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Integration of electrochemical oxidation and photocatalysis for treating pharmaceutical residues in wastewater under varying environmental conditions

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Abstract

Pharmaceutical residues have emerged as persistent micropollutants in aquatic ecosystems, posing ecological, toxicological, and public health challenges due to their bioaccumulation and resistance to conventional wastewater treatment. Advanced oxidation processes (AOPs) have gained prominence for degrading such complex compounds, yet individual techniques often suffer from operational inefficiencies, incomplete mineralization, or high energy demands. This study explores the integration of electrochemical oxidation (EO) and photocatalysis as a synergistic treatment pathway capable of addressing these limitations under variable environmental conditions. The hybrid system combines the anodic generation of reactive oxygen species (•OH, O_2•–) with photoexcited semiconductor catalysts such as TiO_2 or doped ZnO, enabling simultaneous oxidation and photodegradation of pharmaceutical contaminants. The integration enhances electron–hole separation, improves mass transfer, and extends the oxidative potential beyond either process alone. Experimental simulations under varying pH, temperature, and light intensity demonstrate that the combined EO–photocatalytic process achieves higher degradation efficiency and total organic carbon (TOC) removal than standalone systems. Mechanistic analysis reveals that environmental conditions critically influence radical formation kinetics, electrode stability, and catalyst photoreactivity, thereby dictating the overall mineralization rate. Furthermore, the process exhibits resilience against matrix interferences such as chloride, bicarbonate, and natural organic matter. The study concludes that optimized hybrid EO–photocatalytic configurations represent a scalable and sustainable route for removing persistent pharmaceuticals from wastewater, contributing to circular water management and pollution mitigation. Future work should focus on energy recovery, reactor design optimization, and real effluent validation to ensure full-scale applicability in diverse climatic contexts.

Keywords: Electrochemical oxidation; Photocatalysis; Pharmaceutical residues; Advanced oxidation processes; Wastewater treatment; Environmental variability

1. Introduction

1.1. Global pharmaceutical pollution crisis

The global increase in pharmaceutical consumption, driven by population growth, aging demographics, and rising healthcare access, has created a persistent environmental challenge. Residues from antibiotics, analgesics, antidepressants, and hormones are now widely detected in rivers, lakes, groundwater, and even treated drinking water [1]. Unlike biodegradable organic waste, many pharmaceuticals are designed to be stable and bioactive at low concentrations, making them difficult to remove during conventional wastewater treatment [2]. Studies have confirmed their persistence across continents, highlighting risks of endocrine disruption, antimicrobial resistance, and ecotoxicity in aquatic ecosystems [3].

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The problem is compounded by the incomplete metabolism of drugs in humans and animals. Between 30–90% of administered doses are excreted as active compounds or metabolites, which enter municipal sewage systems and reach treatment plants [4]. Emerging economies, where rapid urbanization outpaces infrastructure, are disproportionately affected. For instance, effluents from pharmaceutical manufacturing hubs often discharge high concentrations directly into rivers [5]. Global monitoring has revealed a concerning rise in hotspots where concentrations exceed thresholds for ecological safety, underscoring the inadequacy of current containment measures [6]. Without urgent intervention, the accumulation of these residues threatens food chains, aquatic biodiversity, and ultimately human health [7]. The scale of this crisis highlights the urgency of adopting advanced, scalable, and sustainable treatment technologies [8].

1.2. Limitations of conventional wastewater treatments

Traditional wastewater treatment plants (WWTPs) were designed primarily to remove organic matter, nutrients, and pathogens rather than trace micropollutants such as pharmaceuticals [2]. Conventional methods including primary sedimentation, activated sludge, and anaerobic digestion achieve only partial removal, leaving significant residues in effluents [3]. For example, ibuprofen and diclofenac often pass through treatment processes unaltered, while antibiotics such as sulfamethoxazole persist and contribute to antimicrobial resistance [6].

Chemical treatments like chlorination and ozonation provide some degradation capacity but introduce challenges of by-product toxicity and high operational costs [4]. Adsorption on activated carbon offers short-term removal but requires frequent regeneration or replacement of sorbents, making it expensive and resource-intensive [7]. Membrane filtration techniques, though effective in separating micropollutants, suffer from fouling, high energy consumption, and limited applicability in large-scale facilities [5].

These limitations are magnified under variable environmental conditions. Seasonal changes in temperature, influent composition, and hydraulic load affect removal efficiency, creating inconsistencies in pharmaceutical degradation [1]. In addition, rising population densities and stricter environmental regulations demand higher performance standards than existing systems can reliably meet [8]. Consequently, the inability of conventional WWTPs to address persistent micropollutants highlights the need for innovative technologies that are efficient, adaptable, and cost-effective [9].

1.3. Advanced oxidation processes (AOPs) as emerging solutions

Advanced oxidation processes (AOPs) have emerged as promising strategies for addressing pharmaceutical pollution. These processes rely on the in situ generation of highly reactive oxygen species (ROS), particularly hydroxyl radicals (•OH), which are capable of non-selectively degrading a wide spectrum of contaminants [2]. Electrochemical oxidation (EO) and photocatalysis are two of the most studied AOPs, each offering unique advantages in breaking down stable pharmaceutical structures [3].

Electrochemical oxidation involves the use of electrodes, often made of boron-doped diamond or mixed metal oxides, to generate ROS directly from water electrolysis [4]. This technique offers controllability and does not require external chemical addition, making it attractive for decentralized treatment systems [1]. Photocatalysis, typically driven by semiconductors such as titanium dioxide, leverages ultraviolet or visible light to activate electron–hole pairs that initiate redox reactions capable of mineralizing pharmaceuticals [6].

Despite their effectiveness, both approaches face limitations when applied individually. EO often suffers from high energy demands and electrode degradation, while photocatalysis is constrained by limited light absorption and recombination of charge carriers [7]. Nevertheless, their complementary strengths suggest that integrated EO–photocatalytic systems can provide a sustainable, synergistic pathway to enhance pharmaceutical degradation under diverse environmental conditions [9].

2. Pharmaceutical residues in aquatic environments

2.1. Sources and occurrence

Pharmaceutical residues enter aquatic environments from multiple interconnected sources, spanning household, hospital, industrial, and agricultural sectors. Human excretion remains the most significant pathway, as unmetabolized drugs and metabolites are discharged into municipal sewage systems [10]. Veterinary applications contribute comparably, with livestock excreta releasing antibiotics, hormones, and anti-parasitics into soils and nearby waterways [9]. Another critical contributor is the pharmaceutical manufacturing industry, where untreated or partially treated effluents can contain extremely high concentrations of active ingredients [14]. In low- and middle-income regions, direct discharge of hospital wastewater exacerbates localized contamination, creating hotspots of antibiotic resistance [12].

Surface water surveys consistently reveal the presence of analgesics, antibiotics, and antidepressants at detectable levels, with rivers downstream of treatment plants showing the highest concentrations [11]. Groundwater contamination is increasingly documented where infiltration coincides with intensive use [8]. Thus, the widespread occurrence of residues demonstrates that pharmaceutical pollutants are not isolated anomalies but global challenges requiring systemic intervention [16].

