

Advanced Oxidation Processes for Water Treatment: A Comprehensive Review

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Abstract. Stubborn trace organics—so-called micropollutants—are steadily tainting water bodies, endangering both ecosystems and public health. Because classic treatment trains scarcely touch these compounds, next-generation removal technologies are urgently needed. Advanced Oxidation Processes (AOPs) have stepped to the forefront as a potent counter-strategy. They produce, in situ, an arsenal of indiscriminate $\bullet\text{OH}$ and other ROS that rapidly dismantle trace organics, driving them toward innocuous products or full mineralization. This review delivers an integrated roadmap to AOP fundamentals, reaction pathways, and typologies—spanning ozone, H_2O_2 , photocatalytic, sonochemical, and electrochemical variants. The application of AOPs in water treatment is critically examined, with specific examples from scientific literature illustrating their efficacy against pharmaceuticals, pesticides, and industrial chemicals. Finally, the review discusses the current challenges, such as energy consumption, formation of toxic by-products, and operational costs, and outlines promising future research directions, including the development of novel catalysts, hybrid systems, energy-efficient reactor designs, and process control strategies for full-scale implementation.

Keywords: *Advanced Oxidation Processes, Hydroxyl Radical, Water Treatment, Micropollutants, Wastewater, Catalysis, Ozonation, Photocatalysis.*

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1 Introduction

Water scarcity and contamination top the 21st-century threat list. Alarm has intensified as pharmaceuticals, personal-care residues, endocrine disruptors, and pesticides are routinely detected—at ng L^{-1} to $\mu\text{g L}^{-1}$ levels—in surface, ground, and even tap water [1]. Even at trace levels, these micropollutants can wreak havoc on aquatic ecosystems and may inflict chronic human-health impacts, from antibiotic resistance to hormonal interference.

Built to strip suspended solids, bulk organics, nutrients, and pathogens, conventional plants falter against POPs—shortfall that has catapulted Advanced Oxidation Processes to the spotlight. The concept of AOPs was first introduced in the 1980s for drinking water treatment [2]. AOPs are a set of chemical treatment procedures designed to remove organic and inorganic materials from water and wastewater through oxidation reactions. The core mechanism involves the generation of highly reactive species, most notably the hydroxyl radical ($\bullet\text{OH}$) (Figure 1).

The hydroxyl radical is an extremely powerful oxidant (standard reduction potential $E^\circ = 2.8 \text{ V}$), second only to fluorine. It attacks organics almost without bias at diffusion-limited speeds via four main routes: H-abstraction, electrophilic addition, electron transfer, and self-combination (Buxton *et al.*, 1988). The outcome is a stepwise disintegration of complex pollutants into simpler, less toxic fragments that are ultimately converted to CO_2 and H_2O —i.e., full mineralization.

This review aims to provide a systematic and detailed examination of AOPs. It begins by explaining the fundamental chemistry of $\bullet\text{OH}$ generation and reaction kinetics [3]. Subsequently, it classifies and describes the major types of AOPs, supported by schematic diagrams. A significant portion is dedicated to their practical application in water treatment, illustrated with concrete examples from recent literature. The review concludes with a critical analysis of the current limitations and a forward-looking perspective on the research needed to make AOPs more efficient, cost-effective, and widely applicable [4].

