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*Corresponding author

Moses Adondua Abah, Department of
Biochemistry, Faculty of Biosciences,
Federal University Wukari, Nigeria

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Advanced Oxidation Processes for the Degradation of Organic Pollutants in Wastewater

Moses Adondua Abah^{1,2*}, Micheal Abimbola Oladosu^{2,3}, Sulaiman Luqman Olaitan⁴, Leah Eneotse Adayi⁵, Silas Verwiyeh Tatah¹ and Ochuele Dominic Agida^{1,2}, Okocha Jennifer Uchenna⁶, Ibrahim Ayinla Mahmud⁷, Odimgbe Ezekiel Izudike⁸, Ridwan Musa⁹, Najamu Yau⁹, and Okpanachi Nuhu Oyibo¹⁰

¹Department of Biochemistry, Faculty of Biosciences, Federal University Wukari, Nigeria

²ResearchHub Nexus Institute, Nigeria

³Department of Biochemistry, Faculty of Basic Medical Sciences, University of Lagos, Nigeria

⁴Department of Chemistry, Faculty of Science, University of Abuja, Nigeria.

⁵Department of Water resources and Environmental Engineering, Faculty of Engineering, Ahmadu Bello University, Nigeria

⁶Department Of Chemistry, Faculty of Science, Rivers State University, Nkpulu-Oroworukwo, Port Harcourt, Rivers State, Nigeria

⁷School of Engineering and Built Environment, University of Greater Manchester, Bolton, United Kingdom

⁸Department of Healthcare Administration and Risk Management, Faculty of Health Sciences, Ohio Dominican University, Ohio-USA

⁹Department of Environmental Sciences, Faculty of Physical Sciences, Federal University Dutse, Dutse, Jigawa State, Nigeria

¹⁰Coveup Research Institute, Department of Biochemistry, Faculty of Biological Sciences, University of Nigeria, Nsukka, Enugu State, Nigeria

Abstract

Advanced Oxidation Processes (AOPs) have emerged as a promising technology for degrading organic pollutants in wastewater. These processes involve the generation of highly reactive species, such as hydroxyl radicals, which can effectively break down complex organic molecules. AOPs offer several advantages over traditional treatment methods, including high efficiency, cost-effectiveness, and environmental sustainability. This review aims to provide an overview of the current state of AOPs for wastewater treatment, highlighting the principles, applications, and recent advancements in this field. The study on Advanced Oxidation Processes (AOPs) for wastewater treatment revealed promising results. It was observed that AOPs can effectively degrade organic pollutants, achieving removal rates of up to 90%. The techniques that showed strong potential included ozonation, Fenton process, and photocatalysis. However, it was also discovered that the efficiency of AOPs depends on various operational parameters, such as pH and oxidant dosage, which require careful optimization.

Notably, AOPs not only removed pollutants but also reduced toxicity and improved biodegradability of the treated effluents, making them a viable solution for addressing water pollution challenges. Advanced Oxidation Processes offer a promising solution for degrading organic pollutants in wastewater. This review demonstrates the effectiveness of AOPs in removing a wide range of pollutants, while also highlighting the importance of optimizing operational parameters. As the field continues to evolve, AOPs are expected to play a crucial role in addressing global water pollution challenges, providing a sustainable and efficient treatment solution for wastewater.

Introduction

One of the most important environmental issues facing the world today is water contamination, which is made worse by quick urbanization, industrialization, and intensive farming methods. Untreated or insufficiently treated wastewater is frequently dumped into rivers, lakes, and seas around the world, bringing a variety of pollutants such as pesticides, chemicals that alter hormones, dyes, heavy metals, fertilizers, and pharmaceuticals [1,2]. Since many of these pollutants are persistent, hazardous, and resistant to natural attenuation, they are categorized as contaminants of emergent concern (CECs). Research indicates that agrochemicals, synthetic dyes, and pharmaceuticals and personal care products (PPCPs) are commonly found in surface waters and treated effluents, posing serious threats to human health and the environment [3,4]. The need for sustainable solutions to reduce water pollution is made even more urgent by factors including population growth, climate change and freshwater scarcity [5].

By safeguarding clean water supplies, promoting resource recovery, and preserving aquatic habitats, efficient wastewater management supports sustainable development. The Sustainable Development Goals (SDGs) of the United Nations, especially SDG 6 (Clean Water and Sanitation), highlight wastewater treatment as a vital component of food security, human health, and economic resilience [1]. According to Ulusoy et al. [6], effective wastewater treatment helps to achieve SDGs 12 (Responsible Consumption and Production) and 14 (Life Below Water) by lowering pollutant loading, reducing eutrophication, and facilitating water reuse in industry and agriculture. Its significance in circular economy frameworks is further demonstrated by the fact that treated wastewater can be a useful alternative water source in areas that are experiencing scarcity [7]. Poor care still poses a risk to public health and exacerbates sanitation disparities, especially in low- and middle-income nations.

