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Advances in Organic Pollutant Degradation Technologies for Pharmaceutical Wastewater: Efficiency, Mechanistic Pathways, and Challenges in Application

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Abstract: Against the backdrop of carbon-peaking/carbon-neutrality goals and increasingly stringent discharge standards, this review synthesizes the water-quality characteristics (high salinity, high toxicity, low biodegradability, and compositional fluctuations) and environmental behaviors (persistence, bioaccumulation, and cross-media transport) of organic pollutants in pharmaceutical industrial wastewater. We elucidate the principal degradation mechanisms—oxidation/reduction, radical oxidation by •OH and $SO_4•^-$, and microbial direct metabolism and cometabolism—and underscore the need to identify transformation intermediates and evaluate toxicity evolution. We then compare the applicability and engineering performance of physicochemical methods (adsorption, ozonation/Fenton, photocatalysis, electrochemical processes), biological processes (aerobic/anaerobic systems, MBR/MBBR, bioaugmentation), and hybrid coupled schemes (photo-Fenton, ozone–biological, electro–biological, AOPs+MBR). Physicochemical routes act rapidly but are limited by mineralization and cost; biological routes are economical yet constrained by microbial inhibition and long HRTs; coupled schemes balance biodegradability enhancement with deep mineralization—typical COD and TOC removals reaching ~85%~–95% and 80%~90%, respectively—with superior abatement of antibiotics and endocrine-disrupting compounds (EDCs). Key bottlenecks include process instability under high-salinity/high-toxicity conditions, AOP-induced toxicity transfer and insufficient monitoring of intermediates, challenges in multi-unit coordination and intelligent control, and the constraints that energy and chemical consumption impose on low-carbon objectives. Looking forward, we advocate low-energy, resource-recoverable, and sustainable treatment pathways centered on smart catalytic and anti-fouling membrane materials, salt-/ salt-/toxicity-tolerant and synthetic-biology-enabled microbial consortia, online toxicity monitoring with non-target high-resolution analytics, and digital-twin-based adaptive control.

Keywords: Pharmaceutical wastewater; Organic pollutants; Advanced oxidation processes (AOPs); Biological treatment; Hybrid/coupled processes

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1 Introduction

Against the backdrop of intensifying climate change and resource constraints, green and low-carbon development has become a shared strategic choice for countries pursuing sustainable transitions（Li Huiming & Chen Wenshuo, 2025）. In 2020, China formally proposed its “carbon peaking and carbon neutrality” goals, pledging to peak carbon emissions before 2030 and achieve carbon neutrality before 2060, thereby driving profound changes in societal development models and industrial operations（Gao Ming & Zhang Zhexi，2022）. Under this national strategy, traditional high-energy, high-emission sectors face unprecedented pressure to undergo green transformation. As a resource-intensive and energy-sensitive industry, the pharmaceutical sector not only safeguards public health but also plays a pivotal role in advancing industrial greening （Cai Chun & Lu Xiangyang, 2025）.

As an industry heavily dependent on organic synthesis and biotechnological fermentation, pharmaceutical manufacturing inevitably generates large volumes of highly concentrated, toxic, and recalcitrant wastewater, making it one of the most challenging targets in industrial pollution control （Yao Guangyuan et al., 2021）. In addition to conventional indicators—chemical oxygen demand (COD), ammonia nitrogen (NH_3-N), and suspended solids—such wastewater often contains trace organic pollutants including antibiotics, hormones, solvents, and heterocyclic intermediates. These pollutants are notably toxic, persistent, and mobile in the environment, and readily propagate through hydrological cycles and food webs, thereby disrupting aquatic ecosystems and posing risks to human health. Studies show that antibiotics have been detected in more than 70% of rivers worldwide, with concentrations in some regions exceeding 1 μg/L—well above ecological safety thresholds. Of particular concern, these substances may induce antimicrobial resistance in environmental microbiota and exacerbate the global AMR crisis （Wu Ying et al., 2019）. Meanwhile, endocrine-active compounds can trigger sexual disruption in aquatic organisms at extremely low concentrations, and certain organic solvents and halogenated hydrocarbons are carcinogenic, mutagenic, or endocrine-disrupting, posing serious threats to public health and environmental safety. Although most pharmaceutical enterprises still rely on conventional biological processes such as activated sludge, inhibition of microbial activity by antibiotics and disinfectants, combined with the poor biodegradability of certain pollutants, often leads to treatment performances that fall short of regulatory requirements （Meng Shunlong et al., 2025）. For example, at a cephalosporin production facility employing activated-sludge treatment, the COD removal rate was only 40%, insufficient to meet the COD limit (120 mg/L) specified in the Emission Standard of Water Pollutants for Pharmaceutical Industry (GB 21903-2008). At the same time, jurisdictions in Europe and elsewhere continue to tighten controls on pharmaceutical discharges; for instance, the EU BREF documents propose “zero-emission” targets for certain active pharmaceutical ingredients (APIs), raising the technological bar for treatment （Xu Liya et al., 2024）.