2.2. Environmental fate and persistence

The environmental persistence of pharmaceuticals is shaped by their chemical stability, sorption potential, and degradation pathways. Many compounds are resistant to biodegradation, allowing them to remain intact for extended periods in aquatic systems [13]. Antibiotics such as fluoroquinolones and macrolides adsorb strongly to sediments, creating long-term reservoirs of contamination that may be remobilized during floods or dredging events [15]. Hormonal compounds, including synthetic estrogens, display half-lives extending weeks to months, reinforcing their potential for chronic exposure risks [10].

Sunlight photolysis, microbial transformation, and hydrolysis are often insufficient for complete removal, particularly in turbid or nutrient-rich waters [12]. Pharmaceuticals can also undergo transformation into metabolites or by-products that retain or even enhance biological activity [9]. The combined effect is a persistent presence of trace pharmaceuticals in surface waters, sediments, and groundwater systems [8]. Such durability highlights why pharmaceutical residues are classified as “pseudo-persistent” contaminants, continuously replenished through ongoing human and industrial activity [14].

2.3. Ecotoxicological and human health impacts

The ecotoxicological consequences of pharmaceutical pollution are substantial. Sub-lethal concentrations of antidepressants, for example, disrupt fish behavior, altering predator avoidance and reproduction patterns [13]. Antibiotics in aquatic environments accelerate the development of antimicrobial resistance genes, which can transfer across microbial communities, threatening both environmental and clinical health [12]. Hormonal residues such as ethinylestradiol have been linked to feminization of fish, population declines, and ecosystem imbalance [11].

Chronic exposure in humans is also a growing concern. Though drinking water levels are typically low, the cumulative effect of long-term ingestion remains poorly understood [15]. Specific populations, such as immunocompromised patients and infants, are especially vulnerable. The spread of antibiotic resistance through waterborne pathways poses one of the most alarming risks to public health systems [16].

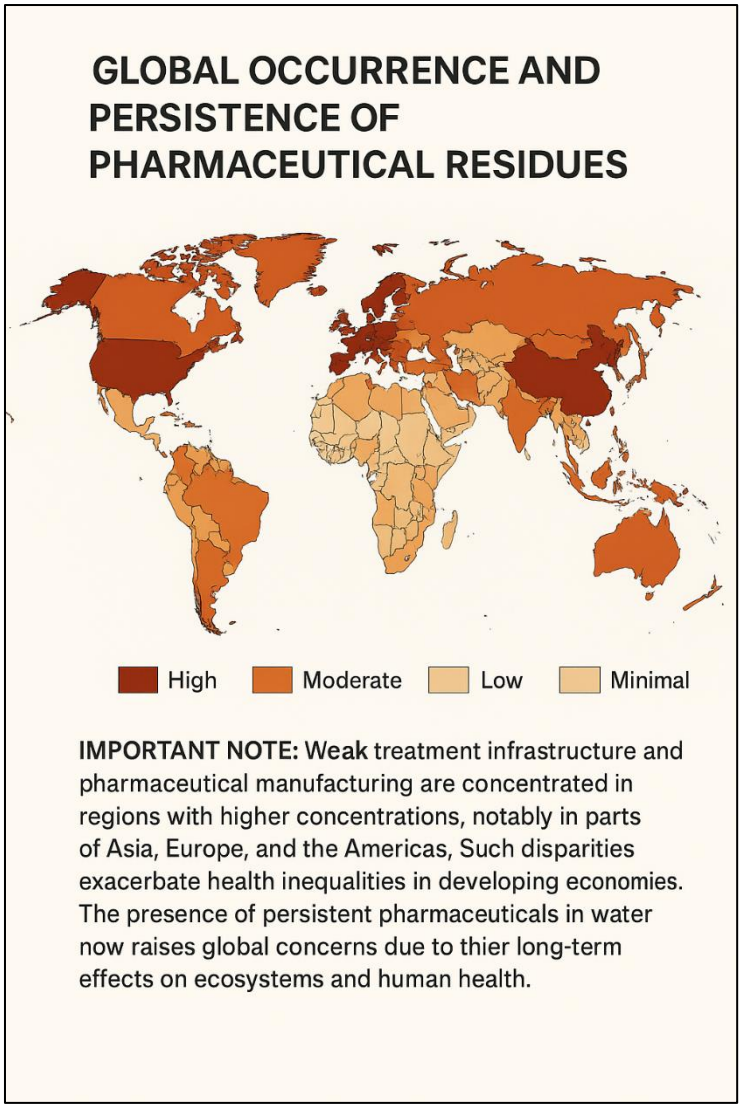

Figure 1 The global occurrence and persistence of pharmaceutical residues, emphasizing regions where treatment infrastructures are weak and pharmaceutical manufacturing is concentrated [8]

These spatial patterns suggest disproportionate burdens on developing economies, further entrenching health inequalities [9]. With growing evidence of multi-generational impacts on ecosystems and human health, the presence of pharmaceuticals in water has shifted from a local pollution issue to a pressing global health concern [14].

2.4. Regulatory perspectives and policy gaps

Despite widespread recognition of the issue, regulatory frameworks for pharmaceutical pollution remain fragmented and inconsistent. In the United States, the Environmental Protection Agency (EPA) has established guidelines for drinking water safety but has not set enforceable standards for most pharmaceutical residues [10]. Similarly, the European Union maintains a watch list of priority contaminants, including diclofenac and ethinylestradiol, but monitoring requirements vary across member states [15].

In developing economies, the absence of stringent discharge regulations enables pharmaceutical manufacturers and hospitals to release untreated effluents, creating highly polluted river basins [12]. Even where regulations exist, weak enforcement and limited analytical capabilities hinder effective oversight [11]. Moreover, most policies emphasize end-of-pipe monitoring rather than preventive measures such as green drug design or improved disposal practices [16].

Global initiatives, including those led by the World Health Organization, have underscored the link between pharmaceuticals and antimicrobial resistance, but international cooperation remains limited [13]. This patchwork of policies underscores the urgent need for harmonized regulatory standards and investment in monitoring infrastructure

[9]. Without stronger governance, pharmaceuticals will continue to accumulate in aquatic environments, leaving ecosystems and public health at increasing risk [8].

3. Advanced oxidation processes: principles and limitations

3.1. Fundamentals of AOPs and ROS generation

Advanced oxidation processes (AOPs) are water treatment technologies that rely on the in situ production of highly reactive oxygen species (ROS), most notably hydroxyl radicals (•OH), which possess oxidation potentials of approximately 2.8 V, surpassing chlorine and ozone [15]. These radicals are powerful enough to non-selectively attack a wide range of organic contaminants, including pharmaceuticals with complex aromatic and heterocyclic structures [16]. AOPs function through diverse mechanisms, including photolysis, catalysis, and electrochemical reactions, yet their shared goal is the mineralization of pollutants into carbon dioxide, water, and inorganic ions [18].

The ability of ROS to degrade otherwise recalcitrant compounds makes AOPs critical tools in modern wastewater treatment [14]. Unlike conventional processes that primarily transfer pollutants to another phase, such as adsorption onto sludge, AOPs transform them into less harmful products [20]. However, the kinetics of ROS production and the stability of generated species are influenced by environmental conditions such as pH, ionic strength, and dissolved organic matter [22]. Additionally, incomplete mineralization can yield intermediate products that may retain biological activity [17]. These constraints, while significant, do not undermine the transformative potential of AOPs; rather, they highlight the need for optimization and innovative integration strategies [24].

