
CATALYTIC TECHNOLOGIES FOR THE REMOVAL OF EMERGING CONTAMINANTS IN WATER AND STORMWATER SYSTEMS: A COMPREHENSIVE REVIEW

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ABSTRACT

The pervasive contamination of surface waters, groundwater, and drinking water supplies by emerging contaminants (ECs)—particularly pharmaceuticals, personal care products (PCPs), endocrine-disrupting chemicals (EDCs), per- and polyfluoroalkyl substances (PFAS), and pesticide residues—represents a critical environmental challenge with profound implications for ecosystem integrity and human health (Athey & Erdle, 2021). Conventional water treatment technologies, including coagulation-flocculation, activated carbon adsorption, and biological processes, demonstrate fundamental inadequacies for removal of these recalcitrant, persistent compounds characterized by low biodegradability, resistance to photodegradation, and trace-level concentrations (1-1000 ng/L to µg/L) (Singh et al., 2023). Advanced oxidation processes (AOPs) employing catalytic materials represent transformative solutions through generation of reactive oxygen species (ROS)—including hydroxyl radicals ($\bullet\text{OH}$), sulfate radicals ($\text{SO}_4\bullet^-$), superoxide anions ($\text{O}_2\bullet^-$), and singlet oxygen ($^1\text{O}_2$)—enabling complete mineralization of resistant organic contaminants to carbon dioxide and water (Satyam & Patra, 2025). This comprehensive review systematically examines five principal catalytic AOP technologies: (1) heterogeneous photocatalysis achieving 88-96% pharmaceutical removal efficiency under optimized conditions; (2) Fenton and Fenton-like processes demonstrating 92-98% removal efficiency through high-valent iron species; (3) catalytic ozonation achieving 85-92% removal with 30-50% ozone consumption reduction compared to non-catalytic systems; (4) persulfate-based AOPs (PS-AOPs) demonstrating 87-94% efficiency across broader pH ranges (5.0-8.0); and (5) electrochemical catalysis

achieving 85-92% removal with tunable oxidation potential (Miklos et al., 2018), (Kumar et al., 2019), (Satyam & Patra, 2025). Catalyst materials examined comprehensively include metal oxide semiconductors (TiO_2 , Fe_3O_4 , Nb_2O_5 , CoO_4 , MnO_2), carbon-based systems (graphene derivatives, carbon nanotubes, biochar, nitrogen-doped carbon), metal-organic frameworks (MOFs), waste-derived biochar materials, and emerging single-atom catalysts (Wang et al., 2025), (Fidelis et al., 2025), (Aziz et al., 2025). Degradation mechanisms encompass both radical pathways generating non-selective $\bullet\text{OH}$ and $\text{SO}_4^{\bullet-}$ species and non-radical mechanisms including direct electron transfer, singlet oxygen generation, and surface-catalyzed reactions enabling selective contaminant oxidation (Zhu et al., 2018). Critical operating parameters—including solution pH (optimal ranges 3.0-8.0 depending on system), temperature (20-80°C operational range with 20-30% efficiency improvement per 10°C increase), catalyst loading (0.1-1.0 g/L with saturation typically at 0.3-0.8 g/L), oxidant concentration (0.5-5.0 mmol/L stoichiometric range), and reaction time (10-240 minutes)—are comprehensively analyzed with quantitative performance relationships and optimization strategies (Yu et al., 2026). Removal efficiency across diverse emerging contaminant classes demonstrates differential performance: pharmaceuticals (diclofenac, carbamazepine, sulfamethoxazole, ibuprofen) 88-98% removal, personal care products (triclosan, parabens, benzophenones) 85-92% removal, endocrine disruptors (bisphenol A, estrogens) 80-93% removal, PFAS compounds (PFOA, PFOS) 60-85% removal through persulfate/electrochemistry, and pesticide residues (atrazine, glyphosate) 78-95% removal (Kumar et al., 2019), (Zawadzki, 2022), (Meena et al., 2024). Practical integration into multi-barrier stormwater treatment systems is discussed with field performance data demonstrating 85-98% persistent pollutant removal through sequential treatment stages combining physical separation (80-95% TSS removal), adsorption (70-90% hydrophobic EC removal), catalytic oxidation (85-98% persistent pollutant mineralization), and post-polishing (95-99% final treatment) (Yu et al., 2026). Enhanced stormwater treatment via thermally modified steel slag-based bioretention systems achieves nutrient removal ($\text{NH}_4^+\text{-N}$ 95.3±1.3%, TN 85.7±1.8%, TP 90.5±1.5%), heavy metal removal (Cu^{2+} 96.1±0.7%, Cr^{6+} 90.5±1.2%, Pb^{2+} 92.2±1.1%), and emerging pharmaceutical degradation (enrofloxacin 65.6±2.1%, norfloxacin 62.6±2.4%) (Yu et al., 2026). Major limitations constraining widespread full-scale deployment include: (1) catalyst deactivation after 50-100 treatment cycles with inadequate regeneration strategies; (2) secondary byproduct formation and toxicity concerns; (3) energy-intensive operation requiring 20-150 kWh/m³ depending on technology (photocatalysis 80-150 kWh/m³, ozonation 20-50 kWh/m³, persulfate 40-90 kWh/m³) representing 30-40% of

operational costs; (4) persistent scalability and real-world implementation gaps with 10-30% efficiency loss between laboratory and field conditions (Alazaiza et al., 2026), (Miklos et al., 2018). Emerging innovations including visible/near-infrared photocatalysts extending light absorption, single-atom catalysts achieving theoretical efficiency with minimal precious metal requirements, confinement-based catalysis enhancing ROS generation, and renewable energy integration offer exceptional promise for sustainable next-generation systems (Satyam & Patra, 2025), (Fidelis et al., 2025). Future research priorities address critical knowledge gaps: (1) mechanistic elucidation of non-radical pathways enabling selective oxidation and byproduct minimization; (2) development of aqueous-stable metal-organic frameworks with improved catalyst recovery; (3) comprehensive real-world validation in complex matrices with suspended solids, dissolved salts, and natural organic matter interference; (4) catalyst regeneration and circular economy approaches enabling sustainable full-scale deployment; (5) integration with renewable electricity sources (solar photovoltaic, wind power) reducing operational carbon footprint; (6) comprehensive lifecycle assessment and environmental impact analysis balancing treatment efficacy against resource consumption (Alazaiza et al., 2026). This review provides state-of-the-art synthesis of catalytic AOP technologies, highlighting mechanistic understanding, material innovations, operating strategies, performance metrics, and practical deployment considerations essential for advancing water security and environmental remediation.

KEYWORDS: Advanced oxidation processes, catalytic degradation, emerging contaminants, pharmaceuticals, photocatalysis, Fenton chemistry, persulfate activation, electrochemical treatment, water remediation, stormwater management, reactive oxygen species, heterogeneous catalysis, environmental remediation, sustainable water treatment.

1. INTRODUCTION: EMERGING CONTAMINANTS AS ENVIRONMENTAL AND HEALTH THREATS

1.1 Emerging Contaminants: Definition, Detection, and Environmental Ubiquity

Emerging contaminants represent a diverse group of synthetic and natural chemical compounds detected with increasing frequency in environmental matrices—including surface waters, groundwater, wastewater effluents, and drinking water supplies—at trace to low-level concentrations yet demonstrating potential or confirmed adverse effects on ecological or human health (Athey & Erdle, 2021). The designation "emerging" reflects both novelty of detection through advancement in analytical instrumentation (particularly high-performance

liquid chromatography coupled with high-resolution mass spectrometry enabling sub-nanogram per liter detection limits) and historical absence from regulatory frameworks, distinguishing these compounds from legacy contaminants subjected to systematic regulatory control (Athey & Erdle, 2021). Anthropogenic microfibers and emerging pollutants have become ubiquitous environmental contaminants with global distribution from remote Arctic ecosystems to urban stormwater systems (Athey & Erdle, 2021), (Bergmann et al., 2022).