In recent years, academia and industry have explored a wide array of control technologies, including advanced oxidation processes (e.g., ozonation, Fenton, photocatalysis), membrane separations (e.g., nanofiltration, reverse osmosis), and biological intensification (e.g., acclimation of resistant strains, enzymatic degradation). While many of these technologies exhibit high removal efficiencies under laboratory conditions, engineering practice frequently encounters high operating costs, risks of by-product formation, persistent membrane fouling, and system instability （He Xuwen et al., 2020）. Accordingly, how to rigorously evaluate process mechanisms, techno-economic suitability, and environmental friendliness has become a critical question for pharmaceutical enterprises, environmental engineers, and policy makers. This review systematically synthesizes the environmental characteristics and hazard mechanisms of typical organic pollutants in pharmaceutical wastewater; focuses on the development status and application boundaries of mainstream treatment technologies; and compares their strengths and weaknesses in pollutant-removal efficiency, energy consumption, and operating costs. Building on distinct wastewater attributes—such as high salinity, high toxicity, and low biodegradability—we further analyze technology–wastewater matching and discuss forward-looking directions in green catalyst development, resource recovery, and intelligent control. The goal is to provide theoretical support and technical references for the pharmaceutical industry's green transition, promoting a shift in industrial wastewater management from "compliance-oriented discharge" to a new stage of "resource recovery, low-carbon operation, and intelligent management."

2 Physicochemical Properties and Environmental Behavior of Organic Pollutants in Pharmaceutical Wastewater

2.1 Characteristics of Pharmaceutical Wastewater and Classification of Pollutants

Pharmaceutical manufacturing generates large volumes of complex, hard-to-treat wastewater across multiple stages—including active pharmaceutical ingredient (API) synthesis, formulation, equipment cleaning, and waste handling （Li Xing, 2023）. The composition of these effluents is determined not only by the specific drug class and process route, but also by raw-material ratios, solvent usage, additives, and reaction conditions, yielding streams characterized by diverse contaminants, high toxicity, and pronounced temporal variability. Compared with general industrial effluents, pharmaceutical wastewater typically exhibits high COD, elevated salinity, poor biodegradability, and strong antimicrobial properties, imposing severe shocks on treatment systems and making it a priority for environmental regulation （Gao Pin et al., 2024）

With respect to pollutant composition, pharmaceutical wastewater commonly contains antibiotics, hormones, organic solvents, synthetic intermediates, heterocyclic compounds, and heavy metals (Table 1)（ Yao Guangyuan et al., 2025; Jiang Kewei et al., 2015）. Among these, antibiotics and hormones are both environmentally persistent and biologically active, potentially promoting the spread of antimicrobial resistance and causing endocrine disruption; organic solvents and aromatic compounds tend to be highly volatile and toxic, readily leading to coupled air–water pollution （Chen Kexin et al., 2024）.

Table 1 Typical pollutant categories and characteristics of pharmaceutical wastewater

Pollutant Type	Representative Compounds	Primary Sources	Key Characteristics	Environmental Hazards
Antibiotics	Sulfonamides; Tetracyclines; Cephalosporins	Antibiotic synthesis; fermentation	High bioactivity; high persistence	Selects for antibiotic resistance genes (ARGs); disrupts microbial community structure
Organic Solvents	N,N-Dimethylformamide (DMF); Methanol; Acetone; Dichloromethane (DCM, Methylene Chloride)	Extraction, Washing, and Reaction Solvents	High volatility; high toxicity	Air pollution, aquatic toxicity; some are carcinogenic
Synthetic Intermediates	Benzene;Toluene (Methylbenzene); p-Nitrophenol (4-Nitrophenol, PNP)	Active Pharmaceutical Ingredient (API) Synthesis Reactions	Poorly biodegradable; highly stable	Long-term persistence reduces the operational efficiency of biological treatment systems.
Hormonal Substances	Estradiol (E2; 17β-estradiol); Progesterone (P4); Testosterone (Androgens)	Hormonal Drug Synthesis	Strong endocrine activity	Induces sex differentiation abnormalities in biota (e.g., intersex/feminization); disrupts aquatic reproductive systems.

