JAEHR
Journal of Advances in Environmental Health Research
J Adv Environ Health Res 2026;14(1):1-17. doi:10.34172/jaehr.1422
http://jaehr.muk.ac.ir

Review Article

How Versatile Are Advanced Oxidation Processes (AOPs) in Addressing Different Wastewater Pollutants in Full-Scale Applications?

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Article history:
Received: February 16, 2025
Revised: April 20, 2025
Accepted: August 5, 2025
ePublished: March 29, 2026

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Abstract

This study presents a comprehensive review of the utilization of advanced oxidation processes (AOPs) for full-scale wastewater treatment. The review included 28 studies conducted in 11 countries across Europe, Asia, and the Americas. The studies investigated various wastewater types municipal, industrial (e.g., textile), and biological- which contain a broad range of pollutants such as micropollutants, antibiotic-resistant bacteria, resistance genes, pharmaceuticals, pesticides, trace pollutants, endocrine disrupting chemicals (EDCs), organic pollutants, and refractory matter. The reviewed studies employed different AOPs, including UV/H2O2, UV/persulfate, UV/chlorine, ozonation, Fenton, electro-Fenton, photo-Fenton, and electrochemical oxidation. The pros and cons of each AOP are summarized, and their performance in wastewater treatment is compared. The review emphasizes the versatility of AOPs in dealing with different environmental concerns and their capability for widespread use in wastewater treatment plants. Moreover, the current study tackles the challenges as to scaling up AOPs, and focuses on the need for further research to improve their efficiency and cost-effectiveness.

Keywords: Advanced oxidation processes, wastewater, Full scale, Hydroxyl radicals, Chemical oxidation

Please cite this article as follows: Pirsaheb M, Hossini H, Massahi T, Nouri M. How versatile are advanced oxidation processes (AOPs) in addressing different wastewater pollutants in full-scale applications?. J Adv Environ Health Res 2026;14(1):1-17. doi:10.34172/jaehr.1422

Introduction

Wastewater treatment has become a critical challenge globally, with environmental, economic, and human implications. International communities have implemented various regulations for effluents discharged from wastewater treatment plants. Conventional treatment technologies have shown low effectiveness in removing persistent and emerging pollutants. The scientific community has been looking for new processes to address these challenges.[1] Advanced oxidation processes (AOPs) have widely been used as highly effective technologies for the degradation of organic contaminants in wastewater systems.[2] Originally developed for potable water treatment, these processes were later adapted for wastewater applications as their broader ability became evident.[3] Their high treatment efficiency is primarily attributed to the in situ generation of extremely reactive hydroxyl radicals (•OH), which non-selectively and rapidly oxidize a wide range of organic compounds. This radical-mediated oxidation pathway enables the extensive transformation of micropollutants and frequently results in near-complete mineralization.[4] AOPs encompass a diverse group of technologies that differ in their approaches to oxidant activation and generation, employing multiple reaction pathways for organic compound degradation. Interest in these processes has intensified due to their proven effectiveness in treating refractory organic contaminants in both natural water bodies and complex industrial effluents. AOPs can be customized to treat a wide range of wastewater types because of their flexibility. A unifying characteristic of all AOPs is the production of highly reactive hydroxyl species, which function as the principal drivers of oxidative degradation.[5] As a result, AOPs are increasingly being developed and integrated within wastewater management sectors and are now regarded as sustainable treatment options, offering strong operational performance while maintaining a relatively low environmental footprint.[6] Different AOPs have decomposed various inorganic and