Primary sedimentation, activated sludge, trickling filters, coagulation-flocculation, and chlorination are examples of traditional wastewater treatment technologies that are widely used but ineffective at eliminating resistant organic compounds. Low biodegradability and chemical stability cause these systems to frequently fail to break down persistent pollutants, leaving behind residues that could enter receiving waterways [3,8]. Biological processes are susceptible to operational variations and toxic influents, whereas chemical disinfection produces hazardous by products such trihalomethanes [2]. According to Matesun et al. [8], conventional plants also have to deal with issues like excessive sludge formation, high energy consumption, and limited adaptation to the growing burden of CECs. Because of these disadvantages, stronger and more sustainable solutions must be sought.

Technologies such as Advanced Oxidation Processes (AOPs) have shown promise in addressing the drawbacks of traditional therapy. AOPs depend on the production of reactive oxygen species (ROS) in situ, particularly hydroxyl radicals ($\bullet\text{OH}$), which have very high oxidation potentials and can break down a variety of organic pollutants non-selectively into mineralized products or biodegradable intermediates [9,10]. Many methods have been researched and used for the degradation of medicines, dyes, agrochemicals, and industrial effluents, including ozonation, Fenton and photo-Fenton reactions, photocatalysis, $\text{UV}/\text{H}_2\text{O}_2$, electrochemical oxidation, sonochemical processes, and plasma systems [11]. Beyond their great efficiency, AOPs can be combined with physical or biological processes to create hybrid systems that are more cost-effective, perform better overall, and produce less sludge. AOPs stand out as cutting-edge, environmentally friendly methods with significant promise for wastewater treatment at the municipal and industrial levels as the world's water emergencies worsen.

The objective of this review is to present a thorough, worldwide summary of advanced oxidation techniques for the breakdown of organic contaminants in wastewater. In particular, it clarifies the basic ideas and reaction mechanisms behind different AOPs; compares and contrasts the main types of AOPs (ozone-based, Fenton/Fenton-like, photocatalysis, $\text{UV}/\text{H}_2\text{O}_2$, electrochemical, sonochemical/plasma) in terms of practicality, efficiency and limitations; surveys the applications of AOPs across pollutant classes (pharmaceuticals, dyes, pesticides, industrial and municipal wastewaters); evaluates important operational parameters (pH, catalyst/light/oxidant dosage, water matrix effects) that affect efficacy, highlights recent developments; and outlines future research directions toward energy-efficient, economical, and sustainable wastewater treatment. In order to help academics, practitioners, and decision-makers choose, develop, and apply AOP-based solutions for water pollution reduction globally, this review will combine theoretical insights with real-world case studies.

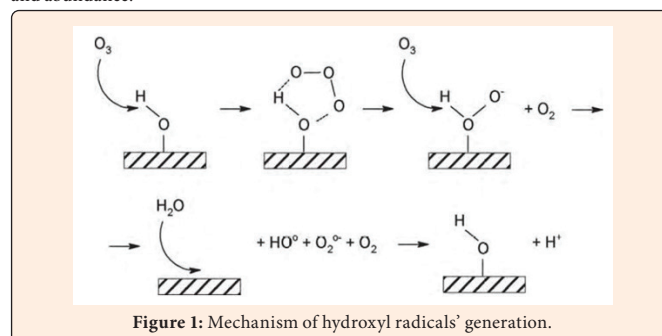
Fundamentals of Advanced Oxidation Processes (AOPs)

One family of water and wastewater treatment methods known as advanced oxidation processes (AOPs) is distinguished by the in-situ production of extremely reactive oxygen species (ROS), mainly hydroxyl radicals ($\bullet\text{OH}$). These radicals are incredibly active oxidants that can attack a variety of refractory organic contaminants through addition processes, electron transfer, and hydrogen abstraction because of their usual redox potential of about +2.8 V [12]. The fundamental idea behind AOPs is to overcome the drawbacks of traditional biological and physicochemical treatment techniques by mineralizing persistent pollutants completely or partially into carbon dioxide, water, and inorganic ions [13].

The idea of AOPs was initially popularized in the 1980s when scientists showed that ozone, hydrogen peroxide, and ultraviolet (UV) light could all be used together to produce hydroxyl radicals and enhance water purification [14]. Since then, the range of AOPs has greatly increased, including classic radical-based systems like Fenton and photo-Fenton reactions as well as more modern techniques like electrochemical advanced oxidation processes (EAOPs), sulfate-radical-based oxidation, heterogeneous photocatalysis, sonolysis, and plasma-assisted oxidation [15].

The non-selective reactivity of hydroxyl radicals, which allows them to break down a wide range of contaminants from colours and endocrine-disrupting chemicals to pesticides and medications, makes them the mainstay of AOPs. But other ROS are also important in a lot of AOPs. Because they are more selective and have a longer half-life than $\bullet\text{OH}$, sulfate radicals ($\text{SO}_4^{\bullet-}$), which are produced by activating persulfate or peroxymonosulfate, are appropriate for use in some industrial effluents [12]. Similar to singlet oxygen ($^1\text{O}_2$), superoxide anions ($\text{O}_2^{\bullet-}$), and even radicals based on chlorine may also aid in the breakdown of pollutants, contingent on the water chemistry and operating conditions [13]. In the end, treatment effectiveness, transformation

pathways, and potential by-product creation are determined by the species' identity and abundance.