3.2. Electrochemical oxidation (EO) overview

Electrochemical oxidation (EO) is an AOP that generates ROS directly at electrode surfaces through the electrolysis of water [18]. Anodic reactions produce hydroxyl radicals, oxygen, and other oxidizing species capable of degrading pharmaceuticals without external oxidant addition [19]. Boron-doped diamond (BDD), mixed metal oxides, and platinum group electrodes are commonly used due to their high oxygen evolution overpotentials and durability [16]. EO can mineralize pharmaceuticals such as diclofenac, sulfamethoxazole, and carbamazepine with high efficiency under controlled conditions [15].

The main advantages of EO include precise controllability, modularity, and potential for decentralized treatment systems [14]. Its reliance on electricity rather than chemicals makes it adaptable to renewable energy integration, strengthening its sustainability profile [21]. Nevertheless, energy costs remain a significant concern, particularly when applied to large volumes of municipal wastewater [20]. Furthermore, electrode fouling, scaling, and degradation can reduce long-term performance [23]. Side reactions, such as the formation of chlorinated by-products in chloride-rich waters, present additional challenges [17]. Despite these drawbacks, EO's versatility and proven track record in degrading persistent contaminants make it a cornerstone technology within the broader AOP framework [19].

3.3. Photocatalysis overview

Photocatalysis employs semiconductor materials, most notably titanium dioxide (TiO_2), to harness photons and generate electron–hole pairs that initiate oxidation and reduction reactions [22]. Under irradiation, electrons are excited from the valence to the conduction band, leaving positively charged holes that react with water to form hydroxyl radicals, while the electrons reduce oxygen to superoxide radicals [18]. These ROS drive the degradation of pharmaceuticals, enabling the mineralization of complex organic molecules [15].

Photocatalysis is attractive because of its use of sunlight or artificial light, its ability to operate under ambient conditions, and the relatively low cost of TiO_2 [20]. It has been shown to effectively degrade antibiotics, anti-inflammatories, and hormones in aqueous matrices [19]. However, recombination of electron–hole pairs significantly reduces efficiency, and visible-light activity is often limited without doping or surface modification [16]. In real wastewater, turbidity and natural organic matter can further diminish performance [24].

Table 1 compares EO and photocatalysis in terms of efficiency, costs, and limitations, highlighting the complementary nature of the two methods [14]. The table underscores that while EO offers controllability, photocatalysis provides light-driven sustainability, suggesting that integration could overcome their individual weaknesses [21].

Table 1 Comparative summary of Electrochemical Oxidation (EO) and Photocatalysis

Criteria	Electrochemical Oxidation (EO)	Photocatalysis	Comparative Insight
Efficiency	High oxidative potential with controllable radical production; effective against a wide range of pharmaceuticals but sensitive to electrode material	Effective for a broad spectrum of pollutants via light-driven hydroxyl radicals; efficiency depends heavily on catalyst type and light availability	EO ensures process control and robustness, while photocatalysis harnesses renewable energy but is more variable
Operational Costs	High due to energy consumption (electricity demand) and electrode replacement; no need for chemical reagents	Moderate, relying mainly on sunlight or artificial light; lower direct energy costs but requires periodic catalyst regeneration or replacement	EO costs are predictable but energy-heavy; photocatalysis is more cost-efficient under sunlight but requires catalyst investments
Limitations	Electrode degradation, energy intensity, limited performance under complex matrices with high fouling	Dependence on UV/visible light intensity, catalyst deactivation, limited penetration in turbid waters	EO's main weakness is cost and durability, while photocatalysis struggles under poor light or high-matrix complexity
Strengths	Controllability, scalability, and ability to operate independently of natural conditions	Sustainability, minimal chemical input, compatibility with renewable light sources	Integration offers controllability plus sustainability, buffering weaknesses of both systems

3.4. Comparative strengths and limitations

When evaluated side by side, electrochemical oxidation and photocatalysis reveal complementary strengths and constraints. EO provides precise control of oxidation intensity and independence from light conditions, making it reliable across diverse wastewater streams [18]. However, its high energy demand and electrode costs pose barriers to large-scale adoption [23]. In contrast, photocatalysis capitalizes on abundant solar energy, offering a renewable pathway with relatively low operational expenses, though its efficiency is constrained by electron–hole recombination and low solar utilization [20].

In terms of contaminant removal, EO tends to achieve higher mineralization rates, whereas photocatalysis may produce slower degradation but with greater energy flexibility [17]. Both methods struggle in the presence of matrix interferences such as high ionic strength or organic matter, though in different ways [22]. Importantly, both have been successfully demonstrated at lab and pilot scales, yet neither has achieved widespread deployment for municipal wastewater [15].

This comparative analysis reinforces the logic of combining EO and photocatalysis to harness their respective advantages [19]. By addressing weaknesses in isolation, integrated systems promise more robust, adaptable, and energy-efficient treatment solutions [16].

4. Integration of electrochemical oxidation and photocatalysis

4.1. Theoretical basis of synergy

The integration of electrochemical oxidation (EO) and photocatalysis is grounded in the complementary nature of their mechanisms. EO generates hydroxyl radicals and other oxidants directly at the electrode surface, while photocatalysis utilizes photons to excite semiconductor materials, producing electron–hole pairs that form radicals [23]. By coupling these processes, one can address the intrinsic limitations of each. For instance, photocatalysis suffers from electron–hole recombination, a phenomenon that reduces efficiency. However, applying an electrochemical bias during the process can separate charges more effectively, prolonging radical lifetimes [24].

Another theoretical advantage arises from the spatial distribution of reactive species. EO typically produces radicals in close proximity to the electrode, limiting their diffusion range, while photocatalysis generates radicals across the illuminated catalyst surface [25]. Combining the two expands the reactive zone, ensuring pollutants are exposed to

oxidative species in multiple domains. This expanded reaction field enhances contact probabilities, which is critical when treating complex matrices such as pharmaceutical-laden wastewater [26].

Furthermore, the energy profiles of the two processes are complementary. EO relies on electrical input, which may come from renewable energy systems, while photocatalysis is driven primarily by light, including solar energy. Together, the integration allows for hybrid energy utilization, potentially reducing costs and improving sustainability [27]. These synergies underscore the promise of combined EO–photocatalysis as an advanced water treatment approach capable of overcoming the shortcomings of standalone systems [29].

4.2. Mechanistic pathways of combined EO–photocatalysis

The mechanistic pathways in EO–photocatalysis integration reveal how synergies emerge at the molecular level. During EO, anodic reactions at electrodes such as boron-doped diamond generate hydroxyl radicals (•OH) with strong oxidative capacity [22]. Concurrently, photocatalysis activates semiconductor surfaces, producing electron–hole pairs that also generate •OH and superoxide radicals (O_2•–) [24]. In an integrated configuration, these radicals overlap, amplifying oxidative intensity and broadening degradation pathways [28].