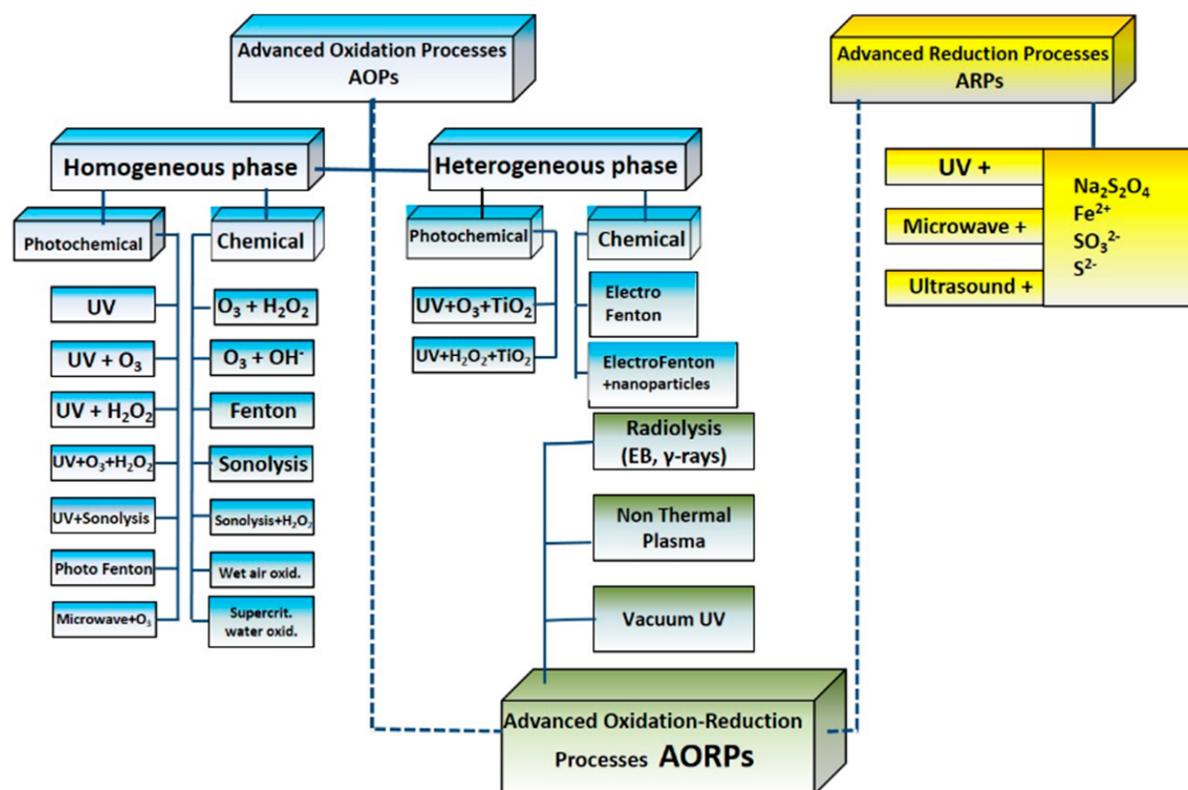


Figure 1. Various process technologies in the ATP realm.

2. Fundamental Principles of AOPs

AOPs represent a cutting-edge toolbox engineered to eradicate organic contaminants from both water bodies and wastewater streams [5]. These processes utilize oxidants such as O_3 , H_2O_2 , UV, and photocatalysts to generate highly reactive free radicals. Through oxidation reactions, AOPs degrade and break down organic pollutants, thereby achieving water purification (Figure 2).

Over the past few decades, AOP technology has been extensively researched and applied. Key research focuses include the design and improvement of catalysts, optimization and control of process parameters, and investigation of catalytic reaction mechanisms. In terms of catalysts, researchers have widely employed various catalytic materials to enhance the efficiency of AOPs. Common catalysts include titanium dioxide (TiO_2) [5], ferrites [6], and transition metal catalysts [7]. By adjusting the composition, morphology, and surface properties of catalysts, their catalytic activity and stability can be enhanced, thereby improving reaction efficiency.

The optimization and control of process parameters are crucial for the performance of AOP technology. Light intensity, pH, and oxidant dose are fine-tuned to the pollutant spectrum and water matrix to maximize removal rates. Additionally, the catalytic reaction mechanism of AOPs is a key area of research. By characterizing and analyzing intermediate and final products generated during the reaction, researchers can explore the generation,

transformation, and quenching processes of active free radicals. This deepens the understanding of reaction mechanisms and guides the optimization and improvement of the technology [8].

Currently, AOP technology is widely applied in water treatment and environmental remediation. It is considered an effective method for removing organic pollutants, suitable for various water quality conditions, and offers high treatment efficiency. However, AOP technology still faces challenges such as catalyst stability and regeneration issues, as well as the feasibility of engineering applications, which require further research and exploration.