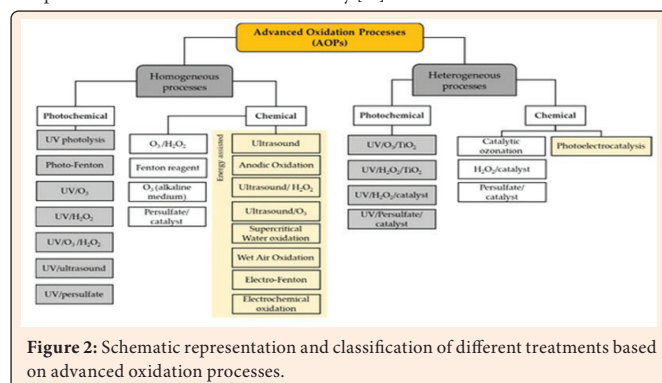


Source: Zhang and Ma [16]

AOPs fall into one of two general categories: homogeneous or heterogeneous systems. The Fenton reaction, in which ferrous iron catalyses the breakdown of hydrogen peroxide to produce hydroxyl radicals, is one example of a homogeneous AOP that only occurs in the aqueous phase. Despite their effectiveness, these procedures frequently call for stringent pH control (typically between 2 and 4) and may produce secondary wastes such iron sludge [13]. Heterogeneous AOPs, on the other hand, depend on solid catalysts or electrode surfaces to promote the production of ROS. Examples include electrochemical oxidation on boron-doped diamond (BDD) electrodes, catalytic ozonation over supported catalysts, and photocatalysis employing semiconductors like TiO_2 . Although these systems have benefits like greater pH tolerance and catalyst reusability, they also have drawbacks including mass transfer restrictions, catalyst deactivation, and problems with light penetration in photocatalytic systems [15].

Depending on the procedure, the response mechanisms behind AOPs can differ significantly. UV irradiation increases efficiency by renewing Fe^{2+} from Fe^{3+} complexes, whereas Fe^{2+} reacts with H_2O_2 to produce hydroxyl radicals in Fenton and photo-Fenton systems. Ozone-based systems, such as O_3/UV and $\text{O}_3/\text{H}_2\text{O}_2$ (peroxone), take use of ozone's breakdown into hydroxyl radicals, especially in alkaline environments [14]. The excitation of semiconductor catalysts is the basis for photocatalytic AOPs. Photon absorption encourages the creation of electron-hole pairs, and the ensuing charge carriers start the production of superoxide anions and hydroxyl radicals at the catalyst surface. In contrast, electrochemical systems produce hydroxyl radicals either directly at the anode surface or indirectly at the cathode through electrogenerated hydrogen peroxide [17].

The impact of background water chemistry is a practical factor to consider while using AOPs. As radical scavengers, constituents including bicarbonate, chloride, and natural organic matter can decrease treatment effectiveness while occasionally producing secondary by-products like bromate from ozonation in waters with a high bromide content [12]. In order to detect dominating reactive species in real-world water circumstances, current research focuses on the use of probe chemicals, radical scavengers, and sophisticated analytical techniques. Additionally, standardized performance measures like oxidant demand per unit of total organic carbon (TOC) eliminated and electrical energy per order (EE/O) are being used more and more to compare AOPs and evaluate their scalability [15].



Source: Amor et al. [18].

Types of Advanced Oxidation Processes

In order to mineralize refractory organic pollutants, advanced oxidation processes (AOPs) use a variety of methods that take advantage of reactive oxygen species (ROS), primarily hydroxyl radicals ($\bullet\text{OH}$) and sulphate radicals ($\text{SO}_4\bullet^-$). AOPs can be broadly classified into a number of types based on the oxidant source and radical generation mechanism. These include ozone-based systems, Fenton and Fenton-like processes, photocatalysis, UV/ H_2O_2 treatment, electrochemical oxidation, and newer techniques like sonochemical and plasma-based technologies. The application of each AOP to various wastewater matrices is determined by its distinct mechanistic pathways, operating conditions, benefits, and limitations. These AOP types are discussed below:

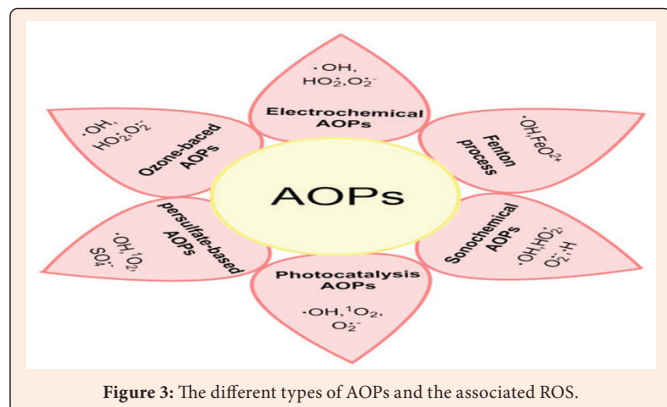


Figure 3: The different types of AOPs and the associated ROS.

Source: Zheng et al. [19].