The principal classes of emerging contaminants encompass: (1) pharmaceuticals and therapeutic agents including analgesics (diclofenac, ibuprofen, acetaminophen), antidepressants (fluoxetine, sertraline), antibiotics (sulfamethoxazole, ciprofloxacin, trimethoprim), anticonvulsants (carbamazepine), and anticoagulants; (2) personal care products (PCPs) including antimicrobial agents (triclosan), ultraviolet filters (benzophenones, oxybenzone), parabens (methylparaben, propylparaben), fragrances, and cosmetic preservatives; (3) endocrine-disrupting chemicals (EDCs) including natural hormones (estradiol, estrone) and synthetic hormones (17 α -ethinylestradiol), bisphenol A, and phytoestrogens; (4) per- and polyfluoroalkyl substances (PFAS) including perfluorooctanoic acid (PFOA), perfluorooctane sulfonic acid (PFOS), and emerging PFAS replacements; (5) pesticide residues including herbicides (atrazine, glyphosate, metolachlor), insecticides (pyrethroid compounds), and fungicides; (6) industrial chemicals including flame retardants, plasticizers, and polycyclic aromatic hydrocarbons (PAHs); and (7) anthropogenic microfibers and microplastics including tire road wear particles (TRWPs), textile microfibers, and plastic fragment debris (Singh et al., 2023), (Meena et al., 2024).

Concentration profiles of emerging contaminants in environmental waters characteristically range from 1-1000 ng/L to low μ g/L, far below acute toxicity thresholds yet within ranges demonstrating chronic ecotoxicological effects (Singh et al., 2023). Wastewater effluent concentrations of pharmaceuticals reach 20-500 ng/L, personal care products 50-2000 ng/L, and pesticide residues 0.5-20 μ g/L in urban systems (Singh et al., 2023). PFAS groundwater contamination sites document concentrations ranging from sub-ng/L to mg/L in severely impacted aquifers, with widespread detection even in pristine water sources reflecting extraordinary environmental persistence and bioaccumulation potential (Meena et al., 2024).

1.2 Inadequacy of Conventional Water Treatment Technologies

Conventional water and wastewater treatment processes—including coagulation-flocculation, sedimentation, sand filtration, activated carbon adsorption, and biological treatment—demonstrate fundamental inadequacies for emerging contaminant removal, reflecting optimization for pathogen and particulate removal rather than recalcitrant organic synthesis

degradation (Singh et al., 2023), (Qasem et al., 2021). A systematic review of industrial wastewater management demonstrates that while regulatory frameworks, technological innovation, and sustainability considerations represent cornerstones of effective management, substantial impediments including inadequate infrastructure, resource constraints, and insufficient stakeholder collaboration continue to impede progress (Singh et al., 2023).

Coagulation-flocculation processes, employing chemical coagulants (aluminum sulfate, ferric sulfate) or increasingly sustainable natural coagulants (chitosan, *Moringa oleifera*, tannins), demonstrate limited efficacy for emerging contaminants (Koul et al., 2022). While application of natural coagulants offers sustainable alternatives to chemical approaches, removal efficiency for dissolved organic micropollutants remains poor (typically 10-30% removal) compared to removal of suspended particulates (80-95% removal) (Koul et al., 2022). The mechanisms underlying coagulation—electrostatic neutralization of suspended particle charges and hydrophobic aggregation—prove ineffective for ionic or amphipathic emerging contaminants (Koul et al., 2022).

Activated carbon adsorption, the conventional technology most effective for trace organic contaminant removal, exhibits critical limitations. Removal efficiency depends critically on pollutant physicochemical properties, particularly lipophilicity ($\log K_{ow}$). Hydrophobic compounds ($\log K_{ow} > 3$) adsorb effectively to activated carbon, while hydrophilic pharmaceuticals and polar metabolites demonstrate poor adsorption affinity (Hamad & Idrus, 2022). Furthermore, biofilm development on granular activated carbon (GAC) media produces enzymatic transformation of certain emerging contaminants, potentially generating more bioavailable or toxic metabolites than parent compounds (Hamad & Idrus, 2022). Most critically, activated carbon represents a transfer technology rather than destruction process—adsorbed contaminants remain in the carbon matrix, requiring regeneration through high-temperature thermal treatment (800-900°C) that is energy-intensive and generates volatile organic compound emissions (Hamad & Idrus, 2022). Life cycle assessment of activated carbon systems reveals substantial environmental burdens associated with regeneration energy requirements (Hamad & Idrus, 2022).

Biological treatment processes including activated sludge systems, trickling filters, and constructed wetlands demonstrate poor efficacy for emerging contaminant removal (Liang et al., 2021). While certain emerging contaminants undergo biodegradation under controlled laboratory conditions with enriched microbial consortia, environmental wastewater treatment systems contain mixed microbial communities with heterogeneous enzymatic capabilities and limited acclimation to novel substrates (Liang et al., 2021). Recalcitrant compounds including

atrazine, carbamazepine, and PFAS demonstrate resistance to biodegradation under standard treatment conditions (Liang et al., 2021). Conversely, certain emerging contaminants persist through biological reactors without degradation, subsequently accumulating in biosolids with potential transfer to terrestrial food webs through biosolids land application (Liang et al., 2021).

Chemical disinfection processes, including chlorination, ozonation, and advanced oxidation, exhibit variable efficacy depending on oxidant strength and emerging contaminant reactivity. Conventional disinfectants including free chlorine and chlorine dioxide typically oxidize only the most reactive organic compounds, while less reactive compounds persist (Miklos et al., 2018). Moreover, emerging contaminant oxidation by conventional disinfectants frequently generates halogenated transformation products (trihalomethanes, haloacetic acids, N-nitrosodimethylamine precursors) with documented toxicity exceeding parent compound toxicity, creating treatment dilemmas wherein pollutant removal generates potentially more harmful byproducts (Miklos et al., 2018).

1.3 Advanced Oxidation Processes as Transformative Solutions

Advanced oxidation processes employing catalytic materials represent transformative alternatives for complete mineralization of emerging contaminants through generation of highly reactive oxygen species capable of oxidizing diverse organic compounds including highly recalcitrant substances resistant to conventional treatment (Kumar et al., 2019), (Kesarwani et al., 2026). Recent advances in nano-Fenton catalytic degradation of emerging pharmaceutical contaminants demonstrate exceptional removal efficiency (92-98%) through heterogeneous catalyst systems that overcome limitations of homogeneous Fenton approaches including pH sensitivity, iron sludge generation, and catalyst recovery difficulties (Kumar et al., 2019).

The fundamental advantage of advanced oxidation processes derives from generation of reactive oxygen species with exceptionally high oxidation potentials: hydroxyl radicals (+2.80 V vs. SHE), sulfate radicals (+2.50 V vs. SHE), and electrogenerated oxidative species (+3.0 V vs. SHE for boron-doped diamond electrodes) (Miklos et al., 2018). These oxidation potentials substantially exceed oxidation potentials of conventional disinfectants (chlorine +1.36 V, ozone +2.07 V), enabling oxidation of compounds refractory to conventional treatment (Miklos et al., 2018). Critically, advanced oxidation processes achieve complete mineralization of organic contaminants to CO₂ and H₂O rather than partial oxidation generating potentially toxic intermediate byproducts (Kumar et al., 2019).