Continued

Pollutant Type	Representative Compounds	Primary Sources	Key Characteristics	Environmental Hazards
High-Salinity Inorganic Salts	Sodium chloride ($NaCl$); sodium sulfate (Na_2SO_4); calcium chloride ($CaCl_2$), etc	Neutralizing Agents; Extractants; Process Additives	High electrical conductivity; high osmotic pressure	Inhibits microbial activity; impairs hydraulic permeability (percolation/ filtration properties)
Surfactant Class	Linear Alkylbenzene Sulfonates (LAS)	Cleaning Agents (Detergents); Wetting Agents (Surfactants); Forming Additives (Molding Aids / Processing Aids)	Strong foaming and emulsifying properties	Increases treatment difficulty; reduces effluent clarity
Trace Heavy Metals	Cu、Zn、Cr、Ni	Catalyst Residues; Raw Material Impurities	High toxicity; non-biodegradable	Inhibits biological treatment systems; poses potential contamination of water bodies and soils

From a water-quality perspective, pharmaceutical wastewater typically shares the following characteristics: (1) High COD and BOD_5, with organic concentrations reaching several thousand to tens of thousands of mg/L—several times those of conventional wastewater; (2) A low BOD_5/COD ratio (often < 0.3), indicating poor biodegradability and constrained biological treatment efficiency; (3) High salinity with large pH fluctuations, due to extensive use of inorganic salts, acids/alkalis, and organic additives in production; and (4) High toxicity, whereby antimicrobial substances and heavy metals significantly inhibit microorganisms within treatment systems （Chen Zhongxiang & Gong Feng, 2021）.

2.2 Environmental Fate and Behavior of Pharmaceutical Wastewater

Organic contaminants in pharmaceutical wastewater generally exhibit pronounced environmental persistence. Their chemical structures often contain stable scaffolds—such as aromatic rings, halogen substituents, or polysubstituted heterocycles—that allow them to remain in natural waters for extended periods, with half-lives ranging from weeks to years, and resist degradation by photolysis, thermal processes, or conventional microbial metabolism （Ma Jiabao et al., 2023）. This persistence leads to continuous accumulation in surface waters, sediments, and soils, imposing chronic exposure pressure on aquatic ecosystems.

Regarding bioaccumulation, some highly hydrophobic pharmaceuticals (e.g., steroidal hormones, lipophilic antibiotics, and certain antiparasitics) have high octanol–water partition coefficients (log Kow) and readily concentrate in the fatty tissues of aquatic organisms. Through trophic transfer, these pollutants may biomagnify along food webs—from plankton to fish, birds, and ultimately humans—posing potential health risks to apex consumers （Li Xuemei et al. 2007）. For example, the accumulation of tetracyclines and fluoroquinolones in aquatic organisms can impair growth and reproduction and promote the dissemination of antibiotic resistance genes within environmental microbial communities. Their mobility is reflected in multipathway transport governed by physicochemical properties. Highly water-soluble small-molecule antibiotics, organic acids, and certain metabolites can migrate with surface runoff and infiltration into groundwater, even reaching drinking-water sources and creating insidious pollution. Volatile organics (e.g., N, N-dimethylformamide, methanol, acetone) can rapidly transfer across the air–water interface into the atmosphere, where photochemical reactions may generate secondary pollutants such as ozone and formaldehyde, affecting regional air quality. In addition, some semivolatile compounds undergo repartitioning at air–water–soil interfaces, enabling intermedia transport and expanding their environmental exposure footprint （Zhao Wenyi et al.，2025）. Compounding these issues, many pollutants undergo dynamic processes such as sorption–desorption and degradation–reformation in the environment. Antibiotics can adsorb to sediments or suspended particulates and be rereleased under hydrodynamic disturbance or changes in pH and salinity; certain transformation intermediates formed during degradation may exhibit greater ecotoxicity and bioavailability than the parent compounds, thereby causing secondary pollution. These processes increase the spatial complexity of pollutant distributions and heighten the difficulty of remediation and long-term risk control.