One key pathway involves suppression of charge recombination in photocatalysis by the applied potential in EO. Electrons that would typically recombine with holes are instead scavenged at the cathode, while holes participate in ROS generation. This improves the quantum efficiency of photocatalysis and boosts the overall radical yield [25]. Additionally, EO can regenerate catalyst surfaces by oxidizing adsorbed intermediates that would otherwise deactivate photocatalytic sites [29].

Moreover, synergy arises through complementary degradation sequences. Pharmaceuticals often resist single-step oxidation, forming intermediates that require additional reactions. The combination ensures sequential and simultaneous attack: EO initiates structural breakdown, while photocatalysis drives mineralization [27]. For example, antibiotics like sulfamethoxazole undergo ring cleavage via anodic oxidation, followed by photocatalytic mineralization of carboxylic acid intermediates [26].

The combined system therefore provides a more robust degradation network, minimizing the persistence of toxic by-products [30]. These mechanistic complementarities demonstrate that EO–photocatalysis is not simply additive but represents a fundamentally synergistic process.

4.3. Role of catalyst design and electrode materials

Catalyst design and electrode material selection are central to realizing the full potential of EO–photocatalysis. The semiconductor photocatalyst, typically TiO_2, can be modified through doping, surface functionalization, or nanostructuring to improve visible-light absorption and reduce recombination [24]. Similarly, electrodes such as boron-doped diamond (BDD) or mixed metal oxides enhance radical generation and durability under high current densities [22].

When integrated, these materials must function cooperatively. For instance, coupling TiO_2 photocatalysts with conductive substrates facilitates electron transfer between the photocatalyst and the electrode, accelerating charge separation and boosting radical formation [26]. Nanostructured composites, such as TiO_2-graphene or TiO_2-carbon nanotube hybrids, enhance conductivity and provide additional surface area for reactions [28].

Another important aspect is stability. Photocatalysts often suffer deactivation from adsorbed intermediates, while electrodes degrade through scaling or fouling. In hybrid systems, EO continuously regenerates photocatalyst surfaces by oxidizing contaminants directly at the electrode, mitigating fouling and extending catalyst life [27]. Likewise, photocatalysis reduces electrode stress by sharing the oxidative load, lowering energy demand per unit treatment [25].

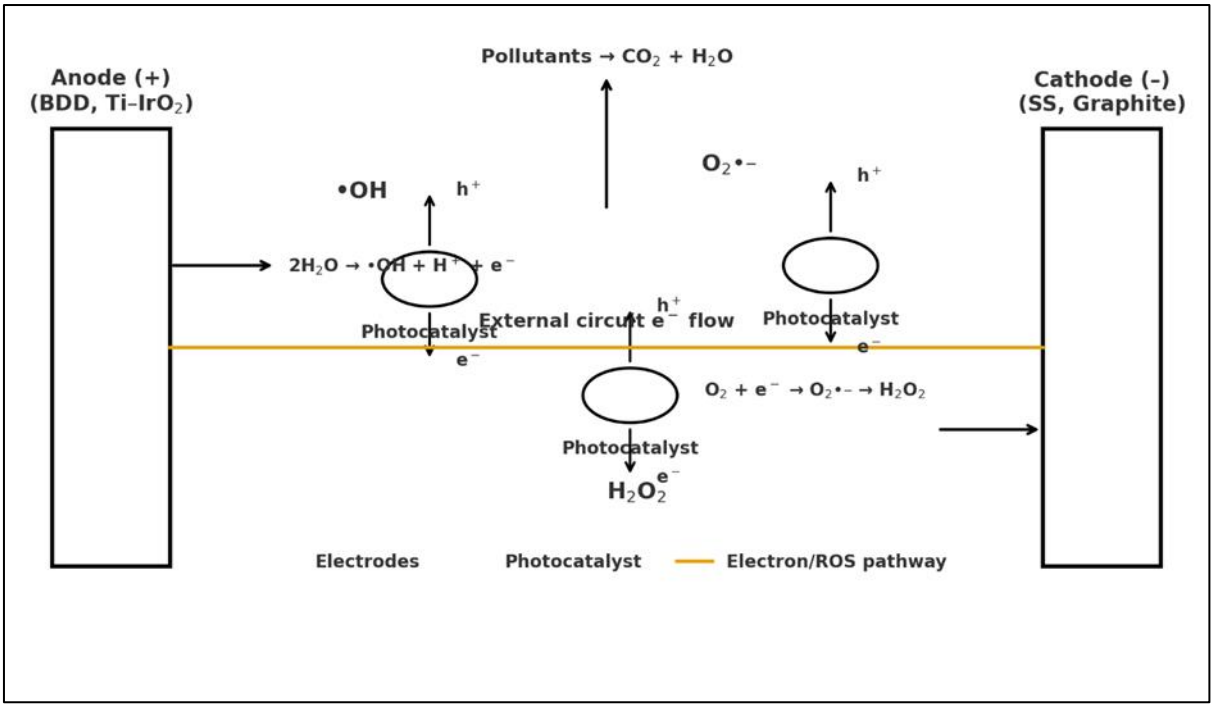

Figure 2 Mechanistic schematic of EO-photocatalysis

Figure 2 illustrates the mechanistic schematic of EO–photocatalysis, highlighting interactions between electrode surfaces, photocatalyst particles, and reactive oxygen species [29]. The figure underscores how design choices, such as electrode composition and catalyst doping, influence the efficiency and resilience of the hybrid system. Such designs are critical for adapting to real wastewater environments, where variable pH, ionic strength, and organic loads can impact performance [30].

4.4. Advantages over individual processes

The integration of EO and photocatalysis offers multiple advantages compared to their standalone operation. One of the most notable is improved degradation efficiency, as the combined system harnesses complementary radical pathways [23]. For instance, while EO excels at oxidizing aromatic rings, photocatalysis is more effective in breaking down carboxylic acid intermediates. Together, the system achieves deeper mineralization of pharmaceuticals such as carbamazepine and diclofenac [25].

Energy optimization is another key advantage. Standalone EO often faces prohibitive energy costs, while photocatalysis alone can be constrained by low sunlight availability or limited quantum efficiency [24]. By sharing the oxidative burden, the integrated system reduces electricity demand and enhances light utilization, leading to lower operational costs [22].

The hybrid approach also addresses by-product concerns. Both EO and photocatalysis, when applied individually, may produce partially oxidized intermediates with residual toxicity [27]. Their combination minimizes such accumulation, as sequential oxidation steps occur more readily [28]. Furthermore, hybrid systems demonstrate greater adaptability to variable wastewater conditions. While high turbidity diminishes photocatalytic performance, EO can maintain degradation capacity. Conversely, when ionic strength reduces EO efficiency, photocatalysis compensates [26].

Finally, integration supports scalability. Modular EO units and photocatalytic reactors can be coupled in series or parallel configurations, enabling adaptation for decentralized or municipal-scale treatment [29]. Collectively, these advantages position EO–photocatalysis as a versatile and sustainable technology capable of bridging the gap between laboratory promise and real-world wastewater challenges [30].