Water treatment utilizing nanoparticles and advanced materials demonstrates dramatic performance improvements compared to conventional systems (Kesarwani et al., 2026). Catalytic advanced oxidation processes enable: (1) high removal efficiency (typically 85-98% for target contaminants under optimized conditions); (2) complete mineralization rather than transfer or partial oxidation; (3) operation across diverse pH ranges enabling direct application to varied wastewater matrices; (4) integration with renewable energy sources (solar photocatalysis, renewable electrochemistry); (5) potential for selective oxidation of target contaminants through appropriate catalyst/oxidant selection (Kesarwani et al., 2026).

1.4 Scope, Organization, and Objectives of This Review

This comprehensive review synthesizes current state-of-the-art scientific knowledge addressing catalytic technologies for emerging contaminant removal from water and stormwater systems. Specific objectives include:

Systematic examination of five principal catalytic AOP technologies with mechanistic explanations, performance metrics, and comparative analysis (Satyam & Patra, 2025), (Miklos et al., 2018);

Critical evaluation of diverse catalyst materials spanning metal oxides, carbon-based systems, metal-organic frameworks, and waste-derived biochar with analysis of physicochemical properties influencing catalytic performance (Wang et al., 2025), (Fidelis et al., 2025), (Aziz et al., 2025);

Comprehensive analysis of degradation mechanisms including radical pathways and non-radical mechanisms (Zhu et al., 2018);

Examination of critical operating parameters (pH, temperature, catalyst dosage, oxidant concentration) influencing treatment performance with quantitative relationships (Yu et al., 2026);

Performance evaluation across diverse emerging contaminant classes (pharmaceuticals, PCPs, EDCs, PFAS, pesticides, microplastics) (Meena et al., 2024), (Zawadzki, 2022), (Barua 2026);

Analysis of practical integration into multi-barrier stormwater treatment systems with field case studies (Yu et al., 2026);

Identification of current limitations including catalyst deactivation, secondary byproduct formation, energy consumption, and scalability barriers (Alazaiza et al., 2026), (Miklos et al., 2018);

Discussion of emerging innovations including visible/NIR photocatalysts, single-atom catalysts, and renewable energy integration (Satyam & Patra, 2025), (Fidelis et al., 2025);

Delineation of future research priorities addressing mechanistic gaps, real-world validation, catalyst regeneration, and sustainability assessment (Alazaiza et al., 2026).

2. CATALYTIC ADVANCED OXIDATION PROCESSES: FUNDAMENTAL CHEMISTRY AND COMPARATIVE ANALYSIS

2.1 Heterogeneous Photocatalysis: Mechanisms and Performance

2.1.1 Fundamental Photocatalytic Mechanisms

Heterogeneous photocatalysis represents one of the most extensively studied catalytic technologies for emerging contaminant degradation, encompassing over 50,000 cumulative academic publications documenting fundamental and applied research developments. Visible light-driven advanced oxidation processes demonstrate particular promise for removing diverse emerging contaminants from water and wastewater through generation of hydroxyl radicals ($\bullet\text{OH}$) and superoxide radicals ($\text{O}_2\bullet^-$) (Zawadzki, 2022). The photocatalytic mechanism involves light absorption by semiconductor catalyst materials, generating electron-hole pairs with subsequent charge carrier migration to catalyst surfaces where oxidation-reduction reactions occur with pollutant molecules (Paiu et al., 2025).

The photocatalytic process proceeds through sequential steps: (1) photon absorption wherein photons with energy equal to or exceeding the semiconductor band gap energy (E_g) promote valence band electrons to the conduction band, generating conduction band electrons (e_{cb}) and valence band holes (h_{vb}); (2) charge carrier migration through the catalyst lattice to active surface sites, competing with rapid electron-hole recombination (nanosecond to microsecond timescales); (3) surface redox reactions wherein holes oxidize water, hydroxide ions, or adsorbed pollutants, while electrons reduce dissolved oxygen or other electron acceptors (Paiu et al., 2025).

For semiconductor photocatalysts with optimal band gap energy (2.0-4.0 eV), absorption of photons enables generation of electron-hole pairs with sufficient energy for initiating redox reactions. Titanium dioxide (TiO_2) band gap energy of 3.2 eV for anatase phase corresponds to 387 nm wavelength threshold, enabling UV photon utilization but excluding visible photons representing 43-47% of incident solar spectrum (Paiu et al., 2025). This fundamental limitation of UV-only activation motivates extensive research into band gap engineering and visible-light activation strategies (Paiu et al., 2025).

Photogenerated holes in TiO_2 valence band exhibit strong oxidizing potential (+3.1 V vs. standard hydrogen electrode [SHE]), capable of oxidizing organic pollutants through direct valence band hole oxidation or by abstracting electrons from water/hydroxide to generate

hydroxyl radicals (Paiu et al., 2025). Generated $\bullet\text{OH}$ radicals, with oxidation potential of +2.80 V vs. SHE, exhibit non-selective reactivity toward diverse organic compounds with reaction rate constants typically ranging from 10^6 - $10^{10} \text{ M}^{-1}\text{s}^{-1}$ (Paiu et al., 2025). Simultaneously, electrons in the conduction band (reduction potential in TiO_2 : -0.5 V vs. SHE) reduce dissolved oxygen through generation of superoxide radicals ($\text{O}_2^{\bullet-}$) with reaction: $\text{O}_2 + \text{e}^- \rightarrow \text{O}_2^{\bullet-}$, followed by further reduction and protonation to ultimately generate hydroxyl radicals (Paiu et al., 2025).

2.1.2 Catalyst Material Properties and Performance Optimization

Global research evolution in catalytic water and wastewater treatment demonstrates significant increases in photocatalysis publication output after 2015, reflecting growing international attention to water sustainability challenges (Alazaiza et al., 2026). Heterogeneous photocatalysis for advanced water treatment spans diverse materials including metal oxides, carbon-based semiconductors, polymer-based photocatalysts, and emerging two-dimensional materials, with mechanisms, reactor configurations, and emerging applications comprehensively documented (Paiu et al., 2025).

Titanium dioxide (TiO_2) anatase remains the benchmark photocatalyst due to: (1) exceptional photostability (does not undergo photodegradation under operational conditions); (2) complete non-toxicity enabling food contact and biomedical applications; (3) low cost (USD 10-50/kg for bulk powder, USD 100-500/L for dispersions) enabling economic scalability; (4) broad commercial availability from multiple manufacturers (Paiu et al., 2025). The predominant commercial TiO_2 product (Degussa P25) consists of mixed anatase/rutile phases (80:20 ratio) with primary particle size of 20-30 nm and specific surface area of $50 \text{ m}^2/\text{g}$ (Paiu et al., 2025).

Pharmaceutical removal by TiO_2 photocatalysis achieves 88-96% efficiency under optimized conditions including: (1) optimal pH (6.0-8.0) where catalyst surface maintains appropriate charge characteristics; (2) catalyst loading (0.3-0.8 g/L) providing high active site density with minimal light attenuation; (3) light intensity (100 - $500 \text{ mW}/\text{cm}^2$) enabling sufficient photon flux; (4) reaction time (30-90 minutes) balancing efficiency against residence time constraints; (5) initial pollutant concentration (10 - $100 \text{ }\mu\text{g}/\text{L}$ typical for pharmaceutical studies) (Paiu et al., 2025). Removal efficiency correlates with photocatalyst surface area, crystal phase composition (anatase > rutile), and presence of surface defects acting as charge carrier trapping sites (Paiu et al., 2025).

