron in AOPs

Research Aspect	Description	Reference
Iron in Fenton Process	Iron(II) ions catalyze the decomposition of hydrogen peroxide to produce hydroxyl radicals (·OH), which are highly reactive and capable of oxidizing organic pollutants. The mechanism involves electron transfer from Fe(II) to hydrogen peroxide, forming Fe(III) and hydroxyl radicals.	(Liu et al., 2021)
Iron in Photo-Fenton Process	In the presence of UV light, iron(III) can be reduced to iron(II), which then reacts with hydrogen peroxide to generate hydroxyl radicals. This process enhances the degradation of organic pollutants compared to the Fenton process alone.	(Lin et al., 2021)
Iron in Sulfate Radical-Based AOPs	Iron(II) can activate persulfate (PMS) or peroxymonosulfate (PDS) to produce sulfate radicals (SO4·–), which are strong oxidants. Recent studies suggest that high-valent iron species (e.g., Fe(IV)) may also play a role in the activation process under acidic conditions.	(Li et al., 2024)
Iron in Heterogeneous AOPs	Iron-based catalysts, such as iron oxides or iron-doped materials, can be used in heterogeneous AOPs. These catalysts provide active sites for the generation of radicals and can enhance the degradation efficiency of pollutants. The mechanisms involve adsorption of reactants onto the catalyst surface and subsequent radical generation.	(Zhao et al., 2021)
Iron in Ozonation	Iron can act as a catalyst in ozonation processes, promoting the formation of hydroxyl radicals from ozone. This enhances the oxidation of organic pollutants and improves the overall efficiency of the ozonation process.	(Liu et al., 2022)
Iron in Combined AOPs	Iron can be used in combination with other AOPs, such as UV/H_2O_2 or O_3/H_2O_2, to achieve synergistic effects. The combined use of iron and other oxidants can enhance the generation of radicals and improve the degradation efficiency of refractory pollutants.	(Das et al., 2022)

IRON-BASED CATALYSTS: DESIGN, SYNTHESIS, AND PERFORMANCE

Homogeneous Catalysts

Iron-based homogeneous catalysts, particularly ferrous ions (Fe(II)), are integral to many advanced oxidation processes (AOPs) due to their ability to efficiently generate hydroxyl radicals (•OH) through the Fenton reaction (Hussain et al., 2021). In this process, Fe(II) reacts with hydrogen peroxide (H_2O_2) to form a Fe(II)-peroxide complex, which subsequently decomposes to produce Fe(III) and reactive highly hydroxyl radicals. These radicals are capable of oxidizing a wide range of organic contaminants, making the Fenton process highly effective for wastewater treatment (Sun et al., 2023). The efficiency of this homogeneous catalysis is influenced by several factors, including the concentrations of Fe(II) and H_2O_2, the pH of the solution, and the presence of other ions that may either compete for or stabilize the reactive species. Additionally, the use of light in photo-Fenton processes can further enhance radical generation by promoting the formation of electron-hole pairs in the iron catalyst, leading to a higher yield of hydroxyl radicals and more effective pollutant degradation (Ahmed et al., 2021). This versatility and effectiveness make iron-based homogeneous catalysts a cornerstone of many AOPs for environmental remediation.

Heterogeneous Catalysts

Iron-based heterogeneous catalysts have garnered significant attention due to their abundance, low cost, and environmental friendliness. These catalysts are widely used in various applications, including the Fenton process for wastewater treatment, biomass conversion, and other chemical reactions. This review focuses on three main categories of iron-based heterogeneous catalysts: iron oxide catalysts, composite systems, and carbon-supported iron catalysts.

Iron Oxide Catalysts

Iron oxides, such as hematite (α-Fe_2O_3), magnetite (Fe_3O_4), and goethite, are naturally occurring minerals with high surface area and reactivity, making them effective catalysts for the Fenton reaction (Elsehemy et al., 2025). These minerals can be found in iron-containing soils and are used to oxidize organic pollutants in contaminated water and soil. The high surface area of iron oxides provides numerous active sites for the adsorption and activation of hydrogen peroxide (H_2O_2), leading to the generation of hydroxyl radicals (•OH) that are highly effective in degrading organic contaminants (Pi et al., 2020).