2.3 Mechanisms Interfering with Conventional Treatment Processes

The complex physicochemical properties of organic contaminants in pharmaceutical wastewater exert cross-unit, compounding interferences across biological treatment, membrane separation, and advanced oxidation, markedly affecting process efficiency and system stability （Chen Hanyang et al., 2025）. First, highly toxic and antimicrobial substances (e.g., antibiotics, antifungals, organic solvents) not only directly inhibit target microorganisms but also disrupt functional microbial consortia in treatment systems, leading to metabolic impairment and floc disintegration; this manifests as sludge bulking and poor settleability in activated-sludge processes, and as biofilm sloughing with reduced nitrogen and carbon removal in biofilm reactors （Zhang Yiming et al., 2020）. Second, strongly hydrophobic and/or high–molecular–weight pollutants readily deposit on membrane surfaces or within particle matrices, forming organic fouling layers and accelerating transmembrane pressure (TMP) rise, thereby shortening membrane lifespan, increasing cleaning frequency and energy demand; macromolecular pharmaceutical by-products can even complex with inorganic ions to block pores and cause irreversible fouling （Sun Chao, 2019）. Third, during advanced oxidation (e.g., ozonation, Fenton, photocatalysis), some pollutants are transformed into more polar yet more toxic intermediates, resulting in “toxicity transfer” that burdens downstream bioprocesses. Fourth, pollutants bearing highly stable structural motifs (e.g., fluorinated aromatics, triazines, perfluoroalkyl chains) exhibit low reactivity toward reactive oxygen species (ROS), severely limiting oxidative degradation efficiency and necessitating higher oxidant dosages or multistage trains, with increased costs and risks of secondary pollution. Collectively, these interferences elevate technical barriers and operational uncertainty, underscoring the need to evaluate toxicity spectra, structural persistence, and fouling propensity at the design stage and to achieve stable, efficient, and sustainable operation via multi-unit synergies, reaction-condition optimization, and real-time online monitoring （Han Wenliang & Dong Linyang, 2021）.

3 Classification and Recent Advances in Degradation Technologies for Organic Contaminants

Degradation technologies for organic contaminants in pharmaceutical wastewater can be broadly classified into physicochemical methods, biological processes, and hybrid (coupled) systems. These approaches differ markedly in removal efficiency, target applicability, operating costs, and by-product control; hence, judicious selection and integration are crucial to achieving efficient and sustainable treatment （Chen Hanyang et al., 2025）.

3.1 Physicochemical Methods

Physicochemical methods remove or transform organic contaminants in pharmaceutical wastewater through physical adsorption, chemical reactions, or electron-transfer processes （Pang Zijun et al.,2024）. They offer fast kinetics and broad applicability—especially for recalcitrant and highly toxic organics—thus occupying a central place in practice and research. However, these technologies often entail high energy demand, higher operating costs, or challenging by-product management, calling for continuous advances in materials and process integration.

(1) Adsorption

Adsorption leverages porous materials with high specific surface area, tailored pore structures, and surface functional groups to concentrate organics via physisorption (van der Waals, electrostatic interactions) or chemisorption (coordination, hydrogen bonding), enabling separation and removal （Cheng Cunxi et al., 2021）. Activated carbon is widely used owing to its availability, moderate cost, and robust pore structure, and it efficiently removes hydrophobic pharmaceuticals and some organic solvents. Its performance for highly polar, low-molecular-weight drugs (e.g., certain antibiotic metabolites) is limited, and saturated sorbents require regeneration to avoid secondary pollution. Metal–organic frameworks (MOFs), featuring tunable pore sizes and abundant coordination sites, provide highly selective uptake and show pronounced enrichment for molecules with sizes commensurate with their channels; functionalized MOFs have reported adsorption capacities for tetracyclines and sulfonamides that are 2–5× those of activated carbon, though water stability and scalable, low-cost synthesis remain hurdles. Functionalized nanomaterials (e.g., graphene oxide, carbon nanotubes, magnetic nanoparticles) can enhance interactions with target pollutants via surface modification and allow magnetic recovery （Zhang He et al., 2017）, but their performance can degrade in high-turbidity/high-salinity matrices, and long-term environmental safety requires further assessment.

(2) Oxidation/Reduction

Redox processes employ chemical oxidants or reductants to generate highly reactive species (e.g., •OH, $SO_4^{\bullet -}$, H•), which rapidly cleave bonds in organics, achieving mineralization or conversion to more biodegradable intermediates. The Fenton system (Fe^{2+}/H_2O_2) efficiently produces •OH at ambient conditions, particularly effective for aromatic and heteroaromatic pharmaceuticals, but is pH-sensitive (optimum ≈3) and generates iron-bearing sludge that needs handling （Zhou Luan et al., 2025）. Ozonation oxidizes pollutants directly or via •OH formed from ozone decomposition, offering rapid degradation and no sludge production; yet ozone stability declines in high-salinity or alkaline media, and removal of strongly hydrophobic compounds can be limited （Jin Suna & Lyu Ruiliang, 2024）. Wet air oxidation at elevated temperature (150–300 °C) and pressure (2–10 MPa) can mineralize high-strength wastewaters with high COD removal, but energy demand and capital costs are substantial, making it more suitable as a pretreatment for small volumes of concentrated wastes.