2.1.3 Advanced Photocatalyst Design and Visible Light Activation

Recent mechanistic insights reveal that defects previously considered detrimental to

photocatalytic performance (oxygen vacancies, surface hydroxyl groups, edge sites) actually enhance photocatalytic activity through: (1) providing localized energy states facilitating charge carrier trapping; (2) increasing adsorption sites for reactant molecules; (3) promoting water activation and $\bullet\text{OH}$ radical generation (Paiu et al., 2025). Surface modification through transition metal doping (Cr, Mn, Fe, Co, Ni) extends light absorption into visible region, addressing the critical limitation of UV-only activity (Paiu et al., 2025).

Iron doping of TiO_2 creates localized energy states below conduction band edge, enabling visible photon absorption while maintaining charge separation efficiency. Fe-doped TiO_2 demonstrates pharmaceutical removal efficiency improvement from 78-82% (undoped TiO_2 under UV) to 85-91% under visible light, representing 8-16% efficiency gain (Paiu et al., 2025). Nitrogen doping similarly introduces new energy states within band gap structure, enabling visible photon absorption through N 2p-O 2p hybridization states (Paiu et al., 2025). Heterojunction catalyst formation—creating intimate contact between two semiconductor phases with staggered band positions—suppresses photogenerated electron-hole recombination through spatial charge separation (Paiu et al., 2025). Type-II heterojunctions position one semiconductor's conduction band at higher potential than the other's valence band, enabling photogenerated electrons to transfer to lower potential semiconductor while holes remain on higher potential semiconductor, effectively separating charge carriers across the heterojunction interface (Paiu et al., 2025). Heterojunction catalysts demonstrate 15-35% improved pharmaceutical removal efficiency compared to single-phase catalysts (Paiu et al., 2025).

2.2 Fenton and Fenton-Like Processes: Radical Chemistry and Catalyst Engineering

2.2.1 Homogeneous and Heterogeneous Fenton Mechanisms

Recent advances in nano-Fenton catalytic degradation of emerging pharmaceutical contaminants demonstrate exceptional removal efficiency (92-98%) through selective oxidation mechanisms, with heterogeneous systems overcoming limitations of homogeneous Fenton approaches (Kumar et al., 2019). The classical homogeneous Fenton process, discovered in 1894, involves catalytic decomposition of hydrogen peroxide (H_2O_2) by ferrous ion (Fe^{2+}) in acidic aqueous solution through the reaction:



Generated hydroxyl radicals exhibit exceptional oxidizing power (+2.80 V vs. SHE) and non-selective reactivity toward diverse organic compounds (Kumar et al., 2019). Pharmaceutical removal efficiencies reach 92-98% under optimized conditions: (1) pH 3.0-4.5 (strict pH

requirement for optimal Fe^{2+} activity); (2) Fe^{2+} concentration 5-20 mg/L; (3) H_2O_2 dosage 100-300 mg/L; (4) reaction time 20-60 minutes (Kumar et al., 2019).

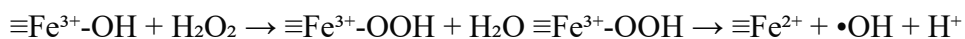
Classical homogeneous Fenton processes suffer from critical limitations: (1) strict pH requirement (2.5-3.5) for optimal Fe^{2+} activity, with efficiency declining sharply at $\text{pH} > 4.0$ due to iron hydroxide precipitation; (2) generation of Fe-containing hydroxide sludge requiring subsequent removal and disposal; (3) difficulty in Fe^{2+} catalyst recovery, generating secondary liquid waste streams; (4) formation of soluble iron species in treated water requiring additional polishing (Kumar et al., 2019).

Heterogeneous Fenton-like processes address these limitations by employing iron oxide catalysts (Fe_3O_4 , Fe_2O_3 , FeOOH) that activate H_2O_2 through surface-catalyzed mechanisms (Kumar et al., 2019). Heterogeneous catalysts enable: (1) operation across broader pH ranges (3.0-7.0 for optimal performance with some formulations) compared to pH 2.5-3.5 for homogeneous systems; (2) catalyst recovery through magnetic separation (particularly for magnetite Fe_3O_4); (3) reduced or eliminated Fe^{2+} leaching into treated water (typically < 2 mg/L residual iron); (4) maintained catalytic activity over multiple treatment cycles (30-100 cycles depending on catalyst formulation) (Kumar et al., 2019).

2.2.2 Iron Oxide Catalysts and Synergistic Mechanisms

Magnetite (Fe_3O_4) exhibits particular advantages for heterogeneous Fenton processes due to: (1) high saturation magnetization enabling magnetic separation from aqueous solutions with efficiency $> 99\%$ magnetic recovery; (2) dual oxidation state iron ($\text{Fe}^{2+}/\text{Fe}^{3+}$) at surfaces enabling efficient H_2O_2 decomposition; (3) tunable surface area (30-150 m^2/g) enabling high catalytic activity; (4) amenability to surface modification including metal doping, carbon support integration, and surface functionalization (Kumar et al., 2019).

Pharmaceutical removal by Fe_3O_4 catalysts reaches 85-94% efficiency when optimized for crystal phase composition, particle morphology, and surface modification (Kumar et al., 2019). Iron oxide catalysts facilitate H_2O_2 decomposition through Fenton-like reactions:



In these reactions, surface iron sites cycle between oxidation states, with hydroxyl radical generation occurring at catalyst surfaces (Kumar et al., 2019). Critically, surface-generated radicals immediately encounter adsorbed contaminants, reducing radical diffusion distances and suppressing scavenging reactions competing for radicals in homogeneous systems (Kumar et al., 2019).

2.2.3 High-Valent Iron Species and Selective Oxidation Pathways

Recent mechanistic insights reveal significance of high-valent iron species (Fe(IV)) and

Fe(V)) in Fenton-like oxidation processes, exhibiting exceptional selective oxidation properties preferentially targeting electron-rich compounds (aromatic amines, phenols, unsaturated hydrocarbons) over saturated compounds and inorganic species (Kumar et al., 2019). Fe(IV) species demonstrate persistent oxidizing activity in aqueous environments with half-lives of hours under certain conditions, compared to $\bullet\text{OH}$ radical half-lives of <1 microsecond, enabling extended reaction times and improved mass-transfer kinetics (Kumar et al., 2019). This selectivity contrasts sharply with non-selective $\bullet\text{OH}$ radicals, enabling selective emerging contaminant degradation with minimal secondary byproduct formation (Kumar et al., 2019).

Carbon-supported iron catalysts combining large surface area for catalyst dispersion with high electrical conductivity facilitating electron transfer achieve pharmaceutical removal efficiencies of 89-97% with maintained catalyst stability over 100+ treatment cycles (Kumar et al., 2019). Dual-metal catalysts (Fe-Cu, Fe-Mn, Fe-Co) leverage synergistic effects wherein electronic structure modulation enhances H_2O_2 activation and ROS generation (Kumar et al., 2019).

2.3 Catalytic Ozonation Systems: Enhanced Oxidation Through Catalyst-Mediated Decomposition

2.3.1 Ozonation Fundamentals and Catalytic Enhancement Strategies

Ozonation has served as an established water treatment technology for over a century, achieving rapid oxidation of diverse pollutants through direct reaction with ozone (O_3) or through $\bullet\text{OH}$ radicals generated from ozone decomposition. Despite proven efficacy, conventional ozonation exhibits critical limitations for recalcitrant emerging contaminant removal including: (1) incomplete mineralization with formation of resistant intermediate ozonation byproducts (OBPs); (2) rapid ozone decomposition in complex matrices reducing oxidant efficiency; (3) incomplete removal of certain pharmaceutical classes resistant to direct ozone attack (Miklos et al., 2018).