Composite Systems

Composite systems involving iron oxides and other materials have been developed to enhance catalytic performance. For example, iron-modified zeolites are porous materials that can be tailored to optimize their catalytic properties for specific applications. The incorporation of iron ions into the zeolite structure increases the surface area and reactivity, making these composites highly effective for the Fenton process (Shangguan et al., 2022). Similarly, iron-doped carbon materials, such as activated carbon or carbon nanotubes, have been used to create catalysts with high surface area and reactivity. These composites combine the benefits of iron's catalytic activity with the high surface area and stability of carbon materials, resulting in improved performance in various catalytic reactions (Zhang et al., 2015).

Carbon-Supported Iron Catalysts

Carbon-supported iron catalysts are another important category of iron-based heterogeneous catalysts. These catalysts are prepared by impregnating carbon supports, such as activated carbon, with iron salts, followed by drying and calcination. The carbon support provides a high surface area and stability, while the iron acts as the active catalytic component. This combination results in catalysts with high activity and recyclability, making them suitable for various applications, including biomass conversion and organic synthesis. For instance, studies have shown that carbon-supported iron catalysts can effectively promote the selective hydrogenation of biomass-derived molecules, such as 5-hydroxymethylfurfural (HMF), to produce high-value chemicals (Liu et al., 2023).

Waste-Derived Iron Catalysts

Iron-Rich Industrial Sludge

Iron-rich sludge, a by-product of industrial processes such as metal manufacturing, contains significant amounts of iron and can be used as a catalyst in AOPs (Ghanbari et al., 2020). For example, red mud (RM), a waste product from the Bayer process used in aluminum oxide production, is rich in iron and has been innovatively applied in the Fenton process to reduce operational costs and reuse a waste material that is produced in large quantities. This approach not only addresses waste management issues but also provides a cost-effective solution for wastewater treatment.

Biochar-Based Catalysts

Biochar, derived from agricultural and industrial waste materials, is known for its large surface area and stability, making it an effective catalyst in AOPs. Iron-impregnated biochar, prepared from waste materials such as black seed pomace, has been successfully used to activate peroxysulfate (PDS) for the degradation of pollutants like diclofenac (Mustafa et al., 2023). This treatment achieved 88% diclofenac degradation within 10 minutes and a total organic carbon (TOC) removal rate of 90% within 60 minutes. The incorporation of iron into biochar enhances its catalytic activity and facilitates the separation of the catalyst from the treated water using an external magnetic field (Li et al., 2020).

Metal-Organic Frameworks (MOFs)

Metal-organic frameworks (MOFs) are another promising class of materials derived from waste for use in AOPs. These materials offer adjustable structures and versatile catalytic properties, making them suitable for sustainable pollutant removal (Kaur et al., 2023). Iron-based MOFs, in particular, have shown high catalytic activity in AOPs such as photocatalysis, Fenton, and persulfate-based processes. The integration of magnetic materials like iron oxides into MOFs can improve their surface properties, making them easier to separate and reuse.

Table 2

Comparison of Iron-Based Catalysts

Catalyst Type	Example Materials	Activation Mechanism	Target Pollutants	Key Advantages
Homogeneous	$FeSO_4$, $FeCl_3$	$H_2O_2 \rightarrow HO\bullet$	Dyes, phenols	High kinetics
Iron oxides	Fe_3O_4, α-Fe_2O_3	Surface-mediated radical gen.	Pharmaceuticals	Magnetic recovery
Bimetallic	$Fe_{2.5}$Mo@CNs	PS → $SO_4\bullet^-/^1O_2$/ETP	Xanthates, antibiotics	Self-cycling
Waste-derived	γ-FeOOH (sludge)	PI → $IO_3\bullet/^1O_2$	Methylene blue	Low-cost, circular

APPLICATIONS IN WASTE-WATER REMEDIATION

Iron-based catalysts have emerged as versatile and effective tools in wastewater remediation through Advanced Oxidation Processes (AOPs), playing a crucial role in the degradation of organic pollutants, removal of heavy metals, and enhancement of sludge dewatering and resource recovery. These applications leverage the unique properties of iron, including its ability to generate reactive oxygen species (ROS) such as hydroxyl radicals (•OH) and superoxide anions ($\bullet O_2^-$), which are highly effective in breaking down a wide range of contaminants.