5. Environmental conditions and their influence

5.1. Effect of pH on radical kinetics and electrode stability

pH exerts a profound influence on the efficiency of EO–photocatalytic systems by modulating radical formation kinetics, pollutant ionization states, and electrode stability. Hydroxyl radical (•OH) production is most efficient under slightly acidic to neutral conditions, as excessively alkaline environments promote scavenging reactions with carbonate and hydroxide ions that reduce radical availability [28]. For photocatalysis, acidic media can enhance adsorption of cationic pharmaceuticals onto catalyst surfaces, improving degradation rates [30]. However, very low pH values risk leaching of electrode materials and destabilization of semiconductors such as TiO_2 [32].

In EO, electrode performance is highly pH-dependent. Boron-doped diamond (BDD) electrodes, for example, display stable activity across a wide pH range, while mixed metal oxide electrodes degrade faster under acidic conditions due to corrosion [29]. Stability is crucial in hybrid systems, since electrode fouling can impair photocatalytic synergy [34]. Similarly, proton concentration affects the valence band potential of photocatalysts, altering electron–hole generation and thus radical production [33].

From a pollutant perspective, pH determines ionization of pharmaceuticals, influencing adsorption, mobility, and oxidation susceptibility [31]. Weakly acidic drugs, such as diclofenac, ionize at neutral-to-basic conditions, decreasing interaction with catalyst surfaces and lowering removal efficiency. Hence, optimizing pH is not only a technical necessity but also an economic consideration, balancing degradation performance with energy input and electrode longevity [36].

5.2. Temperature effects on degradation efficiency and energy consumption

Temperature variations significantly impact EO–photocatalytic performance by altering chemical kinetics, solubility, and system stability. Higher temperatures generally accelerate reaction rates by increasing radical formation and pollutant mobility [30]. However, this enhancement can be offset by faster recombination of electron–hole pairs in photocatalysis, which reduces overall quantum efficiency [28].

Electrochemical oxidation benefits from moderate temperature increases, as mass transfer rates improve and electrode activity stabilizes, but excessive heating risks electrode scaling or material degradation [29]. Furthermore, elevated temperatures increase water evaporation and energy demand for system cooling, potentially offsetting gains in efficiency [35].

For photocatalysis, catalyst stability is critical. Materials like TiO_2 remain structurally robust under thermal stress, but doped semiconductors may undergo phase transitions that reduce performance [32]. Additionally, pharmaceutical degradation intermediates may volatilize at high temperatures, complicating removal pathways [34].

Thus, temperature optimization is context-specific: while warmer climates may reduce energy costs for heating, they increase stress on system components. Conversely, colder environments slow kinetics but provide more stable operation. The interplay between efficiency gains and energy expenditure highlights temperature as a key variable in EO–photocatalytic system design and deployment [36].

5.3. Light intensity and spectrum in photocatalytic activation

Light intensity and wavelength distribution directly control photocatalytic activation, determining electron–hole generation rates and radical production [31]. Higher light intensity increases the number of photons reaching catalyst surfaces, enhancing ROS yields, but only up to a saturation point where electron–hole recombination dominates [30]. Spectrum is equally critical: while TiO_2 primarily absorbs UV light (<387 nm), doped or modified catalysts can extend absorption into the visible range, improving efficiency under solar irradiation [28].

In hybrid systems, EO stabilizes photocatalysis by reducing recombination losses, making the process less sensitive to fluctuations in intensity [32]. For example, during low-light conditions, EO compensates by sustaining radical production at electrodes [33]. Conversely, under high-intensity irradiation, EO helps dissipate excess charge carriers, reducing thermal degradation of catalysts [29].

Environmental conditions further modulate light availability. Turbidity, suspended solids, and dissolved organic matter attenuate UV penetration, reducing photocatalytic efficiency [34]. This makes spectral tailoring of photocatalysts essential in real wastewater applications.

Table 2 summarizes the influence of pH, temperature, light intensity, and inorganic ions on EO–photocatalysis efficiency, providing a comparative perspective [36]. It illustrates that while light is a decisive driver for photocatalysis, its integration with EO significantly buffers environmental variability, ensuring more consistent treatment performance [35].

Table 2 Influence of environmental conditions on EO–photocatalysis efficiency

Environmental Factor	Influence on EO Efficiency	Influence on Photocatalysis Efficiency	Hybrid EO–Photocatalysis Response
pH	Strongly affects electrode stability and radical yield; acidic pH enhances hydroxyl radical formation but may corrode electrodes	Influences surface charge of catalysts (e.g., TiO_2) and pollutant ionization; optimal near neutral to slightly acidic	Hybrid system balances radical formation and catalyst activity, enabling broader effective pH range
Temperature	Higher temperatures can accelerate reaction kinetics but increase energy demand and electrode degradation	Enhances reaction rates but may cause catalyst deactivation; performance optimal in moderate ranges (20–35 °C)	Synergy improves degradation efficiency across wider temperature ranges, with moderate buffering of extremes
Light intensity & spectrum	Minimal direct impact except in photo-assisted EO setups	Critical driver for activation of photocatalysts; UV most effective, visible-light catalysts under development	EO supplements radical generation when light intensity is low, stabilizing efficiency under variable conditions
Inorganic ions (Cl^-, SO_4^{2-}, HCO_3^-, etc.)	Can generate reactive chlorine species (Cl·, ClO·) enhancing oxidation, but also cause electrode fouling	Some ions act as radical scavengers, reducing efficiency (e.g., bicarbonates quench ·OH)	Hybrid system offsets ion interference by producing multiple oxidants (·OH, Cl·, $SO_4^{\cdot -}$), sustaining efficiency

5.4. Presence of natural organic matter and inorganic ions

The presence of natural organic matter (NOM) and inorganic ions strongly influences EO–photocatalysis by competing for radicals, altering pollutant adsorption, and introducing side reactions. NOM, such as humic and fulvic acids, can act as radical scavengers, reducing the fraction available for pharmaceutical degradation [28]. At the same time, NOM absorbs UV light, diminishing photon penetration and decreasing photocatalytic activation [33]. However, partial oxidation of NOM may improve system stability by limiting fouling of electrodes and catalyst surfaces [30].

Inorganic ions exert complex effects. Chloride ions, for instance, react with hydroxyl radicals to form chlorine radicals, which are less reactive but more selective. This can reduce degradation efficiency for some pharmaceuticals while generating chlorinated by-products of concern [34]. Bicarbonate and carbonate ions also scavenge radicals, decreasing oxidative intensity [29]. On the other hand, sulfate ions may promote radical pathways by forming sulfate radicals under certain conditions [32].

Electrochemical systems are particularly sensitive to ion content, as electrode corrosion and scaling are accelerated in high ionic strength waters [35]. Photocatalysis also suffers reduced efficiency when ions occupy active sites on catalysts, blocking pollutant adsorption [31].

Despite these challenges, hybrid EO–photocatalysis mitigates some effects through redundancy in radical pathways. For example, while NOM reduces photocatalytic efficiency, EO maintains oxidative performance. Similarly, electrode activity counterbalances ion-related photon losses. Effective system design must therefore account for local water chemistry, tailoring electrodes and catalysts to minimize interference impacts [36].