organic contaminants in wastewater. These processes include photocatalytic oxidation (using UV light in the presence of a semiconductor catalyst), the Fenton process (a reaction between iron sulfate and hydrogen peroxide (H_2O_2), electrochemical AOP procedures, ultrasound, and ozone-based (O_3/H_2O_2, O_3/H_2O_2) and UV-based AOPs (UV/H_2O_2, O_3/ H_2O_2/UV, etc.).[7, 8] Full-scale AOP techniques have been successful in treating wastewater and drinking water. It is expected that these techniques, as cutting-edge technologies, will essentially remove contaminants from wastewater and transform them into less hazardous or completely non-toxic products, which provides a satisfactory final wastewater treatment solution.[9] Contemporary research increasingly focuses on improving the efficiency of established treatment infrastructures while incorporating supplementary process stages to enhance overall contaminant removal in wastewater facilities. In this regard, ozonation, classified as an advanced oxidation process has shown substantial effectiveness in reducing concentrations of trace level pollutants. Ozone reacts with organic constituents through compound specific oxidative pathways that follow bimolecular reaction kinetics, thereby enabling targeted degradation of susceptible contaminants. In wastewater treatment, a combination of biological treatment and ozone has been found highly efficient. By increasing the biodegradability of resistant compounds and intermediate products, this synergistic process results in the oxidation of compounds.[10] The use of semiconductors as catalysts has been recommended in applying AOPs, for instance; TiO_2, ZnO, ZnS, WO_3, CdS, Fe_2O_3, and $SrTiO_3$. Titanium dioxide (TiO_2) has received attention owing to its exceptional chemical stability, biocompatibility, and advantageous electronic and photophysical properties.[11] Its effectiveness as a photocatalyst particularly under visible light irradiation has been unequivocally shown. Over the past several decades, extensive research has investigated photocatalytic approaches for contaminant removal in aqueous systems.[11] Concurrently, the Fenton reaction, which involves the interaction of hydrogen peroxide with iron based catalysts, is known as one of the most widely used AOPs. This technique has been successfully employed across a broad range of wastewater matrices and is capable of degrading a diverse array of chemical pollutants. Due to the intricate sequence of radical-mediated reactions governing Fenton chemistry, its oxidation mechanisms have been studied in depth, with numerous operational parameters identified as key determinants of overall treatment efficiency.[12]

Despite being recognized as effective treatment technologies, the large-scale performance of AOPs has yet to be comprehensively consolidated. Current literature offers only fragmented insight into their behavior in real -world wastewater treatment systems, with notable gaps in understanding full-scale implementation strategies and mechanistic reaction pathways. To tackle these deficiencies, this review synthesizes studies on the full-scale application of AOPs, highlighting operational configurations, mechanistic underpinnings, and observed treatment outcomes. Furthermore, the analysis identifies critical parameters that govern process efficiency and explores avenues for integrating AOPs with conventional treatment infrastructure to facilitate widespread, scalable deployment.

Research Characteristics and Trends

Table 1 summarizes 28 studies that utilized AOPs in full-scale wastewater treatment. The studies were conducted in different countries and focused on different types of wastewaters, pollutants, and AOPs. In 11 countries, the studies were conducted, with most of them (14) came from Europe, with 7 from Asia, and 4 from the Americas. According to this distribution, AOPs are being widely studied and applied globally, particularly in regions with significant industrial and municipal wastewater generation. Various wastewater types, such as municipal, industrial, biological, and textile wastewater, were studied. The adaptability of AOPs allows them to be effectively used on many different kinds of effluent, demonstrating their utility across various sources. The pollutants targeted by the studies included micropollutants, antibiotic-resistant bacteria, resistance genes, pharmaceuticals, pesticides, trace pollutants, endocrine disrupting chemicals (EDCs), organic pollutants, and refractory matter. This broad range of pollutants highlights the importance of AOPs in addressing various environmental concerns. The studies employed different AOPs, including ozone, Fenton, UV, and photocatalytic processes. The use of multiple AOPs demonstrates the flexibility of these technologies in addressing various wastewater treatment challenges. The operating conditions for the AOPs varied significantly, including pH levels, ozone doses, and UV doses. This variation highlights the need for careful optimization of AOPs to achieve effective pollutant removal. Across the studies, the efficiency of removing pollutants varied, with some achieving efficiency above 90%. This range in efficiency highlights the importance of optimizing AOPs for specific wastewater types and pollutants. The research data outlined in Table 1 show the worldwide adoption of AOPs for treating wastewater. The studies show that AOPs are versatile in addressing different pollutants and wastewater types, but they also emphasize the importance of careful optimization of operating conditions to achieve effective pollutant removal.