(3) Photocatalysis

Photocatalysis excites semiconductor catalysts under irradiation to generate electron–hole pairs that react with water/oxygen to yield reactive species (•OH, $O_2^{\bullet -}$), enabling nonselective oxidative degradation. TiO_2-based catalysts are the most established due to high chemical stability, low toxicity, and facile preparation （Tong Zhenwei & Zhong Zhencheng, 2022）, but they mainly respond to UV (~5% of the solar spectrum), limiting solar utilization （Liu Shouxin & Liu Hong, 2006）. Graphitic carbon nitride (g-C_3N_4) offers visible-light response, tunable band gaps, and easy synthesis; coupling with noble metals or transition-metal oxides can markedly improve charge separation. Other visible-light photocatalysts (e.g., $BiVO_4$, $ZnIn_2S_4$) benefit from band engineering and heterojunction design to enhance activity and reduce energy use, though stability and photo-corrosion still need to be addressed.

(4) Electrochemical Degradation

Electrochemical processes oxidize contaminants directly at the anode or indirectly via in situ generation of H_2O_2 and •OH （Zong Gang & Feng Lanting, 2023）. Anodic electrocatalytic oxidation using high-oxygen-overpotential anodes (e.g., PbO_2, boron-doped diamond, BDD) offers low selectivity but high mineralization efficiency, albeit at higher equipment cost. Electro-Fenton produces H_2O_2 cathodically, which reacts with Fe^{2+} to generate •OH, boosting degradation rates without external chemical oxidants. In hypersaline wastewaters, however, electrode passivation, side reactions, and corrosion can occur; improving electrode materials (e.g., BDD, advanced carbon-based composites) and optimizing operating parameters are essential for stable long-term performance.

3.2 Biological Degradation

Biological degradation relies on microbial metabolism to convert organic pollutants into harmless or less toxic compounds and is among the most widely applied routes for pharmaceutical wastewater treatment. Its strengths include low operating costs, potential for deep mineralization, and tunable removal across diverse contaminants through system optimization. However, the frequent presence of toxic, antibiotic, and/or poorly biodegradable organics can destabilize microbial communities and impair performance, necessitating process selection tailored to pollutant profiles （Wu Jianwen, 2025）.

(1) Aerobic/Anaerobic Treatment

Aerobic processes (e.g., sequencing batch reactor, SBR) oxidize organics to CO_2 and H_2O under aeration and can remove nitrogen via simultaneous nitrification–denitrification. They perform well for wastewaters with reasonable biodegradability ($BOD_5/COD > 0.3$), offering flexible operation and shock resistance, but microbial activity can be inhibited by high levels of antibiotics or biocides, causing effluent variability （Wu Pei et al., 2021）.

Anaerobic processes (e.g., upflow anaerobic sludge blanket, UASB) proceed via hydrolysis–acidogenesis–methanogenesis, degrading organics while generating biogas; they feature low energy demand and low sludge yield and are well-suited as pretreatment for high-strength wastewaters. Sensitivity to temperature and toxicants, a long start-up, and limited efficacy for very low-biodegradability streams are notable constraints （Lin Xilun, 1990）.

A/O (anaerobic–oxic) systems integrate anaerobic phosphorus release with aerobic uptake while coupling organic removal with nitrification/denitrification, thereby enhancing N/P removal. In pharmaceutical applications, pairing front-end advanced oxidation or physicochemical pretreatment to improve biodegradability before the A/O stage can markedly stabilize effluent quality （Liu Mu et al., 2011）.

(2) Biofilm-Based Reactors (MBR, MBBR)

Membrane bioreactors (MBRs) couple activated sludge with membrane separation to achieve near-zero suspended solids and turbidity, enabling direct reuse. Advantages include high biomass concentration, shock tolerance, and compact footprint; membrane fouling remains the chief limitation, which is exacerbated by salinity and toxicity, thus requiring aeration scouring, chemical cleaning, and/or membrane/material modifications to sustain flux （Zhao Junling et al., 2009）.

Moving-bed biofilm reactors (MBBRs) employ carriers to provide attachment area, allowing biofilm and suspended growth to coexist, which increases biomass and enhances resilience to toxic shocks and influent variability. Performance is generally stable in pharmaceutical wastewater, though excessive biofilm thickness can induce mass-transfer limitations and inner-layer anaerobiosis; agitation and hydrodynamic control are used to manage film thickness （Wu Tong et al., 2020）.

(3) Microbial Augmentation and Engineered Consortia

Bioaugmentation with specialist strains: Enriched or acclimated microbes from contaminated niches that tolerate and degrade target pollutants (e.g., quinolones, sulfonamides) can be introduced to increase overall rates and toxicity resilience （Qi Shixin et al., 2020）.