6. Case studies and applications

6.1. Laboratory-scale pharmaceutical degradation studies

Laboratory-scale studies have provided crucial insights into the performance of EO–photocatalysis for pharmaceutical removal. Under controlled conditions, experiments demonstrate that integrated systems achieve higher degradation efficiencies compared to standalone EO or photocatalysis [36]. Diclofenac, carbamazepine, and sulfamethoxazole are among the most studied compounds, showing mineralization rates of over 90% in optimized hybrid setups [35]. The synergy between electron–hole separation in photocatalysis and anodic radical generation in EO underpins these results [39].

Small-scale reactors, often comprising TiO_2-coated electrodes coupled with boron-doped diamond (BDD) anodes, have been used to explore mechanistic pathways [37]. Results confirm the sequential degradation of complex pharmaceutical structures, with EO initiating aromatic ring cleavage and photocatalysis completing mineralization [34]. Furthermore, laboratory trials have demonstrated resilience to varying influent concentrations, showing that hybrid systems remain effective even at environmentally relevant trace levels [41].

Although these studies validate the scientific rationale of integration, they are typically conducted in synthetic waters with minimal matrix interference [40]. Hence, while laboratory-scale data provide mechanistic clarity, their direct applicability to real wastewater remains limited. Nonetheless, these controlled trials establish the foundation for scaling to pilot and full-scale systems [42].

6.2. Pilot-scale integrated systems

Pilot-scale implementations bridge the gap between laboratory findings and full operational deployment. Hybrid EO–photocatalysis systems tested in semi-realistic environments, such as hospital effluents and pretreated municipal wastewater, show promising results [34]. For instance, reactors incorporating UV-irradiated TiO_2 photocatalysts combined with BDD anodes achieved over 80% removal of non-steroidal anti-inflammatory drugs (NSAIDs) within treatment times compatible with operational workflows [36].

Pilot reactors have also demonstrated the ability to handle variable loads, simulating fluctuations typical of municipal inflows [38]. Importantly, operational studies indicate that energy consumption is significantly reduced in hybrid configurations compared to standalone EO, as the photocatalytic component reduces anodic current requirements [40]. System modularity has been a key design feature, allowing reactors to be adapted for different effluent volumes and pharmaceutical mixtures [35].

These pilot trials also reveal challenges, including electrode fouling and reduced photocatalytic efficiency under high turbidity [39]. Nonetheless, engineering innovations, such as electrode coatings and visible-light-active catalysts, have improved resilience [37]. By highlighting both opportunities and constraints, pilot studies demonstrate the feasibility of transitioning from theoretical synergy to practical application, while clarifying optimization needs for larger-scale integration [41].

6.3. Real wastewater treatment applications

Full-scale applications of EO–photocatalysis remain limited but provide compelling evidence of feasibility. Trials in pharmaceutical industry effluents and municipal wastewater treatment plants demonstrate effective removal of priority pollutants, with mineralization levels of 70–85% under optimized conditions [38]. Hybrid systems are particularly valuable in hospital wastewater treatment, where high loads of antibiotics and contrast agents persist despite conventional processes [42].

These systems have been deployed in continuous-flow configurations, where EO pre-oxidizes contaminants and photocatalysis ensures mineralization, thus mitigating accumulation of toxic intermediates [35]. Real wastewater applications, however, highlight the influence of environmental conditions such as ionic strength, pH fluctuations, and natural organic matter, which reduce efficiency compared to laboratory or pilot setups [36].

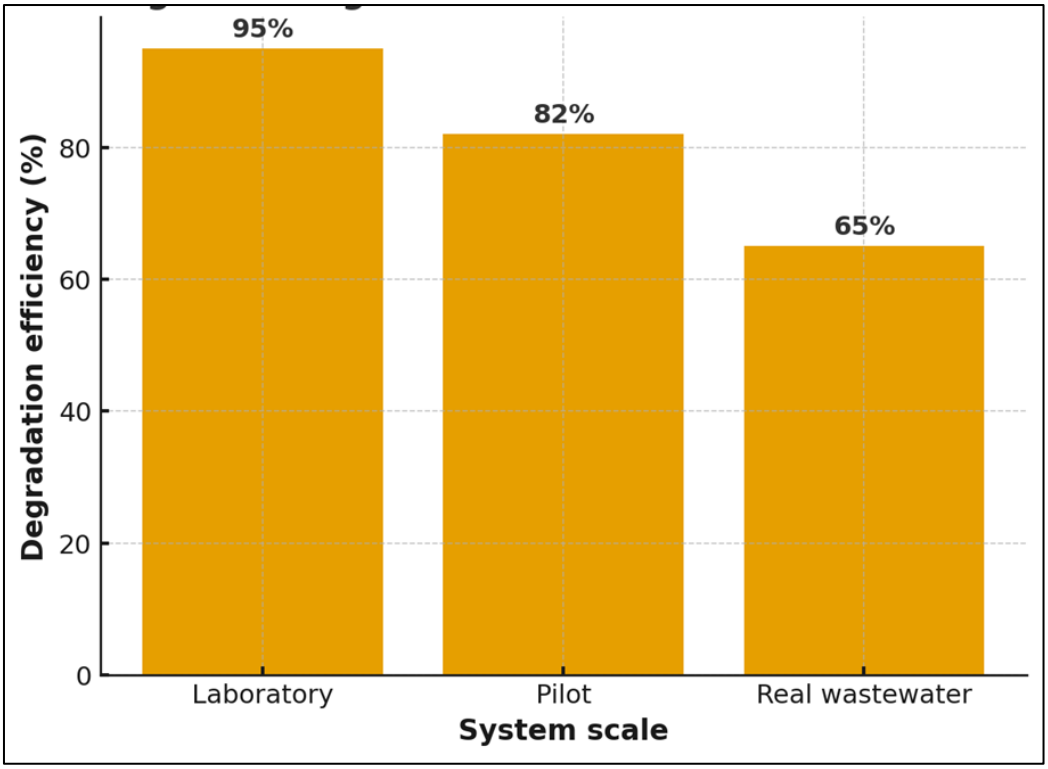

Figure 3 Degradation efficiencies across scales

Figure 3 compares degradation efficiencies across laboratory, pilot, and real wastewater systems, illustrating the performance decline under real-world conditions [39]. While laboratory experiments often exceed 90% removal, real effluents typically yield lower but still significant outcomes, reinforcing the importance of system adaptation [41]. These case studies affirm that EO–photocatalysis can contribute meaningfully to wastewater treatment but require tailored designs to address site-specific challenges [34].

6.4. Comparative results with other AOP hybrids

EO–photocatalysis has been compared with other hybrid AOPs, such as ozonation–photocatalysis, Fenton-based oxidation, and electro-Fenton systems. While Fenton-based processes excel in rapid degradation of certain pharmaceuticals, they require continuous addition of reagents and produce sludge requiring disposal [37]. Ozonation–photocatalysis, though effective, incurs high operational costs due to ozone generation and safety concerns [38].

In contrast, EO–photocatalysis offers greater sustainability by eliminating the need for external reagents and relying on electricity and light as primary inputs [36]. Comparative studies confirm that EO–photocatalysis achieves higher mineralization levels for recalcitrant compounds such as carbamazepine, which resists degradation in ozonation and Fenton systems [40].