Ozone-Based AOPs

Ozone (O_3) is a potent oxidant that can be utilized either by itself or in conjunction with ultraviolet light (O_3/UV) and hydrogen peroxide ($\text{O}_3/\text{H}_2\text{O}_2$). By producing hydroxyl radicals that break down a variety of organic contaminants, these systems accelerate the breakdown of ozone [14]. The effectiveness of ozone-based AOPs against dyes, medications, and pesticides is dependent on pH and the presence of bicarbonates and other radical scavengers. Ozone decomposition generates $\bullet\text{OH}$ radicals, which propel the oxidation process at alkaline pH, whereas direct electrophilic reactions of O_3 predominate at acidic pH. A further regulatory concern is the development of bromate in waters that are rich in bromide [15,20].

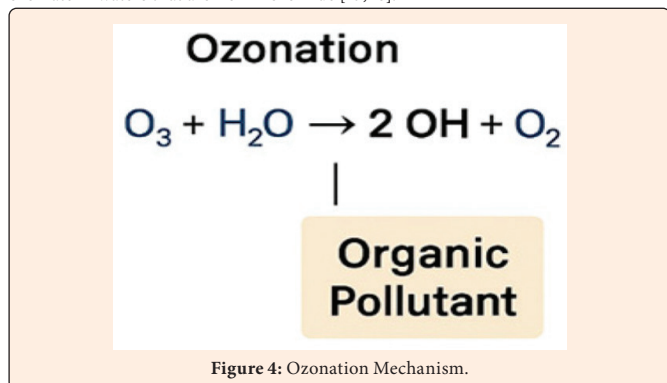


Figure 4: Ozonation Mechanism.

Source: Silva et al. [21].

Fenton and Fenton-Like Processes

Ferrous iron catalyses the breakdown of hydrogen peroxide, generating hydroxyl radicals, which is the basis for the conventional Fenton reaction ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$) [13]. This chemistry is extended by Fenton-like reactions, which use ferric iron, heterogeneous catalysts, or external energy sources. Under natural sunlight, photo-Fenton (also known as UV or solar irradiation) increases efficiency by regenerating Fe^{2+} from Fe^{3+} , which makes it appealing for large-scale wastewater treatment. Further lowering chemical inputs and improving sustainability is Electro-Fenton, where H_2O_2 is electro-generated [22]. Iron sludge production and the requirement for acidic conditions present difficulties, nevertheless, necessitating more optimization.

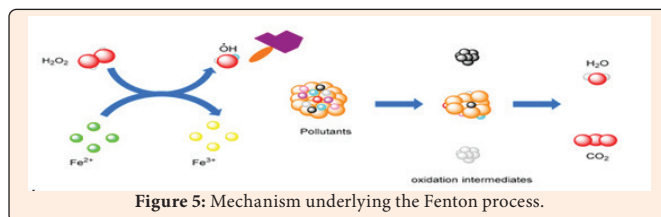


Figure 5: Mechanism underlying the Fenton process.

Source: Zheng et al. [19].

Photocatalysis

The foundation of photocatalytic AOPs is semiconductor excitation, in which photons with energy equivalent to or higher than the bandgap create electron-hole pairs that generate reactive oxygen species (ROS) at the catalyst surface. Water or hydroxide ions are oxidized by the photogenerated holes (h^+) to make $\bullet\text{OH}$, and oxygen is reduced to $\text{O}_2\bullet^-$ by the electrons. Because of its stability, non-toxicity, and potent oxidative power, titanium dioxide (TiO_2) continues to be the industry standard photocatalyst. Recent studies have focused on visible-light-driven photocatalysts (such as perovskite-based materials, $\text{g-C}_3\text{N}_4$, and doped TiO_2) in order to get over the drawback of UV dependence. TiO_2 is combined with membranes, Fenton, or ozonation in hybrid photocatalytic systems to increase degradation rates and expand use in actual wastewater treatment [15].

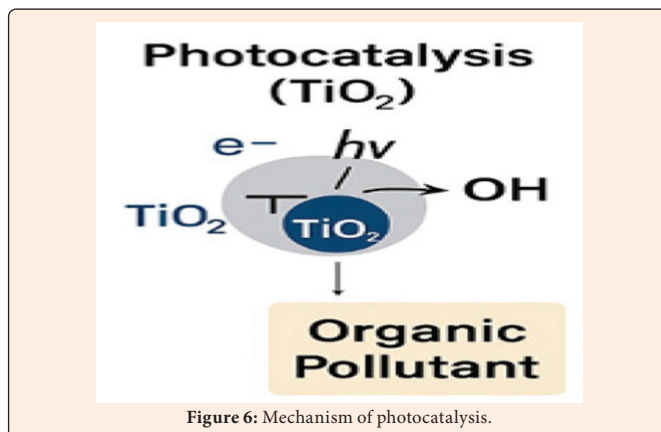


Figure 6: Mechanism of photocatalysis.

Source: Silva et al. [21].

UV/ H_2O_2 Processes

The UV/ H_2O_2 technique directly produces hydroxyl radicals by cleaving hydrogen peroxide with ultraviolet irradiation. Its efficiency is regulated by pH, UV fluence, and matrix composition. This method is frequently used to break down pesticides, medications, and endocrine disruptors, especially when treating drinking water [22]. They can be produced via Fenton reactions involving iron and hydrogen peroxide, ozonation ($\text{O}_3/\text{H}_2\text{O}$), or photolysis of hydrogen peroxide ($\text{H}_2\text{O}_2/\text{UV}$). Once produced, $\bullet\text{OH}$ radicals' fragment and eventually mineralize organic molecules by attacking them through radical addition, electron transfer, or hydrogen abstraction [23]. High energy consumption and scavenging effects from organic materials are among the limitations [12]. Costs can be decreased and efficiency increased by integrating with other therapies, such as biological processes.