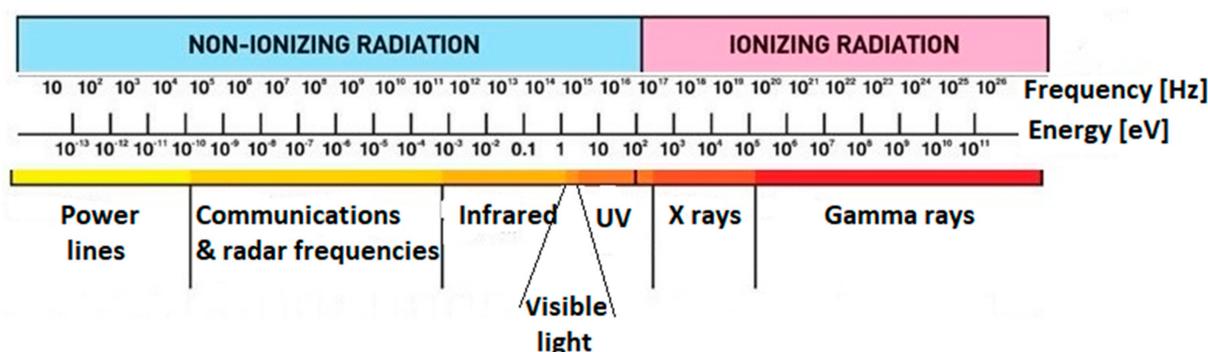
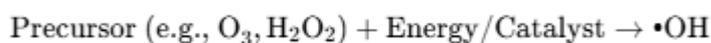


Figure 2 Non-ionizing and ionizing radiation ranges: frequency and energy.

2.1 The Hydroxyl Radical ($\bullet\text{OH}$) and its Generation

The efficacy of any AOP hinges on the efficient and sustained generation of $\bullet\text{OH}$. The radical can be generated by using a single oxidant (e.g., O_3 , H_2O_2) under specific conditions or, more commonly, by combining oxidants, catalysts, and energy sources (e.g., UV light, ultrasound, electricity) [9]. The general reaction for $\bullet\text{OH}$ generation can be represented as:



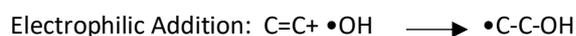
The primary generation pathways in different AOPs are detailed in the following sections.

2.2 Reaction Mechanisms of $\bullet\text{OH}$ with Organic Pollutants

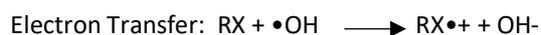
Once generated, $\bullet\text{OH}$ attacks organic pollutants (RH) through several mechanisms:



This is common for aliphatic compounds, generating carbon-centered radicals ($\text{R}\bullet$) that subsequently react with oxygen.



This is the dominant pathway for unsaturated aromatics (e.g., phenol, benzene) and alkenes, forming hydroxylated cyclohexadienyl radicals.



This occurs primarily with halogenated compounds or inorganic ions, leading to the formation of radical cations.

These first steps ignite a cascading radical chain that successively unravels the parent contaminant. The ultimate goal is complete mineralization, but often, the process stops at intermediate degradation products [10].

3. Classification of Advanced Oxidation Processes

AOPs are grouped by phase behavior—homogeneous or heterogeneous—and by the energy source that triggers ROS generation [11]. The following sections detail the most prominent AOPs (Figure 3).

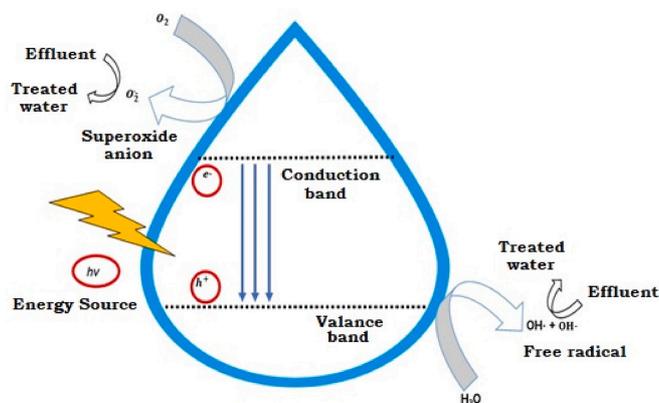


Fig. 1. Mechanism of advanced oxidation process.

3.1 Ozone-Based Processes

Ozone is intrinsically powerful ($E^\circ = 2.07 \text{ V}$), yet its attack on many organics is both selective and sluggish. The power of ozone-based AOPs lies in the promotion of ozone decomposition to yield $\bullet\text{OH}$.

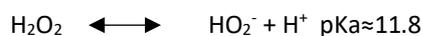
3.1.1 Ozone at High pH (O_3/OH^-)

In alkaline conditions, the hydroxide ion (OH^-) initiates the decomposition of ozone, leading to a chain reaction that produces $\bullet\text{OH}$ (Staehelin and Hoigné, 1982).