Figure 1 is a network graph illustrating keywords used in studies related to AOPs and wastewater. The graph highlights several key concepts that are crucial in the field of AOPs and wastewater. These include "AOPs," "wastewater," "removal," "efficiency," "kinetics," "mechanisms," and "toxicity." These terms have a higher frequency of occurrence in studies, indicating their significance in the research landscape. Also, the thickness of the lines between keywords represents the strength of relationships between these concepts. This suggests that there are strong connections between "AOPs" and "wastewater," as well as between "removal" and "efficiency."

Table 1. Summary of the results of 28 final articles related to application of AOPs in full-scale wastewater treatment that were selected for the present review

Country	Wastewater type	AOP type	Target pollutant	Optimum conditions	Removal efficiency%	Ref.
Switzerland	Municipal	Ozon	Micropollutants	-pH = 7 -Ozone dose > 10^4 $M^{-1}S^{-1}$	> 85	10
Switzerland	Municipal	Ozon	Micropollutants	-pH = 7 -Ozone dose = 0.55 g/L	80	13
Australia	Municipal	Ozon	Nitrosamines	-pH = 10.5-11 -Ozone dose = 28-32 mg/L	75	14
Switzerland	Municipal	Ozon	Antibiotic Resistant Bacteria and Resistance Genes	-pH = 7.2 -Ozone dose = 0.2 mg/L	80	15
USA	Municipal	Ozon	Micropollutants	-pH = 7 -Ozone dose = 0.5 mg/L	89	16
Switzerland	Municipal	Ozon	-Micropollutant -by-product of disinfection	-pH = 7 -Ozone dose = 1.24 g/L	99	17
Australia	Municipal	Ozon	- Pharmaceuticals -pesticides	-pH = 7 -Ozone dose = 2 mg/L	99	18
Germany	Municipal and industrial	Ozon	Trace pollutants	-pH = 6.9-7.6 -Ozone dose = 0.4 to 1 g/L	89	19
Switzerland	Municipal and industrial	Ozon	Micropollutants	-pH = 7.6-8.6 -Ozone dose = 2.7-2.8 mg/L	93	20
Germany	Industrial (with share of confectionery production), private, and hospital	Ozon	EDCs	-pH = Not Assigned -Ozone dose = 0.42- 0.72 mg/L	100	21
Northern Italy	Municipal	Fenton	Organic pollutants	-pH = 5.9 -Fe^{2+} = 88.4 g/kg d.m	72.2	22
Korea	Dyeing	Fenton	Refractory matters and color	-pH = 5.8–6 -Fe^{2+} = 4.2 mM	73	23
Portugal	Olive mill	Fenton	Detoxification	-pH = 3 -Fe^{2+} = 310 mM	90	24
Spain	Olive mill	Fenton	Pollutants	-pH = 3.2-3.8 -Fe^{2+} = 1500 mg/L	90	25
Spain	Municipal	Ozonation And the photo-Fenton process	Micropollutant	-pH = acidic -Fe^{2+} = 9 mg/L -Ozone dose = 12 mg/L	90	26
Spain	Urban	UV-C/sulfate radical	Micropollutants	-PS dose = 0.05–0.5 mM -UV-C contact time = 4–18 s	55	27
Belgium	Industrial and municipal	Ozonation step, a UVC photocatalytic step	Micropollutants	-pH = 6-7 -light intensity = 23 W/m^2 -TiO_2 as photocatalyst	95	28
Spain	Industrial and municipal	UV	Organic micropollutants	-pH = 6.9-7.7 -UV doses = 10–50 mJ/cm^2	90	29
Portugal	Urban	UV	Cefotaxime-resistant Enterobacteriaceae and ESBL producers	-pH = Not Assigned -UV dose = 29.74 mJ/cm^2	90.5	30
Belgium	Synthetic	UV, H_2O_2, O_3	- atrazine (ATZ) and alachlor (ALA) herbicides - bisphenol (BPA), -synthetic hormone 1,7-α-ethinylestradiol (EE2)	-pH = 7 -H_2O_2 dosages = 0.4 – 0.6. -Ozone dose = 0.041-0.73 kWh/m -UV-lamp = 18 W	99.8	31
Belgium	Domestic	UV / H_2O_2	Organic matter	-pH = 7.4-8.2 -UVA = 0.10–0.11 cm^{-1} -H_2O_2 = 0.55 mg/L	97	32
Ecuador	Municipal	UV/H_2O_2	Surfactants	Time = 120 min pH = 7.5	94.3 ± 4.3	33
USA	Municipal	UV	Trace organic compounds	-pH = Not Assigned -UV dose = 750 and 1500 mJ/cm^2	90	34
Canada	Municipal	UV	Human infectious viruses	-pH = 7.2 ± 0.2 -UV dose = 24 mJ/cm^2	98	35
Ethiopia	Textile	Photocatalytic	Pollutants	-pH = 8.1 ± 0.1 -TiO_2 as photocatalyst -dose = 5 mg/L	73	36
Spain	Biological wastewater	Photocatalytic	Bacterial inactivation and micropollutant	-pH = Natural -TiO_2 as photocatalyst -TiO_2 dose = 0.1 g/L	80	37
Indonesia	Batik printing wastewater	Photocatalytic	Pollutant compounds (dye)	-pH = 5 -Ti/$RuIrO_2$ as photocatalyst	60	38
France	Municipal	Electrochemical	Micropollutants	pH = 3	Not reported	39