Electrochemical Oxidation Processes

ROS are produced either directly or indirectly on electrode surfaces by electrochemical AOPs (EAOPs). While the electro-Fenton process produces H_2O_2 in situ, reducing the need for chemicals, anodic oxidation (AO) employing boron-doped diamond (BDD) electrodes can produce hydroxyl radicals with high mineralization efficiency [23]. Ozone breakdown and radical formation are enhanced by electro-peroxone, which mixes ozone with electrochemically produced H_2O_2 . Even with great removal efficiency, electrode stability and capital costs continue to be major obstacles to widespread use.

Sonochemical and Plasma-Based AOPs

Based on acoustic cavitation, sonochemical oxidation produces hydroxyl radicals by causing bubbles to burst due to ultrasonic waves, which results in localized high temperatures and pressures [24]. In contrast, active electrons and reactive species in partially ionized gas are used in cold plasma processes to break down contaminants at room temperature. Both techniques have potential for microbial inactivation and developing pollutants, but their widespread use is constrained by their energy requirements and viability of scaling up [15].

Table 1: Major advanced oxidation processes (AOPs) in wastewater treatment.

AOP Type	Dominant Reactive Species	Strengths	Limitations	Typical Applications	References
Ozone-based (O_3 , O_3/H_2O_2 , O_3/UV)	$\bullet OH$, O_3 radicals	Effective for dyes, pharmaceuticals, disinfection	High energy cost; bromate risk	Textile effluents, pharmaceuticals	[20,25]
Fenton & Fenton-like	$\bullet OH$ (Fe^{2+}/H_2O_2)	Strong oxidation; well-established	Acidic pH needed; iron sludge	Pesticides, phenols	[13]
Photocatalysis (TiO_2 , visible-light)	$\bullet OH$, h^+	Solar potential; complete mineralization	Catalyst recovery; UV dependence	PPCPs, endocrine disruptors	[26]
UV/ H_2O_2	$\bullet OH$	Effective in clear waters	Energy intensive; scavenging effects	Drinking water polishing, PPCPs	[12,25]
Sonochemical / Plasma-based	$\bullet OH$, atomic O, plasma radicals	No added chemicals; effective for recalcitrant	High energy demand; scale-up issues	Pharmaceuticals agrochemicals	[24]

Application of AOPs in Wastewater Treatment

The application of advanced oxidation processes (AOPs) in wastewater treatment has attracted global attention due to the increasing presence of persistent and emerging contaminants that conventional technologies fail to remove effectively. Organic pollutants such as pharmaceuticals, dyes, pesticides, and industrial effluents often resist biodegradation and pose risks to ecosystems and human health even at trace concentrations. AOPs, through the generation of highly reactive oxygen species, provide a versatile platform for the degradation of these complex pollutants into harmless end-products like carbon dioxide, water, and inorganic salts. In recent years, both laboratory and pilot-scale studies have demonstrated the potential of AOPs across diverse wastewater streams, highlighting their adaptability and efficiency [15,27].

Degradation of Pharmaceuticals and Personal Care Products (PPCPs)

Because of their bioactivity and endurance in aquatic environments, pharmaceuticals and personal care products (PPCPs) are acknowledged as micropollutants. They are frequently found in surface waters all around the world since conventional treatment facilities are unable to fully eliminate them. AOPs that have been shown to be successful in breaking down antibiotics, analgesics, and endocrine disruptors include UV/ H_2O_2 , ozonation, and photocatalysis. For example, fluoroquinolone antibiotics were significantly removed by electro-Fenton processes, while hormones such as 17 β -estradiol have been degraded by TiO_2 photocatalysis [17,28]. Transformation products, which can still have biological activity, need to be taken into consideration.

Removal of Dyes and Textile Effluents

Textile effluent contains very stable and hazardous synthetic dyes, surfactants, and auxiliary compounds. AOPs have been successfully used for textile dye mineralization and colour removal, especially ozonation and Fenton procedures. While heterogeneous photocatalysis using TiO_2 and doped catalysts yields encouraging results under sun irradiation, Fenton and photo-Fenton treatments efficiently break down azo and anthraquinone dyes [24]. Because of their quick decolorization ability, ozone-based methods are especially well-suited for industrial effluents; nonetheless, bromate generation and energy consumption are still issues.

Treatment of Pesticides and Agrochemical Residues

The biological activity and recalcitrance of pesticides and agrochemicals make it difficult to remove them from wastewater. It has been demonstrated that AOPs are highly effective at breaking down fungicides, insecticides, and herbicides. For instance, atrazine and chlorpyrifos can be eliminated by photo-Fenton treatment in the presence of sunlight, while organophosphorus pesticides can be effectively eliminated by AOPs

based on sulphate radicals [12,29]. In agricultural areas where pesticide-contaminated runoff contributes to groundwater pollution, these procedures are especially alluring.