3.1.2 Ozone/Hydrogen Peroxide ($\text{O}_3/\text{H}_2\text{O}_2$ or Peroxone)

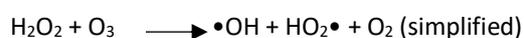
This combination remains one of the most intensively researched and deployed AOP configurations worldwide. Hydrogen peroxide (H_2O_2) acts as a promoter for ozone decomposition, significantly accelerating $\bullet\text{OH}$ generation.



The Peroxone process is highly effective and is often used for groundwater remediation and drinking water treatment.

3.1.3 Ozone/Ultraviolet Radiation (O_3/UV)

UV radiation photolyzes ozone in water to produce H_2O_2 , which then reacts with residual ozone to form $\bullet\text{OH}$.

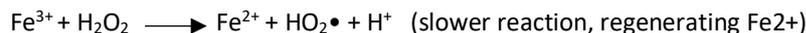
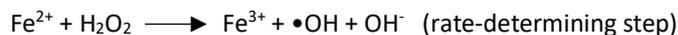


This combination is synergistic and can be more effective than either O₃ or UV alone.

3.2 Hydrogen Peroxide-Based Processes

3.2.1. Fenton and Photo-Fenton Processes

The classic Fenton reaction, discovered in the 1890s, uses ferrous ions (Fe²⁺) to catalyze the decomposition of H₂O₂, producing •OH under acidic conditions (pH 2.5-3.5).



Shining UV-Vis light on the classic Fenton cocktail accelerates the cycle, giving rise to the Photo-Fenton variant. Light irradiation helps regenerate Fe²⁺ from Fe³⁺ complexes (e.g., Fe(OH)²⁺) more efficiently, leading to a higher •OH production rate and allowing for lower iron concentrations (Pignatello et al., 2006).



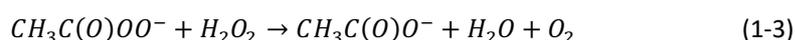
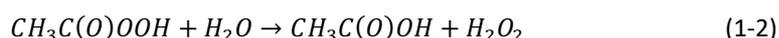
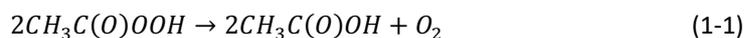
The Photo-Fenton process is considered one of the most cost-effective AOPs for industrial wastewater treatment, especially in regions with high solar irradiation (solar photo-Fenton).

3.2.2. PAA-Based Advanced Oxidation Processes (AOPs)

As an efficient hybrid disinfectant, PAA (peracetic acid) is composed of hydrogen peroxide (H₂O₂), water, and acetic acid. Its strong oxidizing capability stems from its high redox potential (E_o = 1.96 V), which exceeds that of H₂O₂ (E_o = 1.8 V) and chlorine dioxide (E_o = 1.5 V) [12], enabling PAA to exhibit effective inactivation against a wide range of microorganisms. PAA offers advantages such as a high redox potential, high oxidation efficiency, and low harmful byproduct formation [49]. Furthermore, conformational analysis of PAA reveals weak acidic behavior caused by intramolecular hydrogen bonding. This weak acidity benefits the oxidation process, as the intramolecular hydrogen bonds stabilize protonated PAA, and the protonated form possesses stronger oxidizing power than the deprotonated form [12].

Once triggered, PAA unleashes an array of ROS—•OH (2.72 V), •CH₃, peracyl (CH₃C(O)•, 2.24 V) and peroxyacyl (CH₃C(O)OO•, 1.60 V) radicals, among others [51]. In complex water matrices containing constituents like natural organic matter and bicarbonate ions (HCO₃⁻), PAA-based AOPs may demonstrate superior performance compared to other AOPs.

PAA decomposition occurs via two primary pathways: non-radical decomposition and radical decomposition. Non-radical decomposition includes the self-decomposition of PAA and its reaction with water (Equations (1-1) and (1-2)), while H₂O₂ present in the system can react with PAA anions (Equation (1-3)). Radical decomposition, which is the desired pathway in AOPs requiring activation techniques, includes energy activation, metal activation, and catalyst activation.

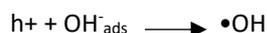


3.3 Heterogeneous Photocatalysis

Heterogeneous photocatalysis employs a solid semiconductor catalyst, most famously titanium dioxide (TiO₂), which is activated by UV light. Absorption of a photon whose energy exceeds the TiO₂ band-gap—≈3.2 eV for anatase, λ < 388 nm—excites an electron from the valence to the conduction band, generating a hole (h⁺) in the VB [14].