These connections indicate that researchers are actively exploring the relationships between these concepts to better understand and improve AOPs in wastewater treatment. The figure shows that most studies concentrate on using AOPs for treating wastewater, prioritizing how effectively contaminants are eliminated and the underlying processes involved. This highlights the importance of developing effective AOPs for wastewater treatment, which is a critical area of research. Additionally, the presence of keywords like "kinetics" and "mechanisms" suggests that researchers are taking an interdisciplinary approach, combining principles from chemistry, engineering, and environmental science to better understand and optimize AOPs. In summary, Figure 1 provides insights into the key concepts, relationships, and research focus in the field of AOPs and wastewater. It highlights the importance of removal efficiency, mechanisms, and interdisciplinary approaches, and suggests that the field is dynamic and continues to evolve.

AOPs

Ozone (O_3)

Ozone is a strong oxidizing agent with a standard redox potential of 2.07 V, capable of driving both direct and indirect oxidative transformations. In the direct pathway, O_3 preferentially reacts with ionized organic species over their neutral counterparts. Alternatively, the indirect route is initiated through the decomposition of ozone to generate highly reactive •OH, which subsequently mediates extensive oxidation of contaminants.[9] A distinguishing characteristic of ozone is its broad-spectrum reactivity toward both organic and inorganic compounds, making it particularly advantageous in wastewater treatment applications.[20] Coupling ozonation with biological processes has emerged as a key strategy for enhancing pollutant removal efficiency. Within the spectrum of chemical oxidation techniques, ozone continues to gain prominence as an effective and cost-efficient oxidant in the purification of wastewater streams.[40] Reusing or discharging wastewater, complying with high-level environmental requirements, and using reliable technical equipment are the reasons for the widespread use of this method. To use an ozone system at a municipal wastewater treatment plant (WWTP), the required ozone dose must be determined, which is used to calculate the necessary amount of ozone. The system components include ozone production, gas supply, reactive system requirements, gas displacement, and extraction. Effective regulation and monitoring of operating conditions are critical for maintaining optimal performance of ozonation systems and for achieving the desired treatment outcomes.