Industrial Wastewater Treatment

Complex wastewaters with refractory organic matter, heavy metals, and hazardous by-products are produced by industrial sectors such petrochemical, tannery, pulp and paper, and pharmaceutical industries. AOPs provide efficient pre-treatment and polishing processes for certain kinds of wastewaters. In the petrochemical industry, phenolic compounds have been significantly degraded by ozonation and biological treatment. Electrochemical oxidation has demonstrated potential in the removal of chromium and colours from wastewater from tanneries. Similarly, to remove lignin and chlorinated organics from pulp and paper mill effluents, photocatalytic and Fenton-based methods are used [27]. Despite their efficacy, sludge production and high operating costs continue to be obstacles to widespread use.

Municipal Wastewater and Sludge Treatment

A significant source of newly discovered pollutants, nutrients, and pathogens is municipal wastewater. Even while many trace organics are partially removed by traditional activated sludge techniques, they nevertheless remain. AOPs have been included into tertiary treatment stages, particularly ozonation and UV/ H_2O_2 , to enhance the removal of micropollutants prior to discharge or reuse. Pharmaceuticals and endocrine disruptors, for instance, have been shown to be removed from municipal effluents by more than 80% in Switzerland's full-scale ozonation plants [20]. Additionally, AOPs have been investigated in sludge treatment, where photocatalysis and ozonation enhance biodegradability and decrease sludge volume, supporting circular economy and resource recovery initiatives [25].

Factors Influencing the Performance of AOPs

The effectiveness of advanced oxidation processes (AOPs) is highly dependent on operational and environmental parameters that govern the generation, stability, and reactivity of radical species. AOPs are not "one-size-fits-all" technologies; instead, their performance varies with wastewater characteristics, pollutant load, and process conditions. Understanding these factors is critical for optimizing treatment efficiency, improving cost-effectiveness, and enabling scale-up for real-world applications [12,25].

Effect of pH, Temperature, and Initial Pollutant Concentration

Since pH has an impact on catalyst stability, pollutant ionization, and radical production, it is a significant factor in AOPs. For example, ozonation works better in alkaline environments where hydroxyl radicals are more likely to develop, yet Fenton reactions need acidic conditions (pH=3) to maximize Fe^{2+} activity [13,20]. According to Bautista et al. [30], temperature affects reaction kinetics. While moderate heating



speeds up the production of radicals, high temperatures can cause oxidants to break down too soon. Likewise, increased concentrations of pollutants raise the demand for radicals, which could lower the efficiency of mineralization if the supply of oxidants is inadequate [22].

Influence of Natural Organic Matter (NOM) and Scavengers

Wastewater's natural organic content, bicarbonates, and halides can reduce treatment efficiency by competing with target contaminants for reactive oxygen species (ROS). Carbonate and chloride ions create less reactive secondary radicals, which lowers degradation rates, while NOM, in particular, functions as a light attenuator and radical scavenger in photocatalysis [31]. To lessen these interferences, pre-treatment or process changes are frequently necessary.

Catalyst Type, Dosage, and Regeneration

Catalyst characteristics have a direct impact on performance in catalytic AOPs such photocatalysis and Fenton-type reactions. The efficiency of radical generation is determined by the active site availability, bandgap energy, and catalyst surface area. While catalyst deactivation by fouling or leaching lowers long-term stability, overdosing might result in aggregation, light scattering, or scavenging effects. Therefore, regeneration techniques like chemical washing or calcination are essential for long-term operation [29].

Light Intensity and Wavelength in Photocatalysis

In photocatalytic AOPs, the incident light intensity and wavelength strongly affect electron-hole pair generation. UV light ensures efficient TiO₂ activation, but visible-light photocatalysts are increasingly explored to exploit solar irradiation. Excessive light, however, may cause recombination of photogenerated charge carriers, reducing efficiency. Optimizing reactor design for uniform light distribution is thus essential [26].

Reactor Design and Operational Conditions

Batch, continuous flow, and pilot-scale reactor designs have an impact on mass transfer, light penetration, and hydrodynamics. For example, immobilized photocatalyst reactors may have a lower active surface area yet reduce catalyst recovery problems. Similar to this, for the best pollutant degradation, electrochemical AOPs rely significantly on the electrode material, current density, and cell arrangement. Performance must be balanced with operational expenses and energy efficiency while scaling up [25].

Table 2: Factors influencing the performance of AOPs.

Factors	Effect on Performance	Design/ Operational Guidance	References
pH	Controls radical yield (e.g., Fenton at ~pH3, O ₃ decomposition at alkaline pH)	Adjust to optimum for each AOP	[13,20]
Temperature	Speeds up reactions but may promote radical recombination	Operate near ambient/moderate	[12,25]
Initial pollutant load	Higher concentration increases oxidant demand	Apply staged dosing	[22,25]
Natural organic matter/scavengers	Compete with target pollutants for radicals	Pretreatment or increased oxidant dosing	[31]
Catalyst type and regeneration	Determines radical generation and stability	Use immobilized/magnetic catalysts; plan regeneration	[32]
Light intensity/wavelength	Affects photocatalyst efficiency	Use solar/visible-light catalysts	[26]

Combination of AOPs with other Treatment Methods

Although advanced oxidation processes (AOPs) are powerful for degrading recalcitrant organic pollutants, they are often limited by high energy and chemical costs, incomplete mineralization, and potential formation of toxic by-products. To overcome these drawbacks, researchers have increasingly focused on combining AOPs with complementary treatment methods such as biological systems, membrane technologies, and adsorption-based processes. These integrated approaches harness the advantages of AOPs in breaking down complex or toxic molecules into biodegradable intermediates, which can then be more efficiently removed by subsequent processes. The synergistic effect not only enhances treatment performance but also improves cost-effectiveness, making such hybrid systems promising for large-scale and sustainable wastewater management [25].