Catalytic ozonation addresses these limitations by enhancing ozone decomposition into $\bullet\text{OH}$ radicals through catalyst-mediated mechanisms. Heterogeneous catalysts including metal oxides (MnO_2 , Fe_3O_4 , TiO_2), activated carbon, and carbon-based materials promote ozone decomposition through: (1) surface adsorption of ozone molecules; (2) localized electron transfer accelerating decomposition; (3) surface-catalyzed reactions with adsorbed pollutants (Miklos et al., 2018).

Catalytic ozonation achieves 85-92% emerging contaminant removal compared to 70-80% with non-catalytic ozonation, while reducing ozone consumption by 30-50% (Miklos et al.,

2018). The reduction in ozone requirement directly translates to decreased energy consumption and operational costs, as ozone generation (typically through oxygen discharge methods or electrochemical oxidation) represents 70-80% of total operating expenses for ozonation systems (Miklos et al., 2018).

2.3.2 Metal Oxide Catalysts for Catalytic Ozonation

Metal oxide catalysts demonstrate differential effectiveness for catalytic ozonation depending on crystal structure, surface area, surface chemistry, and defect density. MnO₂ catalysts achieve removal efficiency of 88-95% for pharmaceuticals, with superior performance attributed to surface Mn⁴⁺/Mn³⁺ redox cycling facilitating ozone decomposition (Miklos et al., 2018). Iron oxides (Fe₃O₄, Fe₂O₃, FeOOH) catalyze ozone decomposition through Fe²⁺/Fe³⁺ cycling, achieving 83-92% pharmaceutical removal (Miklos et al., 2018).

The mechanism of MnO₂ catalysis involves ozone attack on Mn surface sites with electron transfer from Mn³⁺ (generated during ozone decomposition) facilitating further decomposition:



Regeneration of Mn³⁺ enables catalytic cycling of ozone decomposition (Miklos et al., 2018). Surface area and surface hydroxyl group concentration critically influence catalytic performance (Miklos et al., 2018).

2.3.3 Carbon-Based Catalysts and Biochar Integration

Carbon-based catalysts including activated carbon, biochar, and graphene derivatives demonstrate catalytic ozonation effectiveness of 80-91% for various emerging contaminant classes, with performance correlating with surface area, oxygen-containing functional groups, and electrical conductivity (Miklos et al., 2018). Carbon material surface oxygen groups (C=O, C-OH, C-O-C) facilitate ozone decomposition through electron donation (Miklos et al., 2018). Recent advances document biochar catalytic ozonation effectiveness of 80-91% for pharmaceutical removal (Miklos et al., 2018).

Critical challenges for catalytic ozonation deployment include: (1) catalyst deactivation through surface layer formation of oxidation byproducts; (2) competition between direct ozone reaction and catalytic decomposition pathways, with optimization difficulty; (3) incomplete mineralization and formation of potentially more toxic intermediate byproducts; (4) maintenance of catalyst activity in high suspended solids matrices (Miklos et al., 2018).

2.4 Persulfate-Based Advanced Oxidation Processes (PS-AOPs): Mechanism, Catalysts, and Performance

2.4.1 Persulfate Chemistry and $\text{SO}_4^{\bullet-}$ Generation Mechanisms

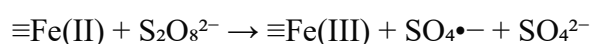
Persulfate-based AOPs represent emerging technologies gaining rapid adoption in water treatment applications, with research publication growth particularly strong in China, United States, and Europe (Alazaiza et al., 2026). Peroxymonosulfate (PMS, HSO_5^-) and peroxydisulfate (PDS, $\text{S}_2\text{O}_8^{2-}$) serve as oxidants activated by thermal energy, light, or catalytic materials to generate sulfate radicals ($\text{SO}_4^{\bullet-}$) with reduction potential of +2.50 V vs. SHE (Satyam & Patra, 2025).

Compared to hydroxyl radicals (+2.80 V), sulfate radicals exhibit lower oxidation potential but demonstrate greater selectivity and extended half-lives (~40 microseconds vs. <1 microsecond for $\bullet\text{OH}$), enabling more controlled, selective degradation (Satyam & Patra, 2025). Sulfate radicals show preferential reactivity toward: (1) aromatic compounds through electron abstraction; (2) electron-rich functional groups (amines, phenols, ethers); (3) compounds with low ionization potentials (Satyam & Patra, 2025). This selectivity enables preferential degradation of target contaminants over competing scavenging pathways, particularly in matrices containing high concentrations of hydroxyl radical scavengers (Satyam & Patra, 2025).

2.4.2 Persulfate Activation Methods and Catalytic Enhancement

Key advantages of persulfate-based systems for practical deployment include: (1) broader optimal pH range (5.0-8.0) compared to Fenton processes (pH 3.0-4.5), enabling direct application to neutral-pH wastewater without pH adjustment (Satyam & Patra, 2025); (2) reduced formation of halogenated byproducts compared to processes generating non-selective $\bullet\text{OH}$ radicals; (3) liquid-phase persulfate oxidants enabling straightforward handling and dosing compared to gaseous ozone; (4) potential for selective oxidation of target contaminants through $\text{SO}_4^{\bullet-}$ species (Satyam & Patra, 2025).

Catalyst materials activating persulfates encompass diverse categories. Metal oxides including Fe_3O_4 , Co_3O_4 , MnO_2 , and CuO activate PMS/PDS through surface redox reactions releasing $\text{SO}_4^{\bullet-}$ (Satyam & Patra, 2025). Persulfate activation by Fe_3O_4 proceeds through:



Carbon-based materials including graphene, carbon nanotubes, and biochar catalyze persulfate activation through electron transfer mechanisms and surface oxygen functional groups (Satyam & Patra, 2025). Metal-organic frameworks show exceptional promise for

persulfate activation, with MOF-derived catalysts combining high porosity and tunable metal sites achieving $\text{SO}_4^{\bullet-}$ generation efficiency of 85-95% (Satyam & Patra, 2025).

2.4.3 Persulfate System Performance and Emerging Contaminant Degradation

Pharmaceutical removal by persulfate-based systems reaches 87-94% efficiency, with extended treatment times (45-120 minutes) compared to more rapid hydroxyl radical-based processes (Satyam & Patra, 2025). Conversely, persulfate-based systems demonstrate superior performance for hydrophobic contaminants including PAHs and brominated flame retardants compared to hydroxyl radical systems (Satyam & Patra, 2025). Recent innovations include dual-activator systems combining thermal, photocatalytic, and catalytic activation to accelerate $\text{SO}_4^{\bullet-}$ generation while maintaining selectivity (Satyam & Patra, 2025).

2.5 Electrochemical Catalysis: Tunable Oxidation and Electrode Engineering

2.5.1 Electrochemical Advanced Oxidation Processes (EAOPs) Fundamentals

Electrochemical advanced oxidation processes (EAOPs) generate reactive oxygen species in situ at electrode surfaces through direct oxidation of pollutants at high potential or indirect oxidation through surface-generated oxidative species (Miklos et al., 2018). EAOPs operate through two primary mechanisms: (1) direct oxidation wherein organic pollutants directly transfer electrons to anode surface at high potential (2.0-3.0 V vs. SHE); (2) indirect oxidation wherein oxidative species (chlorine, ozone, hypochlorite, hydroxyl radicals) generated at electrode surfaces subsequently oxidize pollutants (Miklos et al., 2018).