These photogenerated carriers diffuse to the surface where the hole acts as a potent oxidant: it can attack organics directly or, more often, extract H from adsorbed $\text{H}_2\text{O}/\text{OH}^-$ to release $\bullet\text{OH}$. Meanwhile, the electron reduces O_2 to superoxide ($\text{O}_2^{\bullet-}$), a precursor that is quickly converted into additional $\bullet\text{OH}$.



A major research focus is on modifying TiO_2 (e.g., doping with nitrogen, carbon) or developing new catalysts (e.g., ZnO , WO_3 , $g\text{-C}_3\text{N}_4$) to enable activation by visible light, which constitutes a larger portion of the solar spectrum.

3.4 Other AOPs

3.4.1 Sonolysis (Ultrasound)

Sonicating water at 20 kHz–1 MHz triggers acoustic cavitation: micro-bubbles explosively form, expand, and implode, creating hot spots of several thousand kelvin and hundreds of atmospheres. Under these conditions, water molecules undergo pyrolysis to form $\bullet\text{OH}$ and $\text{H}\bullet$ atoms.

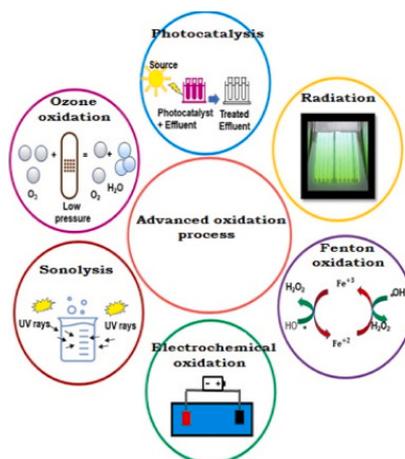


Fig. 2. Types of advanced oxidation process.



The $\bullet\text{OH}$ generated inside the bubbles can react with volatile pollutants that have diffused into the bubble, while those released into the bulk liquid can degrade non-volatile compounds. Sonolysis is often combined with other AOPs (e.g., sonophoto-Fenton) for synergistic effects.

3.4.2 Electrochemical Advanced Oxidation Processes (EAOPs)

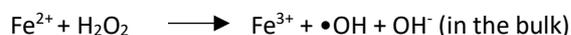
EAOPs generate $\bullet\text{OH}$ electrochemically. There are two main types:

1. Anodic Oxidation: Surface-adsorbed $\bullet\text{OH}$ are generated directly on the anode (M) via discharge of water molecules.



The nature of the anode material is critical. Non-active anodes such as BDD yield loosely bound $\bullet\text{OH}$ that desorb readily, driving near-complete mineralization. (Brillas et al., 2009).

2. Electro-Fenton: H_2O_2 is generated in situ by the cathodic reduction of dissolved oxygen, while Fe^{2+} is added as a catalyst. This creates a continuous Fenton reaction in the bulk solution.



EAOPs offer excellent control and avoid the need for chemical storage and transport.

4. Applications of AOPs in Water Treatment: Literature Examples

AOPs have been extensively researched and applied for the degradation of various micropollutants in different water matrices. The following examples illustrate their effectiveness.

4.1 Removal of Pharmaceuticals

AOPs have been exhaustively tested and deployed to eliminate a broad spectrum of micropollutants across diverse water matrices. The following examples illustrate their effectiveness [15].

Example 1: $\text{O}_3/\text{H}_2\text{O}_2$ vs. Carbamazepine. Carbamazepine (CBZ), an antiepileptic drug, is notoriously resistant to conventional treatment. Huber et al. (2003) showed that ozonation efficiently strips carbamazepine from treated wastewater. The study found that the reaction was primarily due to direct reaction with O_3 . However, the $\text{O}_3/\text{H}_2\text{O}_2$ process (Peroxone) was shown to be even more efficient, especially in waters with high alkalinity that scavenge $\bullet\text{OH}$, because H_2O_2 promotes a faster and more complete $\bullet\text{OH}$ -mediated oxidation pathway, leading to greater mineralization.