Synthetic-biology-enabled consortia: Genetic engineering can endow hosts with specific catabolic enzymes (e.g., ring-dioxygenases for aromatics, defluorinases for organofluorines), while co-cultures distribute metabolic burdens and complement pathways, thereby broadening the degradable pollutant spectrum （Wang Weiwei et al., 2021）.

3.3 Integrated Hybrid Processes

Given the complex composition, low biodegradability, and high toxicity of organic contaminants in pharmaceutical wastewater, single-unit technologies rarely achieve high removal while maintaining reasonable cost and operational stability. In recent years, hybrids that couple physicochemical and biological methods have become prominent. The core idea is to employ a front-end, high-efficiency oxidative or electrochemical step to cleave recalcitrant structures and reduce toxicity, followed by a back-end biological stage to achieve deep mineralization—thereby harnessing complementarities across units.

(1) Photo-Fenton Coupling; Ozone–Biological Integration

Photo-Fenton uses UV/visible/solar irradiation to accelerate the Fe^{2+}/Fe^{3+} redox cycle and sustain •OH generation. Light input not only boosts oxidation of aromatics and N-heterocycles but also broadens the effective pH window from the ~3 typical of conventional Fenton toward near-neutral conditions. Studies report that photo-Fenton markedly shortens reaction times and reduces H_2O_2 dosage for tetracycline- and sulfonamide-laden streams, lowering operating costs and secondary-pollution risks （Sun Yi et al., 2017）.

In ozone–bio trains, ozonation cleaves large or structurally stable molecules (e.g., quinolones, steroidal drugs) into smaller organic acids/alcohols, increasing biodegradability (higher BOD_5/COD). Subsequent biological units (e.g., A/O, MBR) then polish residual organics and remove N/P. This pairing is widely applied in upgrades for medium- to high-strength pharmaceutical effluents, balancing performance with OPEX optimization （Duan Xilei et al., 2009）.

(2) Electro-Biological Synergies

Embedding electrochemical steps within bioreactors enables direct anodic oxidation and/or in situ generation of reactive species (e.g., H_2O_2, •OH) to attack recalcitrants while facilitating internal cycling of electron donors/acceptors （Shi Jinzhuo et al., 2024）. Such coupling can enhance microbial metabolism, improve resilience to antibiotics and salinity, and, to some extent, suppress the dissemination of resistance genes. Electric fields also modulate extracellular electron transfer (EET), fostering cooperation between electroactive and degradative guilds. Design and operation are nontrivial: electrode materials, spacing, applied potential/voltage gradients, and contact time must be tightly controlled to avoid side reactions and energy penalties.

(3) AOPs-MBR Trains and Pathway Optimization

Positioning advanced oxidation processes (AOPs) upstream of an MBR can nonselectively cleave aromatic, heterocyclic, and even perfluoro-chain motifs, improving biodegradability and lowering toxicity before high-biomass/high-HRT biological polishing. Membrane separation then ensures stable, compliant effluent [38]. Success hinges on coordinated optimization: AOP intensity must be tuned to avoid generating large loads of low-biodegradability, membrane-permeable by-products or highly toxic intermediates; meanwhile, aeration management, periodic backwashing, and membrane/material modifications are used to slow fouling. Reported ozone–MBR and UV/H_2O_2–MBR configurations have achieved >90% COD removal, with effluent antibiotic concentrations below detection limits.

4 Major Degradation Mechanisms and Reaction Pathways

4.1 Oxidation–Reduction Mechanisms

In pharmaceutical wastewater treatment, oxidative pathways employ oxidants (e.g., O_3, H_2O_2, ClO_2) to cleave C–C, C–N, C–O and related bonds, converting organic pollutants to smaller molecules or inorganic end products; for instance, ozone attacks C=C, aromatic rings, and amino groups to achieve decolorization and detoxification. Reductive pathways transfer electrons from donors (e.g., zero-valent iron, sulfides) to pollutants, enabling dehalogenation, denitration, and related transformations; zero-valent iron can reduce chlorinated organics to less chlorinated—or fully dechlorinated—products, thereby improving biodegradability. In practice, oxidation and reduction are often coupled (e.g., catalytic wet peroxide oxidation combined with ZVI reduction) to markedly enhance the removal of antibiotics and steroidal compounds.