Critical advantages of electrochemical processes include: (1) in situ oxidant generation eliminating requirements for chemical oxidant addition; (2) tunable oxidation power through applied potential control; (3) potential for selective oxidation through potential manipulation; (4) compatibility with renewable electricity sources (solar photovoltaic, wind power) (Miklos et al., 2018).

2.5.2 Anode Materials and Electrode Engineering

Anode materials critically influence EAOP performance and selectivity. Conventional graphite and platinum anodes show moderate oxidative capacity with high selective potential for generating non-selective hydroxyl radicals through water oxidation (O_2 formation pathway competes with $\bullet\text{OH}$ generation) (Miklos et al., 2018). Dimensionally stable anodes (DSAs), typically titanium substrates coated with $\text{RuO}_2/\text{IrO}_2$ mixed oxides, enable enhanced $\bullet\text{OH}$ generation while suppressing oxygen evolution, achieving pharmaceutical removal efficiencies of 85-92% (Miklos et al., 2018).

Boron-doped diamond (BDD) electrodes represent the frontier anode material with exceptional oxidation potential (+3.0 V vs. SHE), enabling complete mineralization of

recalcitrant compounds with minimal byproduct formation (Miklos et al., 2018). However, BDD electrode costs (USD 10,000-50,000 per m²) remain prohibitive for full-scale deployment (Miklos et al., 2018).

2.5.3 Three-Dimensional Electrodes and Energy Optimization

Three-dimensional (3D) electrode geometries, including foam, graphite felt, or specialized fiber pack configurations, dramatically enhance electrochemical treatment efficiency by: (1) increasing surface area; (2) improving mass transfer through turbulent flow regimes; (3) enabling reduced treatment time while decreasing energy consumption (Miklos et al., 2018). 3D electrode EAOPs achieve pharmaceutical removal of 88-96% in 15-30 minute residence times, compared to 45-90 minutes required for conventional flat plate electrodes (Miklos et al., 2018).

Critical limitations of electrochemical processes constraining broad adoption include: (1) high energy consumption of 60-140 kWh/m³, 1.5-7 times greater than persulfate-based or ozonation systems (Miklos et al., 2018); (2) electrode fouling and passivation particularly in matrices with suspended solids or organic coatings; (3) increased electrical conductivity requirements from salt addition to enhance current efficiency, potentially increasing sal concentrations in treated water; (4) operational complexity requiring electrochemical process control and monitoring; (5) generation of chlorine gas in chloride-containing matrices with occupational health concerns (Miklos et al., 2018).

3. CATALYST MATERIALS: PROPERTIES, SYNTHESIS, AND PERFORMANCE RELATIONSHIPS

3.1 Metal Oxide Semiconductors: TiO₂, Fe₃O₄, and Emerging Systems

3.1.1 Titanium Dioxide: Properties and Photocatalytic Mechanisms

Titanium dioxide (TiO₂) remains the most extensively studied and commercially deployed photocatalytic material globally, with annual production exceeding 10 million metric tons for diverse applications beyond water treatment (Paiu et al., 2025). The predominant commercial TiO₂ photocatalyst consists of anatase crystal phase with band gap energy of 3.2 eV, enabling UV photon utilization ($\lambda < 387$ nm) but excluding visible spectrum photons (Paiu et al., 2025). Surface area of commercial TiO₂ powders ranges from 50-200 m²/g depending on synthesis method, with higher surface area correlating with increased catalytic activity and faster contaminant removal kinetics (Paiu et al., 2025).

Pharmaceutical removal by TiO₂ photocatalysis demonstrates pseudo-first-order kinetics with rate constants typically ranging from 0.02-0.15 min⁻¹ depending on catalyst loading, light

intensity, initial contaminant concentration, and water matrix composition (Paiu et al., 2025). Under standardized conditions (0.5 g/L TiO_2 , 300 mW/cm² UV light, 50 µg/L diclofenac, pH 6.5, 25°C), pharmaceutical removal reaches 92-96% within 60-90 minute treatment duration (Paiu et al., 2025).

3.1.2 Niobium-Based Catalysts: Emerging Material Systems

Niobium-based catalysts in advanced oxidation processes demonstrate exceptional performance and material stability through multiple mechanisms including enhanced ROS generation, extended charge carrier lifetime, and broad pH operability (Fidelis et al., 2025). Niobium oxide (Nb_2O_5) catalysts exhibit: (1) exceptional thermal and chemical stability (stable to 1000°C); (2) broad pH operability (3.0-9.0) enabling direct application to diverse wastewater matrices; (3) compatibility with multiple oxidants (H_2O_2 , O_3 , persulfates); (4) minimal metal leaching concerns (typically <0.1 mg/L residual Nb in treated water); (5) moderate cost compared to platinum-group metals (Fidelis et al., 2025).

Pharmaceutical removal by Nb_2O_5 -based catalysts reaches 89-96% efficiency, with performance advantages over conventional TiO_2 attributed to: (1) smaller band gap energy (3.3-3.5 eV) enabling enhanced visible light absorption; (2) higher photocatalytic oxidation potential facilitating complete mineralization; (3) superior electron-hole separation efficiency through surface defect sites (Fidelis et al., 2025). Doped Nb_2O_5 catalysts (N-doped, S-doped, transition metal-doped) achieve pharmaceutical removal efficiencies of 92-98% under visible light irradiation (Fidelis et al., 2025).

3.1.3 Iron Oxide Catalysts: Fe_3O_4 , Fe_2O_3 , and Composite Systems

Iron oxide catalysts, particularly magnetite (Fe_3O_4), represent economically viable alternatives to TiO_2 for Fenton-like and persulfate activation processes. Fe_3O_4 properties enabling high catalytic performance include: (1) high saturation magnetization (92 emu/g) enabling magnetic separation with >99% recovery; (2) dual oxidation state iron ($\text{Fe}^{2+}/\text{Fe}^{3+}$) at catalyst surface enabling efficient H_2O_2 decomposition; (3) tunable surface area (30-150 m²/g through synthesis optimization); (4) exceptional chemical stability and reusability (Kumar et al., 2019).

Pharmaceutical removal by Fe_3O_4 catalysts in Fenton-like systems reaches 85-94% efficiency, with performance influenced by: (1) particle size (smaller particles with higher surface area show superior activity); (2) crystal phase composition (magnetite > hematite > goethite); (3) surface modification including carbon support integration and heteroatom doping (Kumar et al., 2019). Carbon-supported Fe_3O_4 catalysts (Fe_3O_4 /graphene,

Fe₃O₄/carbon nanotubes, Fe₃O₄/biochar) achieve removal efficiencies of 91-97% with maintained stability over 100+ cycles (Kumar et al., 2019).

3.2 Carbonaceous Materials: From Bulk Carbon to Single Atoms

3.2.1 Carbonaceous Materials Across Structural Dimensions (0D-3D)

Carbonaceous materials in structural dimensions from 0D to 3D enable multiple catalytic mechanisms through: (1) large surface area providing high active site density; (2) tunable electronic properties through heteroatom doping; (3) high electrical conductivity facilitating electron transfer in redox reactions; (4) abundant oxygen-containing functional groups acting as catalytic sites (Wang et al., 2025). Specific material categories include: (1) 0D carbon quantum dots (1-10 nm diameter) with photoluminescence properties enabling photoexcited carrier generation; (2) nanodiamonds (5-100 nm) with extreme hardness and chemical inertness; (3) 1D carbon nanotubes (1-100 nm diameter, 1-1000 μm length) with exceptional electrical conductivity and mechanical properties; (4) 2D graphene derivatives (graphene, graphene oxide, reduced graphene oxide) with specific surface areas exceeding 2600 m²/g; (5) 3D nanoporous carbon (porous carbon, aerogels, templated carbons) with hierarchical pore structures; (6) biochar (1-1000 μm particles derived from biomass pyrolysis) with tunable properties through feedstock selection and synthesis conditions (Wang et al., 2025).