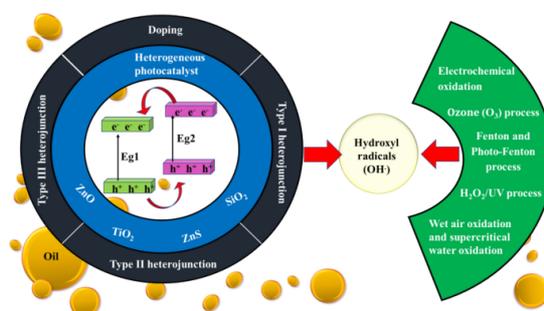


Fig. 5 Photocatalytic process for wastewater treatment

Example 2: $\text{UV}/\text{H}_2\text{O}_2$ vs. Diclofenac. Diclofenac, a common anti-inflammatory drug, is frequently detected in surface waters. Real et al. (2016) assessed $\text{UV}/\text{H}_2\text{O}_2$ for diclofenac abatement; adding H_2O_2 not only accelerated decay but also suppressed formation of toxic photoproducts compared with UV alone. With a near-diffusion-controlled rate constant ($\sim 10^{10} \text{ M}^{-1} \text{ s}^{-1}$) for diclofenac + $\bullet\text{OH}$, $\text{UV}/\text{H}_2\text{O}_2$ is exceptionally efficient for this target [16-20].

- Example 3: Solar Photo-Fenton vs. Antibiotics. The removal of antibiotics is critical to combat the spread of antibiotic resistance genes. Klammerth et al. (2010) treated secondary effluent spiked with a mixture of antibiotics (e.g., sulfamethoxazole, trimethoprim) using solar photo-Fenton. Under real sunlight in a pilot CPC, >90 % of the target micropollutants were eliminated. Optimizing the $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratio and iron redox speciation to operate near neutral pH was identified as the key to practical wastewater implementation [21-24].

4.2 Degradation of Pesticides

Example 4: TiO_2 Photocatalysis vs. Atrazine. Atrazine is a widespread herbicide that is persistent in the environment. Pelizzetti et al. (1990) were among the first to demonstrate the complete mineralization of atrazine to CO_2 , Cl^- , and NH_4^+ using UV-illuminated TiO_2 suspensions. The study meticulously identified the intermediate degradation products, illustrating the stepwise breakdown of the complex triazine ring structure by $\bullet\text{OH}$ attack [25-27].