AOPs Coupled with Biological Treatment

One of the best methods for treating refractory wastewater is to combine AOPs with biological processes. AOPs increase the effectiveness of later biological therapy by pre-oxidizing persistent organics into smaller, more biodegradable molecules. This mixture has been effectively used to break down textile colours, insecticides, and medications. For example, high mineralization rates with decreased toxicity have been demonstrated by photo-Fenton followed by activated sludge [22,28].

AOPs Combined with Membrane Technologies

Because AOPs decrease fouling potential and degrade pollutants that flow through membranes, they can also be used in conjunction with membrane processes like reverse osmosis (RO) and nanofiltration (NF). On the other hand, membranes can increase process efficiency by keeping oxidants and catalysts inside reactors. A developing field of study is integrated photocatalytic membrane reactors (PMRs), in which pollutants are simultaneously degraded and separated. Although recent reviews show that PMR materials and reactor layouts have advanced quickly, they also point to real-world issues such as scale-dependent hydrodynamics, catalyst leaching, polymer membrane photodegradation, and light delivery in turbid matrices. Translating PMRs from lab to practice still heavily relies on design optimization, including reactor optics, membrane material selection, and catalyst immobilization [33].

Hybrid Processes (AOP + Adsorption, Coagulation, etc.)

The combination of AOPs with adsorption or coagulation processes can address the limitations of each method. Adsorption using activated carbon or biochar effectively removes residual organics and by-products after AOP treatment, while coagulation enhances the removal of suspended solids and colloids. Such hybrids have been particularly effective in treating industrial effluents with complex pollutant mixtures [34].

Integrated Treatment Trains for Wastewater Reuse

Integrated treatment trains, where AOPs are embedded within multi-step systems, are gaining traction in municipal and industrial wastewater reuse applications. For example, ozonation combined with biological activated carbon (BAC) filtration has been widely implemented in Europe for micropollutant removal in municipal wastewater. These trains ensure both pollutant removal and water disinfection, enabling safe reuse and contributing to circular economy frameworks [20].

Recent Advances and Emerging Trends

The design of catalysts, energy efficiency, and integration with sustainable treatment approaches have all experienced notable advancements in advanced oxidation processes (AOPs) in recent years. Metal-organic frameworks (MOFs), graphene-based composites, and doped TiO₂ are examples of nanomaterials that have been produced to improve photocatalytic stability and activity [32]. Solar-driven AOPs are becoming more and more possible thanks to these materials' enhanced charge separation and visible-light responsiveness. One significant development is the move to AOPs fuelled by renewable energy. As less expensive substitutes for UV-driven systems, solar photocatalysis and photo-Fenton processes are becoming more popular since they have both financial and environmental benefits. For the breakdown of complex pollutants, such as medications and microplastics, sonochemical and plasma-based oxidation are being investigated concurrently [35].

Additionally, the field is changing due to digital tools. These days, by-product generation prediction, reaction condition optimization, and hybrid treatment train design are all accomplished through the use of AI and machine learning [36]. It is anticipated that this combination of experimental research and data-driven methodologies will speed up scale-up. Recent developments generally indicate that AOP systems will become smarter, more efficient, and greener in line with sustainable wastewater reuse and the circular economy.

Table 3: Recent advances in hybrid AOP systems.

Hybrid approach	Key advances	Main benefits	References
AOP + Biological (sequential)	AOP pre-oxidation (ozonation, photo-Fenton) improves biodegradability of refractory organics.	Enhanced mineralization, reduced toxicity, shorter biological treatment times.	[27]
Photocatalytic Membrane Reactors (PMRs)	Immobilized catalysts reduce leaching; simultaneous degradation and separation achieved.	Catalyst retention, combined pollutant removal + filtration	[32]
Solar-driven AOPs (photo-Fenton, TiO ₂ /UV-solar)	Pilot-scale reactors using solar collectors for energy-efficient treatment.	Low energy cost, suitable for regions with high solar radiation.	[25]
Integrated multi-barrier trains (AOP + membrane + bio + adsorption)	Site-specific trains designed by techno-economic and LCA frameworks to balance removal, cost and footprint.	Tailored reuse quality, regulatory compliance, robust to variable influents.	[25]

Challenges and Future Perspectives

Although advanced oxidation processes (AOPs) are one of the most effective technologies for breaking down persistent pollutants in wastewater, there are a number of technical, financial, and environmental obstacles that must be overcome before they can be used widely. Incomplete mineralization is a significant problem since it can produce toxic by-products that are even more dangerous than the initial contaminants [20,25]. While photocatalysis has challenges with catalyst recovery and limited light penetration in actual wastewater matrices, Fenton-based systems necessitate highly acidic conditions (pH~3), which results in post-neutralization procedures and sludge production [22].