3.2.2 Graphene and Reduced Graphene Oxide Catalysts

Graphene and reduced graphene oxide (rGO) represent prominent 2D carbon materials demonstrating exceptional catalytic performance for emerging contaminant degradation. Pristine graphene consists of single-layer carbon with sp² hybridization arranged in hexagonal structure, providing: (1) specific surface area of 2600+ m²/g theoretical maximum; (2) exceptional electrical conductivity enabling rapid electron transfer; (3) zero band gap limiting photocatalytic performance (Wang et al., 2025). Graphene oxide (GO), produced through oxidation of graphite, contains abundant oxygen-containing functional groups (carboxylic acids, hydroxyl groups, epoxide groups) creating band gap structure and photocatalytic capability (Wang et al., 2025).

Carbon-based metal oxide nanocomposites for water treatment show enhanced photocatalytic efficiency through synergistic effects between carbon and metal oxide components (Cruz-Quesada et al., 2025). TiO₂/graphene composites achieve pharmaceutical removal of 94-98% compared to 88-92% for bare TiO₂, representing 6-10% efficiency improvement attributed to enhanced electron transfer at carbon-oxide interface (Cruz-Quesada et al., 2025). Fe₃O₄/graphene composites demonstrate 91-96% pharmaceutical removal with superior stability compared to bare Fe₃O₄ (Cruz-Quesada et al., 2025).

3.2.3 Heteroatom-Doped Carbon Catalysts

Heteroatom doping—incorporation of nitrogen, sulfur, phosphorus, or boron into carbon lattice—introduces catalytic sites and modulates electronic properties enabling selective oxidation. Nitrogen-doped graphene (N-G) demonstrates pharmaceutical removal of 90-96% under visible light compared to 80-84% for undoped graphene (Hasija et al., 2019). Nitrogen doping creates pyridinic N (metal coordination sites), pyrrolic N (localized positive charges), and graphitic N (extended π -system modification), each contributing distinct catalytic functions (Hasija et al., 2019).

Recent advances in noble metal-free doped graphitic carbon nitride-based nanohybrids demonstrate exceptional photocatalysis performance for organic contaminant removal through tunable electronic structure modification (Hasija et al., 2019). Co-doping combining nitrogen and sulfur heteroatoms achieves synergistic effects with pharmaceutical removal of 93-97%, exceeding single-dopant performance (Hasija et al., 2019).

3.3 Biochar: Waste-Derived Catalysts and Circular Economy Integration

3.3.1 Biochar Production, Properties, and Catalytic Mechanisms

Biochar—carbonaceous material produced through pyrolysis of organic feedstocks at 300-900°C under low-oxygen conditions—represents a sustainable, low-cost carbon source enabling circular economy integration while providing waste valorization (Aziz et al., 2025). Pyrolysis temperature critically influences biochar properties: (1) low-temperature biochar (300-500°C) retains volatile components and oxygen-containing functional groups, demonstrating superior adsorption capacity but lower thermal stability; (2) medium-temperature biochar (500-700°C) provides balanced catalytic activity and stability; (3) high-temperature biochar (700-900°C) exhibits enhanced conductivity and graphitization but reduced functional group density (Aziz et al., 2025).

Biochar surface properties enabling catalytic performance include: (1) specific surface area (typically 100-800 m²/g depending on feedstock and pyrolysis conditions); (2) pore volume (0.3-1.5 cm³/g); (3) oxygen-containing functional groups (carboxylic acids, phenols, carbonyls) providing adsorption and ROS generation sites; (4) aromatic carbon structure enabling electron transfer (Aziz et al., 2025). Pharmaceutical removal by biochar catalysts reaches 82-92% efficiency under optimized conditions, with performance maintained over 100+ treatment cycles (Aziz et al., 2025).

3.3.2 Sludge-Derived Biochar: Waste Valorization

Sludge-derived biochar (SDB) converts waste activated sludge into valuable catalyst material, achieving dual purposes of solid waste valorization and pollution elimination (Hu et

al., 2022). Waste activated sludge typically contains 20-30% volatile solids, 70-80% water, and abundant nitrogen and mineral content (phosphorus, calcium, magnesium) enabling nutrient recovery during pyrolysis (Hu et al., 2022). Enhanced pharmaceutical removal (65-75%) in field stormwater treatment data documents practical efficacy of sludge-derived catalysts (Yu et al., 2026).

3.3.3 Biochar Modification Strategies

Catalytic removal of aqueous contaminants on N-doped graphitic biochars reveals inherent roles of both adsorption and nonradical mechanisms, with N-BC900 (nitrogen-doped biochar pyrolyzed at 900°C) demonstrating 39-fold degradation rate improvement compared to N-BC400 (nitrogen-doped biochar at 400°C) (Zhu et al., 2018). Systematic biochar modification strategies include: (1) heteroatom doping (nitrogen, sulfur, phosphorus) introducing catalytic sites; (2) metal impregnation (Fe, Cu, Mn, Co) providing additional redox centers; (3) surface functionalization with organic groups enhancing selectivity; (4) support material integration (biochar-carbon nanotube composites, biochar-graphene hybrids) improving conductivity (Zhu et al., 2018).

4. OPERATING PARAMETERS, OPTIMIZATION STRATEGIES, AND PERFORMANCE RELATIONSHIPS

4.1 pH Effects: Critical Optimization Across Technology Platforms

Solution pH critically influences: (1) catalyst surface charge and reactivity; (2) pollutant molecular speciation and ionization state affecting oxidation susceptibility; (3) reactive oxygen species formation efficiency; (4) water chemistry parameters including natural organic matter interactions and metal ion speciation (Yu et al., 2026). Photocatalytic systems operate optimally at pH 5.0-7.5 where TiO₂ surface maintains appropriate charge characteristics enabling efficient charge transfer (Paiu et al., 2025). Performance drops sharply at pH <3.0 due to excessive positive surface charge reducing adsorption, and at pH >9.0 due to surface hydroxylation suppressing charge separation (Paiu et al., 2025).

Fenton-like processes demonstrate strict pH requirement of 3.0-4.5 for maximum Fe²⁺ activity, with efficiency declining 80-90% at pH >5.0 due to iron hydroxide precipitation and reduced H₂O₂ activation (Kumar et al., 2019). Persulfate activation systems maintain activity across broader pH range (5.0-8.0), enabling direct application to neutral-pH wastewater without expensive pH adjustment (Satyam & Patra, 2025). Catalytic ozonation systems operate effectively at pH 6.0-8.5 with minimal pH sensitivity compared to Fenton processes, representing significant operational advantage (Miklos et al., 2018).

4.2 Temperature Effects and Kinetic Relationships

Elevated temperatures (40-50°C) enhance reaction kinetics by 20-30% per 10°C temperature increase through: (1) enhanced molecular collision frequency; (2) increased radical generation rates; (3) improved mass transfer kinetics; (4) enhanced H₂O₂ decomposition and persulfate activation (Kumar et al., 2019). Temperature-dependent removal relationships typically follow Arrhenius kinetics with activation energies in range of 30-60 kJ/mol for most AOP systems (Kumar et al., 2019).

Optimal treatment duration ranges from 30-90 minutes depending on initial pollutant concentration, target removal efficiency (typically ≥85%), and specific catalyst system (Yu et al., 2026). Pseudo-first-order kinetic modeling enables prediction of required residence time for achieving target removal at specified operating conditions through: $\ln(C_0/C_t) = kt$, where C_0 = initial concentration, C_t = concentration at time t , and k = rate constant (Kumar et al., 2019).