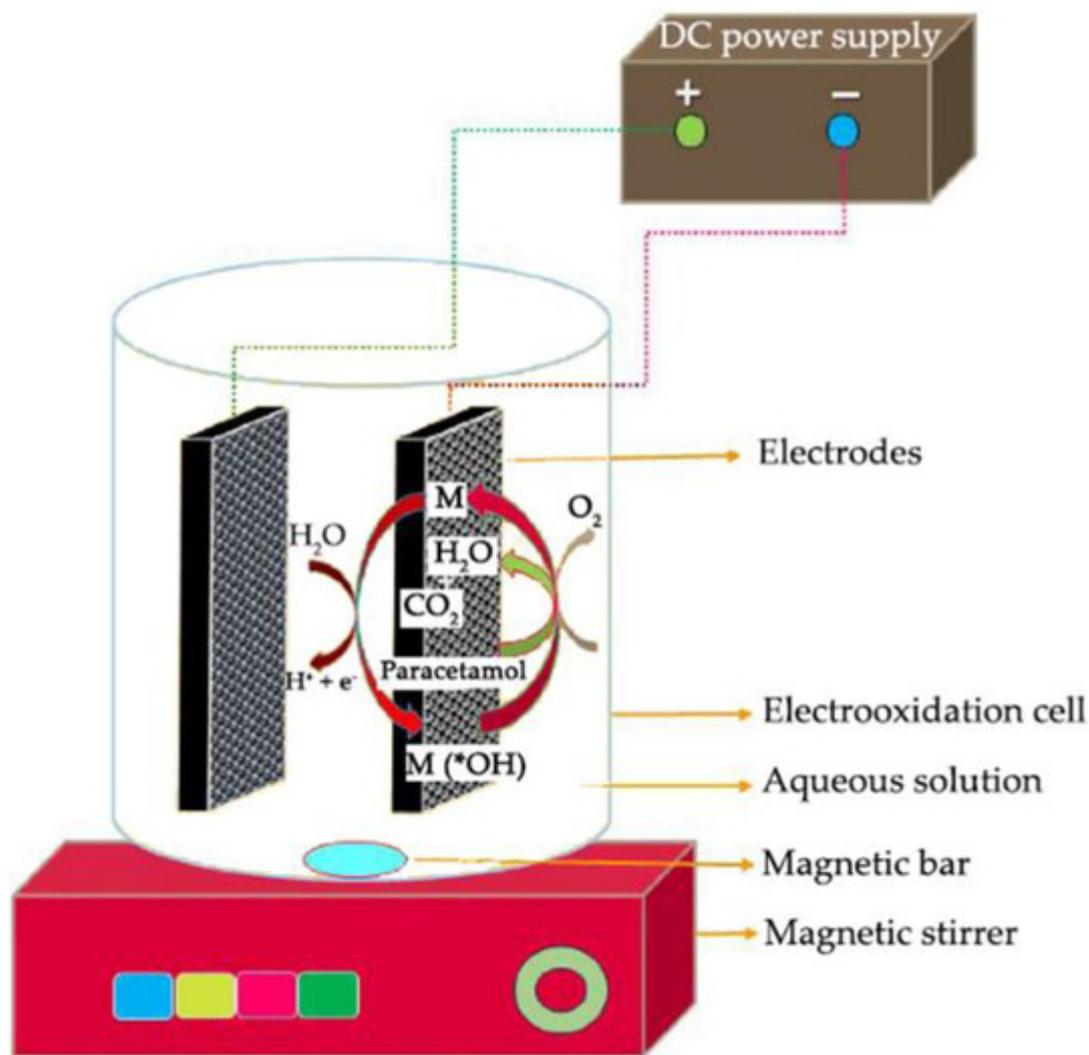


Figure 2. Diagram of the electrochemical reactor, using a glass beaker. The solution was stirred continuously throughout the process with a magnetic bar on a magnetic stirrer. The graphite anode was used as a working anode and a distance of 2 mm.

Example 5: Electro-Fenton vs. Chlorophenols. Pentachlorophenol (PCP) is a toxic wood preservative. Brillas et al. (2003) deployed an electro-Fenton cell equipped with a carbon-felt cathode and Pt anode for pentachlorophenol destruction; the set-up produced H_2O_2 in situ, and dosing Fe^{2+} triggered fast $\bullet\text{OH}$ formation. Near-total mineralization was attained, chloride ions were stoichiometrically released, and a stepwise route—sequential dechlorination followed by ring cleavage—was proposed [27-30].

4.3 Treatment of Industrial Wastewater

Example 6: For toxic, high-strength industrial effluents that defy biological treatment, thermal options such as Wet Air Oxidation (WAO—high-pressure O₂ at elevated temperature) or its catalytic variant (CWAO) offer a viable oxidative route. Mishra et al. (1995) reviewed the application of WAO and its catalytic variant (CWAO) for wastewaters from chemical and pharmaceutical industries. The addition of heterogeneous catalysts (e.g., supported noble metals) allows the process to operate at lower temperatures and pressures, significantly reducing operating costs while achieving high TOC removal [31, 32].

5. Challenges and Future Perspectives

Yet proven performance is only half the battle; broad adoption of AOPs is still hampered by a set of hurdles that define tomorrow's research agenda.

5.1 Current Challenges

Energy and Chemical Consumption: Many AOPs (e.g., UV-based, ozonation, sonolysis) are energy-intensive. The cost of chemicals (O₃, H₂O₂, catalysts) can also be prohibitive for large-scale applications.

Matrix Effects: Natural organic matter, carbonate/bicarbonate, and chloride in real waters scavenge •OH, vying with target pollutants and curtailing treatment efficiency [33].

Formation of Toxic By-Products: When oxidation stops short of full mineralization, the intermediates formed can prove more harmful than the original pollutant; ozonating bromide-laden water, for instance, generates the carcinogen bromate (BrO₃⁻). Similarly, oxidation of nitrogen-containing compounds can generate nitrosamines.

Process Complexity and Control: Scaling up laboratory-scale AOPs to full-scale treatment plants requires sophisticated monitoring and control systems to adjust oxidant doses and energy input in response to fluctuating water quality [34].

5.2 Promising Research Directions

5.2.1 Development of Novel Catalysts and Materials

Visible-Light Responsive Photocatalysts: Intensive research is needed to develop stable, efficient, and non-toxic photocatalysts (e.g., doped TiO₂, g-C₃N₄, MOFs) that can harness visible light from the sun or LEDs, drastically reducing energy costs.