4.2 Radical (•OH, $SO_4{\bullet}^-$)–Induced Mechanisms

Advanced oxidation processes (AOPs) rely on highly reactive species—primarily hydroxyl radicals (•OH) and sulfate radicals ($SO_4{\bullet}^-$)—to nonselectively degrade organics. •OH ($E^0 \approx 2.8$ V) can cleave aromatic rings, ether linkages, and amines on millisecond timescales (e.g., Fenton-generated •OH rapidly disrupts tetracycline scaffolds). $SO_4{\bullet}^-$ ($E^0 \approx 2.5$–3.1 V) features a longer lifetime and often outperforms •OH against electron-poor functionalities; it is also less susceptible to scavenging by common anions in high-salinity matrices, yielding greater stability in saline antibiotic wastewaters. Both radicals can be generated via photolysis, persulfate activation, or electrochemical routes and can interconvert during reaction, extending oxidative action and improving mineralization.

4.3 Microbial Metabolism and Cometabolic Pathways

Biodegradation converts pollutants to low-toxicity products via enzyme-catalyzed reactions and proceeds through direct metabolism or cometabolism. In direct metabolism, pollutants serve as carbon/energy sources and enter canonical routes—for example, phenolic drugs can be funneled through the catechol (o-dihydroxybenzene) pathway to cis,cis-muconic acid, then into the TCA cycle for complete mineralization. Cometabolism occurs when pollutants cannot support growth by themselves; in the presence of other substrates (e.g., glucose, acetate), nonspecific enzymes transform the pollutants—e.g., methanotrophs, in the presence of methane, use methane monooxygenase to degrade chloramphenicol. In pharmaceutical wastewater, cometabolism is particularly important for recalcitrant and toxic antibiotics/hormones; optimizing C/N ratios, adding readily degradable cosubstrates, or employing mixed consortia can markedly improve removal.

4.4 Identification of Intermediates and Toxicity Evolution

Degradation often yields intermediates with structures and toxicities distinct from the parent compounds—sometimes with higher environmental risk. Identification typically uses HRMS, GC–MS, or LC–MS/MS to resolve pathways; for example, ozonation of ciprofloxacin can produce defluorinated products, carboxylic acids, and ketones. Toxicity evolution is assessed via acute toxicity assays (e.g., Vibrio fischeri bioluminescence), algal growth inhibition tests, and QSAR modeling. Studies show certain ketone/aldehyde intermediates can exert stronger acute toxicity to algae and aquatic invertebrates than the parent drug. Consequently, process design/optimization should track toxicity removal alongside COD/TOC reduction. Where toxicity rebound is possible, terminal activated-carbon polishing, biological finishing, or secondary oxidation units should be incorporated to remove high-risk intermediates and ensure ecological safety of the effluent.

5 Comparative Assessment of Key Technologies and Application Efficiency

There are pronounced differences in degradation efficiency, applicability, and economics among pharmaceutical wastewater treatment technologies (Table 2). Physicochemical methods (e.g., Fenton, ozonation, photocatalysis, electrochemical oxidation) offer rapid kinetics and are suitable for structurally stable, poorly biodegradable organics, but they typically entail higher reagent and energy consumption and often limited mineralization. Biological processes (aerobic, anaerobic, biofilm reactors) feature low operating costs and suit large flow rates, yet exhibit slower degradation for highly toxic or antibiotic-bearing streams that inhibit microbes, requiring longer hydraulic retention times (HRT). Hybrid trains (ozone–biological, photo-Fenton–biological, AOPs + MBR) couple enhanced biodegradability with deep mineralization and generally provide the best overall performance, particularly for standards-tightening upgrades and high-risk effluents.

In terms of COD, TOC, and characteristic micropollutant removal, hybrids commonly achieve 85–95% COD and >80% TOC removal within relatively short reaction times, while driving antibiotic and endocrine-disrupting compound levels below detection. Cost analyses indicate that physicochemical methods are preferable for high-strength, low-volume wastes as pretreatment or polishing; biological routes suit more biodegradable, moderate-load streams; and hybrid configurations fit scenarios requiring stable, compliant effluent or reuse. Engineering experience shows that pairing front-end high-efficiency oxidation with back-end robust bioprocessing not only improves overall removal but also reduces operational variability—and, in some cases, enables energy recovery and a favorable operating-cost balance.