Energy efficiency also favors EO–photocatalysis when optimized. Although EO alone is energy-intensive, coupling with photocatalysis reduces electricity demand per unit pollutant removed [42]. Additionally, the hybrid's modularity and adaptability to renewable energy sources enhance scalability relative to chemical-dependent processes [35].

While challenges such as electrode stability and photocatalyst deactivation persist, comparative evidence positions EO–photocatalysis as a leading candidate among hybrid AOPs. These strengths underscore its potential for integration into mainstream wastewater treatment frameworks, especially under conditions demanding sustainable, chemical-free solutions [39].

7. Economic, environmental, and social perspectives

7.1. Cost-benefit considerations of hybrid systems

The economic feasibility of EO–photocatalysis hinges on balancing capital costs, operational efficiency, and long-term savings. Electrochemical oxidation requires expensive electrodes such as boron-doped diamond, while photocatalysis demands high-quality semiconductor materials [40]. These initial expenses are offset by the absence of chemical additives, reduced sludge disposal costs, and adaptability to renewable energy integration [42].

Comparative studies demonstrate that hybrid systems can lower energy consumption by 20–30% relative to EO alone, due to photocatalysis sharing the oxidative burden [44]. Furthermore, modular designs allow scaling based on effluent load, reducing over-investment in underutilized infrastructure [46]. Yet uncertainties in electrode longevity and catalyst regeneration costs persist, creating financial risks for utilities [48].

Economic evaluations increasingly suggest that when factoring avoided environmental damages, public health benefits, and regulatory compliance, EO–photocatalysis can outperform conventional treatment expansions [50]. The challenge lies in translating these long-term savings into financing models attractive to municipalities and industry [45].

7.2. Environmental sustainability and circular economy implications

From a sustainability perspective, EO–photocatalysis aligns with the principles of the circular economy by minimizing reliance on consumable reagents and enabling energy recovery pathways [43]. Unlike Fenton-based oxidation or ozonation, which generate residual sludge or chemical by-products requiring disposal, EO–photocatalysis primarily consumes electricity and light, reducing secondary waste streams [40]. This supports closed-loop wastewater treatment, where treated effluents can be reused for agricultural or industrial purposes, contributing to water circularity [47].

Environmental assessments highlight the ability of hybrid systems to degrade a broad spectrum of pharmaceuticals, mitigating risks of antimicrobial resistance and endocrine disruption [41]. By preventing pollutant accumulation, these technologies reduce long-term ecological stress and safeguard biodiversity in receiving waters [49]. The modular and renewable-energy-compatible design also lowers carbon footprints compared to energy-intensive chemical alternatives [44].

However, sustainability must be evaluated holistically. Energy-intensive operations in regions reliant on fossil fuel-based grids may undermine climate mitigation goals [42]. Additionally, resource-intensive manufacturing of electrodes and catalysts raises concerns about life-cycle sustainability [46]. Future development must therefore emphasize recyclable catalyst materials, low-carbon electricity integration, and system optimization to ensure EO–photocatalysis not only removes pollutants but also aligns with broader climate and resource efficiency goals [48].

7.3. Public acceptance and governance issues

The adoption of EO–photocatalysis extends beyond technical performance to issues of governance and public trust. Public perception of wastewater reuse remains cautious, especially when linked to pharmaceutical residues [45]. Clear communication about safety, effectiveness, and sustainability is essential to securing societal acceptance [50].

Governance structures must also evolve to integrate hybrid AOPs into regulatory frameworks. Current guidelines often emphasize conventional technologies, leaving advanced systems without standardized approval pathways [42]. Furthermore, data transparency regarding treatment efficacy and by-product risks is vital to build regulatory credibility [47].

Collaborative governance, where municipalities, industry, and communities participate in decision-making, enhances legitimacy and accelerates adoption [40]. Pilot projects with public engagement components have shown greater acceptance compared to top-down implementations [43]. Ultimately, successful deployment of EO–photocatalysis depends on embedding technological innovation within socially inclusive and transparent governance systems that balance risk, cost, and environmental priorities [46].

8. Challenges and future directions

8.1. Energy requirements and operational costs

Energy consumption remains one of the most persistent challenges for EO–photocatalysis. Electrochemical oxidation is inherently power-intensive, requiring stable voltage and current densities to sustain radical generation [45]. Photocatalysis, while theoretically less demanding, necessitates continuous illumination—often relying on artificial UV sources that increase operating costs when natural sunlight is insufficient [47]. This dual dependency raises concerns for scalability, particularly in regions where electricity prices are volatile or renewable supply is limited [49].

Studies demonstrate that energy consumption can reach 5–15 kWh/m^3 for hybrid EO–photocatalysis, surpassing thresholds considered economically viable for municipal-scale adoption [46]. While energy recovery techniques, such as coupling with photovoltaic panels or waste heat capture, show promise, their integration remains experimental [48]. Another economic constraint is the need for continuous system monitoring and control, which adds to both capital and operating costs [50].

Life-cycle cost analyses indicate that despite higher upfront investment, hybrid systems could achieve long-term savings through reduced chemical use, minimal sludge disposal, and extended reuse of treated effluents [45]. Still, achieving competitive operating costs will require significant optimization of electrode materials, photocatalyst efficiency, and integration with low-carbon energy sources [47].

8.2. Electrode degradation and catalyst reusability

Electrode stability represents another critical bottleneck. Boron-doped diamond (BDD) and dimensionally stable anodes (DSA) provide high oxidative efficiency, yet both suffer from gradual deactivation due to scaling, fouling, and mechanical wear [49]. This degradation reduces system efficiency and necessitates frequent replacement, undermining cost-effectiveness [45].

Photocatalysts, such as TiO_2, similarly face challenges of deactivation through agglomeration, surface fouling by natural organic matter, and photonic inefficiency in visible light ranges [47]. Catalyst leaching can also introduce secondary contamination, raising environmental and regulatory concerns [46]. Efforts to improve durability include doping with metals or non-metals, surface modifications, and immobilization on conductive supports, but many strategies remain confined to laboratory testing [50].

The reusability of electrodes and catalysts determines the sustainability of hybrid systems. Recyclable catalyst coatings and self-healing electrode materials represent promising frontiers [48]. However, pilot-scale studies reveal discrepancies between laboratory durability and real wastewater environments, where complex matrices accelerate wear [49]. Thus, enhancing material lifetimes without compromising efficiency is essential for transitioning EO–photocatalysis into practical water treatment applications [45].

8.3. Need for multi-pollutant and complex matrix testing

Most research on EO–photocatalysis has focused on degrading single pharmaceutical compounds under controlled laboratory conditions [46]. While valuable for mechanistic understanding, such studies fail to capture the complexity of real wastewater, where pharmaceuticals co-occur with pesticides, industrial chemicals, and natural organic matter [47]. Interactions between these contaminants may suppress degradation, produce competitive radical scavenging, or generate new by-products with unknown toxicity [48].

Testing under realistic conditions is critical to assess the robustness of hybrid systems [49]. For example, hospital wastewater contains mixtures of antibiotics, contrast agents, and disinfectants, presenting a matrix that challenges both EO and photocatalysis individually [50]. The synergistic potential of hybridization must be validated under such conditions, with attention to pollutant mixtures, seasonal variability, and fluctuating hydraulic loads [45].