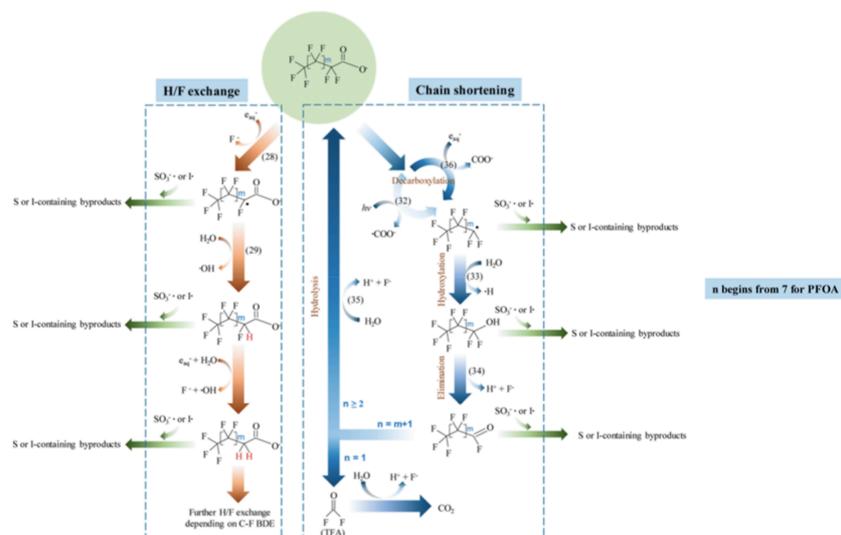
Heterogeneous Fenton-like Catalysts: Crafting robust solid catalysts—iron clays, zeolites, or doped carbons—that activate H₂O₂ or persulfate across neutral pH would remove the acid requirement and the iron-sludge disposal burden tied to classic Fenton chemistry [35].

5.2.2 Integration with Other Treatment Processes (Hybrid Systems)

AOPs as Pre-treatment for Bioremediation: Using a mild AOP to partially oxidize recalcitrant pollutants into more biodegradable intermediates can make them amenable for subsequent low-cost biological treatment.

AOPs as Polishing Step after Biological Treatment: AOPs are ideally suited as a final barrier for micropollutant removal in wastewater reuse and drinking water production. Combining membranes (e.g., UF/NF) with AOPs in photocatalytic membrane reactors can offer simultaneous separation and degradation.

Combination of AOPs: Synergistic effects can be exploited by combining AOPs, such as ultrasound with photocatalysis (sonophotocatalysis) or electrochemistry with photocatalysis (photoelectrocatalysis), to enhance •OH yield and mitigate catalyst fouling [36].



Proposed major pathways of reductive degradation of PFOA. Adapted with permission from reference.

5.2.3 Energy Optimization and Renewable Energy Integration

LED-based Photoreactors: Replacing traditional mercury-vapor UV lamps with UV-LEDs offers longer lifetimes, lower energy consumption, and flexible reactor designs [37].

Solar-Driven AOPs: In sun-rich regions, harvesting solar photons directly for photo-Fenton or photocatalytic reactors (e.g., CPCs) offers a green, low-cost route—yet reliability and economic competitiveness still demand further refinement.

5.2.4 Advanced Oxidation and Process Control

Real-Time Monitoring and Adaptive Control: Developing sensors for real-time measurement of oxidant concentration, UV transmittance, and even specific micropollutants can enable dynamic, adaptive control of AOPs, optimizing chemical and energy use.

Computational Modeling and AI: Advanced modeling of reaction kinetics and computational fluid dynamics (CFD) for reactor design, coupled with machine learning for process optimization, can accelerate the design and operation of efficient AOP systems [38].

5.2.5 Comprehensive Risk Assessment

Toxicity-Driven Process Optimization: Future studies should move beyond pollutant removal efficiency to assess the formation of transformation products and the overall toxicity reduction (using bioassays) throughout the oxidation process. The goal should be to design AOPs that minimize toxicity, not just concentration.

6. Conclusion

Advanced Oxidation Processes represent a powerful and versatile toolbox for addressing the critical challenge of removing persistent and hazardous pollutants from water. Their core strength lies in the potent and non-selective action of the hydroxyl radical. This review has detailed the mechanisms of various AOPs, from established ones like $\text{O}_3/\text{H}_2\text{O}_2$ and Fenton to emerging technologies like electrochemical and solar-driven processes. The wealth of literature demonstrates their successful application in degrading a wide array of contaminants in diverse water matrices.

However, for AOPs to transition from a specialized technology to a mainstream solution, future efforts must focus on overcoming the barriers of cost and complexity. The most promising path forward involves the intelligent development of novel materials, the strategic integration of AOPs into hybrid treatment trains, and the smart application of process control and renewable energy. By focusing research on these areas, AOPs can fulfill their potential as a cornerstone of sustainable water management, ensuring the safety and quality of our precious water resources for generations to come.

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