Cost is still another significant barrier. AOPs' economic viability at full scale is limited by their frequent requirements for costly chemical inputs like ozone or hydrogen peroxide as well as substantial energy for plasma reactors or UV lamps. Furthermore, hydroxyl radicals can be quenched by the presence of scavengers such bicarbonates and natural organic matter in wastewater, which lowers efficiency [28]. These elements lead to inconsistent performance across wastewater types and make process optimization more difficult. Concerns about secondary contamination emerge from an environmental standpoint. Under some circumstances, ozonation can yield bromate, however Fenton-type procedures produce a lot of iron sludge that needs to be disposed of [20]. According to life cycle assessment (LCA) research, certain AOPs may have substantial carbon footprints that outweigh their environmental benefits if they are fuelled by non-renewable energy.

Innovations are influencing how AOPs will develop in the future. To increase efficiency and lower costs, photocatalysts driven by visible light, nanomaterials, and renewable energy sources are being developed [32]. There is significant potential for balancing resource and energy efficiency with pollutant degradation through integration with biological and membrane processes. Furthermore, it is becoming possible to predict the creation of by-products, optimize operational parameters, and

create more sustainable treatment plans with the help of artificial intelligence and machine learning [36].

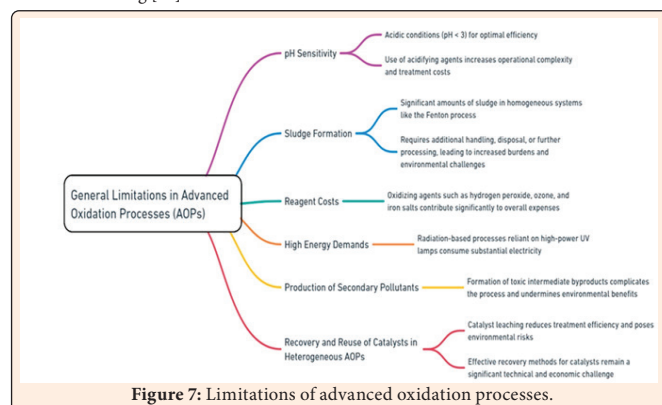


Figure 7: Limitations of advanced oxidation processes.

Source: Satyam and Patra [36].

Conclusion

The effectiveness of Advanced Oxidation Processes (AOPs) in breaking down persistent and developing organic contaminants that traditional treatments are unable to eliminate is becoming more widely acknowledged. Their power comes from producing extremely reactive radicals that allow pollutants to mineralize almost completely. Catalytically driven AOPs, which exhibit increased efficiency but also confront difficulties such catalyst stability and energy consumption, have shown promise in recent research [19]. Hybrid systems, which offer a balance between environmental sustainability, cost-effectiveness, and efficiency, have also drawn interest. These systems integrate AOPs with biological or membrane processes.

Furthermore, assessments indicate that AOPs, especially when fueled by renewable energy, might improve effluent biodegradability and support global sustainability goals [21]. Barriers still exist in spite of these advancements. Large-scale adoption is still constrained by energy consumption, operating expenses, and by-product generation. Reactor design optimization, long-lasting catalysts, and thorough life-cycle analyses are necessary to address these problems. All things considered, AOPs are moving closer to being a vital component of environmentally friendly wastewater treatment. They have enormous potential for widespread use and long-term water security with further development, particularly in hybrid configurations and renewable-powered systems.

Table 4: Summary of key findings.

Domain	Key findings
Pollutant Degradation Efficiency	AOPs demonstrate high efficiency in degrading pharmaceuticals, pesticides, dyes, and industrial pollutants, often achieving near-complete mineralization, unlike conventional treatments [19].
Mechanistic Insights	Hydroxyl and sulfate radicals are the primary oxidizing agents, with process-specific pathways (ozone, Fenton, photocatalysis, electrochemical) dictating degradation kinetics and by-product formation [37].
Process-Specific Strengths	Ozone-based AOPs are effective for dyes and PPCPs; Fenton processes excel in aromatic pollutant removal; photocatalysis enables solar-driven applications; electrochemical oxidation eliminates the need for chemical dosing [21].
Operational Challenges	Major barriers include energy intensity (UV, electrochemical), pH sensitivity (Fenton), catalyst deactivation (photocatalysis), and toxic by-product generation (ozonation, plasma), hindering large-scale deployment [28].



Hybrid & Integrated Systems	Coupling AOPs with biological or membrane processes enhances biodegradability, reduces energy costs, and achieves higher overall treatment performance, showing promise for wastewater reuse applications [33].
Catalyst and Material Innovations	Advances in nanomaterials, visible-light photocatalysts, and stable electrode designs are improving efficiency, durability, and scalability of AOPs [19,37].
Sustainability & SDGs	When integrated with renewable energy (solar, hydropower), AOPs align with UN Sustainable Development Goal 6 (clean water and sanitation) and promote circular economy strategies [20].
Emerging Trends	Artificial intelligence and machine learning are increasingly applied to optimize AOP system design, monitor performance, and reduce energy use, marking a transition toward smart wastewater treatment systems [19].

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