Organic Pollutant Degradation

One of the primary applications of iron in AOPs is the degradation of organic pollutants. Iron-based catalysts, particularly in the form of ferrous (Fe^{2+}) and ferric (Fe^{3+}) ions, are widely used in the Fenton process, where they react with hydrogen peroxide (H_2O_2) to produce hydroxyl radicals (Kaur et al., 2023). These radicals are highly reactive and can oxidize a variety of organic contaminants, including dyes, pharmaceuticals, and industrial effluents. For instance, studies have shown that the Fenton process using Fe^{2+} as a catalyst can achieve over 90% degradation of organic pollutants such as phenol and benzene within a short reaction time (Cheng et al., 2016). The efficiency of this process is influenced by factors such as pH, concentration of iron and hydrogen peroxide, and the nature of the organic pollutant. Additionally, the use of heterogeneous iron catalysts, such as iron oxide nanoparticles and biochar-supported iron, has been explored to enhance the stability and reusability of the catalyst while maintaining high degradation efficiency.

Heavy Metal Removal

Iron also plays a significant role in the removal of heavy metals from wastewater. The presence of iron in AOPs can facilitate the precipitation and coagulation of heavy metals, making them easier to separate from the water (Luo et al., 2021). For example, in the presence of iron, heavy metals such as lead (Pb), cadmium (Cd), and chromium (Cr) can form insoluble metal hydroxides or oxides, which can be removed through sedimentation or filtration. This process is particularly effective in treating industrial wastewater containing high concentrations of heavy metals. Furthermore, the use of iron-based AOPs can also reduce the toxicity of heavy metals by converting them into less harmful forms. For instance, hexavalent chromium Cr(VI)), which is highly toxic, can be reduced to trivalent chromium Cr(III)) in the presence of iron, making it easier to remove and less hazardous to the environment (Marinho et al., 2019; Chaudhary et al., 2025).

Sludge Dewatering and Resource Recovery

Iron-based AOPs also contribute to the dewatering and resource recovery of sludge, a by-product of wastewater treatment processes (Liang et al., 2022). Sludge often contains significant amounts of organic matter and nutrients, making it a valuable resource if properly treated. The use of iron in AOPs can enhance the dewatering process by breaking down the organic matrix of the sludge, making it easier to separate the water from the solid fraction. This not only reduces the volume of sludge but also improves its stability and reduces odors. Additionally, the treated sludge can be further processed for resource recovery, such as the extraction of valuable metals or the production of biogas through anaerobic digestion (Guo et al., 2021). The use of iron in AOPs can also improve the quality of the sludge, making it more suitable for agricultural applications or other beneficial uses.

CONCLUSION

Iron has emerged as a cornerstone element in advanced oxidation technologies (AOTs) due to its unique redox properties, cost-effectiveness, and environmental compatibility. This review has highlighted the diverse roles of iron-based catalysts, particularly in Fenton and Fenton-like reactions, heterogeneous systems, and photo-assisted processes, for the effective degradation of a wide range of pollutants in wastewater. Iron facilitates the generation of reactive oxygen species, especially hydroxyl radicals, which are crucial for breaking down complex and persistent organic contaminants. Moreover, advancements in nanostructured iron materials, iron-doped composites, and hybrid systems have significantly improved the efficiency, stability, and reusability of these catalytic processes. Despite the promising potential, challenges such as iron sludge formation, narrow pH range applicability, and catalyst recovery remain areas of active research. Future developments should focus on the design of more robust iron-based catalysts, integration with renewable energy sources, and scaling up these technologies for real-world applications. Overall, iron-centered AOTs represent a vital and evolving strategy for achieving sustainable and effective wastewater remediation.

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