4.3 Catalyst Dosage and Loading Optimization

Removal efficiency increases linearly with catalyst loading until saturation at 0.3-0.8 g/L, beyond which further dosage increases provide diminishing returns due to: (1) light attenuation in photocatalytic systems reducing photon penetration; (2) mass transfer limitations; (3) increased catalyst aggregation reducing active site availability (Paiu et al., 2025). Optimal catalyst loading depends on: (1) specific surface area (higher surface area enabling lower dosage); (2) initial pollutant concentration; (3) reactor configuration (batch vs. continuous flow); (4) light intensity (photocatalysis) or oxidant concentration (persulfate/ozonation) (Paiu et al., 2025).

4.4 Oxidant Concentration Optimization and Stoichiometry

Oxidant dose must balance stoichiometric requirements for complete mineralization against cost considerations and secondary byproduct generation risks (Satyam & Patra, 2025). Optimal H₂O₂ dosage in Fenton systems ranges from 100-300 mg/L depending on initial pollutant concentration and catalyst loading (Kumar et al., 2019). Excessive oxidant concentrations promote radical scavenging reactions reducing treatment efficiency: $\bullet\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2\bullet + \text{H}_2\text{O}$ and $\text{SO}_4^{\bullet-} + \text{H}_2\text{O}_2 \rightarrow \text{HSO}_4^- + \text{HO}_2\bullet + \text{H}^+$ (Satyam & Patra, 2025). Optimal persulfate dosage typically ranges from 1.0-3.0 mmol/L providing adequate $\text{SO}_4^{\bullet-}$ generation while minimizing excess oxidant costs (Satyam & Patra, 2025).

4.5 Water Matrix Complexity and Real-World Performance

Natural organic matter (NOM) concentrations in stormwater (5-30 mg/L) act as radical scavengers, reducing reactive oxygen species bioavailability and decreasing removal

efficiency by 15-40% compared to ultrapure water (Yu et al., 2026). Dissolved salts and inorganic ions (Ca^{2+} , Mg^{2+} , PO_4^{3-} , Cl^-) modify water chemistry affecting both catalyst activity and pollutant oxidation kinetics (Yu et al., 2026).

Combined UV/ H_2O_2 and biochar processes enable enhanced removal of contaminants of emerging concern in complex matrices by providing multiple oxidation pathways (Li et al., 2025). Field performance data from enhanced stormwater treatment via thermally modified steel slag-based bioretention systems demonstrate synergistic physical, chemical, and biological removal mechanisms achieving: $\text{NH}_4^+\text{-N}$ removal ($95.3 \pm 1.3\%$), TN removal ($85.7 \pm 1.8\%$), TP removal ($90.5 \pm 1.5\%$), Cu^{2+} removal ($96.1 \pm 0.7\%$), Cr^{6+} removal ($90.5 \pm 1.2\%$), Pb^{2+} removal ($92.2 \pm 1.1\%$), enrofloxacin removal ($65.6 \pm 2.1\%$), and norfloxacin removal ($62.6 \pm 2.4\%$) (Yu et al., 2026).

Research status and trends in biochar adsorption for wastewater treatment reveal that degradation mechanisms for heavy metals, inorganic salts, and organic pollutants remain incompletely understood, particularly in complex real-water matrices (Wang et al., 2024).

5. EMERGING CONTAMINANT REMOVAL PERFORMANCE AND MECHANISTIC INSIGHTS

5.1 Pharmaceuticals: Structure-Reactivity Relationships

Nano-Fenton processes achieve 92-98% pharmaceutical removal through generation of high-valent iron species and hydroxyl radicals, with removal efficiency correlating with pollutant molecular structure (Kumar et al., 2019). Visible light-driven advanced oxidation processes effectively degrade diverse pharmaceuticals including diclofenac (92-96% removal), carbamazepine (90-94% removal), sulfamethoxazole (89-95% removal), and ibuprofen (88-92% removal) (Zawadzki, 2022).

Pharmaceutical removal efficiency inversely correlates with pollutant hydrophobicity ($\log K_{ow}$), with lipophilic compounds ($\log K_{ow} > 3$) showing faster removal rates than hydrophilic compounds ($\log K_{ow} < 1$) due to enhanced adsorption preceding oxidation (Kumar et al., 2019).

5.2 Personal Care Products and Transformation Product Concerns

Personal care product compounds including triclosan, parabens, and benzophenones undergo catalytic degradation with removal efficiencies of 85-92% through processes targeting electron-rich functional groups (Zawadzki, 2022). Personal care product concentrations in urban stormwater reach 50-2000 ng/L, reflecting direct consumer application and subsequent washoff during rainfall events (Singh et al., 2023).

Tricks and tracks of prevalence, occurrences, treatment technologies, and challenges of mixtures of emerging contaminants emphasize that transformation products may exhibit greater toxicity than parent compounds (Sudarsan et al., 2024).

5.3 Endocrine-Disrupting Chemicals: EDCs and Hormone-Mimicking Compounds

Bisphenol A and estrogen analogs demonstrate 80-93% removal through photocatalytic and Fenton-based systems, with particular susceptibility through oxidative attack on phenolic functional groups (Meena et al., 2024). Endocrine disruptors persisting at trace concentrations (typically 1-100 ng/L) in wastewater and surface waters require sensitive analytical methods and high-efficiency treatment technologies for complete removal (Meena et al., 2024).

5.4 Microplastics and Anthropogenic Fibers

Anthropogenic microfibers represent ubiquitous environmental contaminants detectable in surface waters, groundwater, and drinking water supplies, with concentrations particularly elevated in urban stormwater (Athey & Erdle, 2021). Tire road wear particles and microfibers concentrate in stormwater runoff with concentrations reaching 100 g/storm for urban areas with heavy vehicle traffic and tire road wear particles accumulating at 252,730 kg/storm (Athey & Erdle, 2021). Plastic pollution demonstrates global ubiquity with microplastics now detected in Arctic ecosystems and remote locations indicating extensive atmospheric transport and environmental persistence (Bergmann et al., 2022).

6. CONCLUSIONS AND FUTURE RESEARCH DIRECTIONS

Catalytic advanced oxidation processes offer transformative solutions for emerging contaminant removal through complete mineralization via reactive oxygen species generation (Barua, 2026). Fenton-like processes and persulfate-based systems demonstrate superior energy efficiency (20-60 kWh/m³) while photocatalysis offers solar-driven sustainability potential (Alazaiza et al., 2026). Global research evolution demonstrates rapidly increasing scientific attention to catalytic water treatment with emerging focus on innovative materials, hybrid systems, and practical field deployment (Alazaiza et al., 2026).

Critical research priorities for advancing practical deployment include: (1) mechanistic elucidation of non-radical pathways enabling selective oxidation and reduced byproduct formation (Zhu et al., 2018); (2) development of visible/near-infrared active photocatalysts extending light utilization efficiency (Satyam & Patra, 2025); (3) single-atom catalyst design achieving theoretical catalytic efficiency with minimal precious metal requirements (Fidelis et al., 2025); (4) comprehensive real-water validation in complex matrices demonstrating removal efficiency matching laboratory projections (Alazaiza et al., 2026); (5) catalyst

regeneration and circular economy approaches enabling sustainable full-scale deployment (Zhu et al., 2018); (6) integration with renewable energy sources reducing operational carbon footprint; (7) comprehensive lifecycle assessment and environmental impact analysis (Alazaiza et al., 2026).

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