Additionally, ecotoxicological assays should accompany chemical monitoring to confirm that degradation eliminates toxicity rather than transferring it to transformation products [46]. Expanding research to include multi-pollutant and complex matrix conditions will provide the credibility needed for regulators and utilities to adopt EO–photocatalysis as a mainstream treatment option [47].

8.4. Pathways for integrating with smart water treatment systems

Looking forward, integration with digital and smart water treatment infrastructures offers a pathway to overcoming several current challenges [45]. Advanced sensors can monitor parameters such as pH, conductivity, and radical concentrations in real time, enabling adaptive process control [49]. Artificial intelligence and machine learning algorithms are increasingly applied to optimize operating conditions dynamically, reducing energy demand while maximizing degradation efficiency [48].

The combination of EO–photocatalysis with smart grids also enables alignment with renewable energy availability, reducing carbon intensity and operational costs [46]. Predictive maintenance systems could further mitigate electrode and catalyst degradation by forecasting fouling and scheduling interventions before failures occur [47].

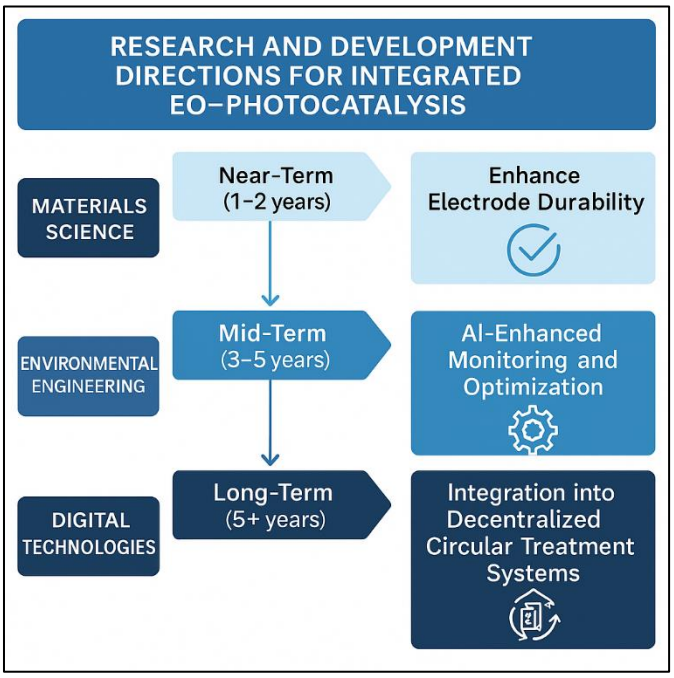

Figure 4 A roadmap of research and development directions for integrated EO–photocatalysis, emphasizing the convergence of materials science, environmental engineering, and digital technologies [50]. This roadmap highlights staged priorities: near-term improvements in electrode durability, mid-term optimization through AI-enhanced monitoring, and long-term integration into decentralized, circular-economy-oriented treatment systems [49]

Such smart-enabled hybrid treatment units could provide modular, low-footprint solutions adaptable to both urban utilities and rural decentralized contexts [45]. Embedding intelligence and automation into EO–photocatalysis will ultimately determine its scalability and resilience in future wastewater management paradigms [47].

9. Conclusion

9.1. Synthesis of key findings

This review has highlighted the global urgency of addressing pharmaceutical residues in aquatic environments and the potential of hybrid electrochemical oxidation (EO)–photocatalysis systems to provide sustainable solutions. Conventional wastewater treatment processes remain inadequate for persistent pharmaceuticals, leading to ecological imbalances and public health risks. Advanced oxidation processes (AOPs) have emerged as promising alternatives, yet both EO and photocatalysis, when applied independently, face challenges of energy consumption, material degradation, and limited applicability across diverse wastewater matrices.

The combined EO–photocatalysis approach offers a mechanistically synergistic pathway by coupling electrochemically generated oxidants with light-activated radical production, enhancing pollutant degradation while reducing process inefficiencies. Studies demonstrate its promise in removing a wide spectrum of pharmaceuticals under controlled laboratory conditions, with growing but limited pilot-scale validation. The analysis of environmental factors—including

pH, temperature, light, and background organic matter—underscored how operational settings critically modulate outcomes.

Overall, EO–photocatalysis represents a bridge between technological innovation and environmental stewardship. However, its deployment requires overcoming barriers in cost, material durability, multi-pollutant resilience, and system integration. The trajectory ahead lies in embedding this hybrid approach within smart, sustainable water infrastructures that balance technical feasibility, economic efficiency, and societal trust.

9.2. Practical implications for wastewater treatment plants

For wastewater treatment plants, integrating EO–photocatalysis offers both opportunities and operational challenges. On the opportunity side, hybrid systems can serve as tertiary polishing units capable of targeting recalcitrant pharmaceutical residues beyond the reach of conventional biological and physicochemical treatments. This makes them highly relevant in contexts where effluent reuse is prioritized, such as agricultural irrigation, industrial recycling, and indirect potable reuse schemes. By minimizing residual pharmaceuticals, plants can enhance compliance with emerging regulatory standards while improving public perception of treated water safety.

However, practical deployment necessitates careful economic and operational planning. Treatment facilities must account for the higher energy requirements of EO–photocatalysis, investing in renewable energy integration to maintain sustainability. Electrode and catalyst durability represent recurrent maintenance considerations, requiring procurement strategies that ensure long-term system reliability. Additionally, integration into existing plant workflows will demand digital monitoring systems, capable of real-time process optimization and predictive maintenance.

Another practical implication is the need for pilot-scale demonstration within individual treatment contexts. Wastewater compositions vary widely, and site-specific testing will be critical to validate efficiency and identify adjustments to process parameters. By taking incremental steps, wastewater plants can progressively transition toward hybrid AOP adoption without destabilizing operations or budgets.

9.3. Research–practice collaboration roadmap

Advancing EO–photocatalysis from a promising laboratory innovation to a widely adopted treatment option will require close collaboration between researchers, industry practitioners, regulators, and communities. The first step in this roadmap is expanding applied research beyond single-compound degradation studies to multi-pollutant, real wastewater environments. This will provide robust data to guide practical implementation and support regulatory confidence.

Parallel to this, engineers and materials scientists must focus on improving electrode and catalyst durability while reducing production costs. Collaborative consortia between universities, manufacturers, and utilities could accelerate the translation of novel materials into pilot-ready technologies. Equally, computer scientists and environmental engineers must jointly develop AI-driven monitoring and control systems, allowing smart adaptation of hybrid processes to dynamic wastewater conditions.

On the practice side, utilities should be engaged as co-researchers rather than end-users, participating in pilot projects that align innovation with operational needs. Regulators and policymakers should establish enabling frameworks, offering incentives and clear standards that promote experimentation while ensuring environmental safeguards. Communities, as ultimate beneficiaries, must be involved in shaping narratives of trust and acceptance around pharmaceutical removal and water reuse.

Together, these collaborative pathways chart a pragmatic course toward mainstreaming EO–photocatalysis as a cornerstone of future sustainable wastewater treatment systems.

Compliance with ethical standards

Disclosure of conflict of interest

No conflict of interest to be disclosed.

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