Table 2 Comparative performance and application scenarios of key treatment technologies

Technology Type	Typical Processes	COD Removal	TOC Removal	Performance on Characteristic Pollutants	Advantages	Limitations	Typical Application Scenarios
Physicochemical Methods	Fenton; ozonation; photocatalysis; electrochemical oxidation	70–90% (1–3 h)	50–75%	Antibiotics and hormones: removal >90%	Fast reactions; suited to recalcitrant pollutants	High reagent/energy demand; limited mineralization; possible formation of toxic intermediates	High-strength, low-flow wastes as pretreatment or polishing
Biological Processes	Aerobic; anaerobic; MBR; MBBR	75–90% (6–24 h)	40–65%	Best performance for biodegradable streams	Low cost, low energy use; stable operation	Slow start-up; sensitive to toxicants; long HRT	Large-flow wastewater with good biodegradability
Integrated/Hybrid Trains	Ozone–biological; photo-Fenton–biological; AOPs + MBR	85–95% (<12 h)	80–90%	Antibiotics and endocrine-disrupting compounds (EDCs): removal >95%; estrogenic activity ↓ >90%	Improves biodegradability while enabling deep mineralization; stable effluent quality.	Higher capital cost; more complex operation/ management	Standards-upgrade projects; high-risk wastewater; reuse treatment

Continued

Technology Type	Typical Processes	COD Removal	TOC Removal	Performance on Characteristic Pollutants	Advantages	Limitations	Typical Application Scenarios
Engineering Cases (Examples)	Ozone–bio contact oxidation; electro-catalysis + MBR; photo-Fenton + A/O; wet air oxidation + UASB + MBR	COD < 50 mg/L; antibiotics < detection limit	≥80%	Estrogenic activity reduced by >90%	Stable compliance; reusable effluent; potential energy recovery	Requires a higher technical level and O&M capability	Pharmaceutical parks; centralized/combined wastewater treatment plants

6 Challenges and Future Trends in Technology Application

Despite substantial advances in laboratory studies and select engineering projects, significant challenges remain in adapting treatment technologies to high-salinity, high-toxicity conditions, managing the toxicity of transformation intermediates, optimizing multi-unit synergies, and advancing green transitions under the "dual-carbon" agenda (carbon peaking and carbon neutrality). The coexistence of elevated salinity and multiple toxic organics suppresses microbial metabolism, accelerates membrane failure (e.g., swelling, embrittlement, fouling), and reduces electrochemical reaction efficiency. Priority directions, therefore, include developing salt-/ salt-/toxicant-tolerant microbial consortia, anti-swelling/anti-fouling membrane materials, and staged salt-removal schemes to improve stability and long-term operability.

In advanced oxidation and certain biotransformations, structurally simpler yet more toxic intermediates can form (e.g., oxidative derivatives of quinolones) with higher acute toxicity and resistance risks than their parents. Current practice still relies heavily on COD/TOC, with limited real-time toxicity monitoring and non-target screening of intermediates. Accordingly, high-resolution mass spectrometry (HRMS) and online bioassays should be integrated, and "toxicity removal rate" should be incorporated as a core performance metric.

Operationally, pharmaceutical wastewater treatment typically requires concurrent physicochemical, oxidative, and biological units. Differences in reaction kinetics, load responses, and energy profiles complicate system-level optimization; many facilities depend on manual, experience-based adjustments, lacking data-driven, mechanistic intelligent control. Future systems should implement "real-time water-quality sensing → process prediction → adaptive control," and explore digital-twin models for end-to-end monitoring and predictive maintenance.

Driven by carbon-peaking/carbon-neutral goals, conventional high-energy, high-reagent paradigms must transition to low-carbon operations, leveraging solar-driven photocatalysis, low-energy membrane separations, biogas recovery in anaerobic units, and in situ generation of greener oxidants to shrink the carbon footprint. Research hotspots will include smart catalytic materials with self-regulation and anti-fouling traits; synthetic-biology-designed microbial consortia for synergistic multi-pollutant degradation and ARG control; multi-omics (genomics, transcriptomics, metabolomics) to decode functional microbial responses; and co-treatment strategies targeting antibiotics, endocrine disruptors, and microplastics. These advances aim to deliver treatment that is efficient, stable, and sustainable.

7 Conclusions and Outlook

A comparative analysis of degradation technologies for organic pollutants in pharmaceutical wastewater indicates: physicochemical methods are best suited to high-strength, poorly biodegradable, structurally persistent contaminants in low-to-moderate volumes; biological processes are preferable for large-flow streams with higher biodegradability and lower toxicity; and hybrid trains excel by coupling biodegradability enhancement with deep mineralization, making them particularly suitable for standards-upgrade projects and high-risk effluents. Mechanistic elucidation is critical for optimizing operating parameters, anticipating reaction pathways, and preventing secondary pollution, while multi-technology integration enables complementarity and synergy, improving stability and overall performance.

Looking ahead—and guided by the dual-carbon strategy—development should prioritize low-energy, resource-recovery, and greener treatments. By leveraging intelligent catalysts, salt-/toxic-tolerant microbiomes, digitalized control (including digital twins), and multi-omics-informed process design, the sector can build a high-efficiency, low-carbon, and sustainable treatment framework that aligns pollution control with environmental protection.

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