The ozone gas produced by the ozone generator is transferred to the reaction chamber through stainless steel pipes. This can be done by a liquid oxygen tank and an on site air preparation unit to supply gas. Diffusers provide gas, and unique concrete ponds serve as

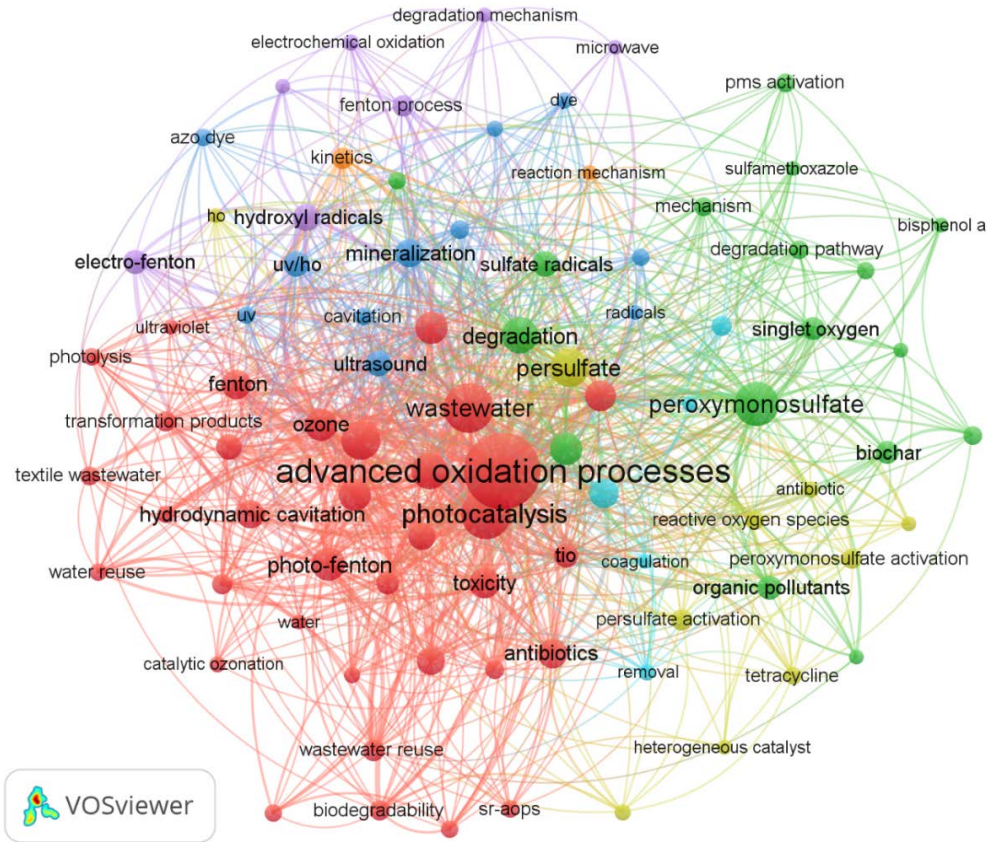

Figure 1. Keyword co-occurrence network of publications on AOPs and wastewater treatment, constructed using VOSviewer (version 1.6.20). Node size reflects the frequency of keyword occurrence, indicating their prominence in the literature, while edge thickness represents the strength of associations between keywords. The network highlights major research themes such as AOPs, wastewater, removal, efficiency, kinetics, mechanisms, and toxicity, illustrating the conceptual structure and research focus within this field.

reaction chambers for municipal wastewater treatment. An injector is used to mix ozone gas with water flow.[40] In wastewater treatment plants, ozone is commonly produced in situ via electrical discharge, employing high voltage alternating current typically between 6 and 20 kV across a dielectric gap infused with oxygen-rich gas. Owing to its intrinsic chemical instability, ozone cannot be stored and must be generated on-site, where it rapidly decomposes into molecular oxygen following formation. As a potent oxidant and antimicrobial agent, ozone's efficacy in disinfection is governed by the delivered concentration, exposure time, and the inherent sensitivity of the target microorganisms.[41] A study by Prieto-Rodríguez et al achieved 90% micropollutant breakdown after 20 min of purification and consumption of 3.4 mg/L of ozone. Even highly polluted effluents, such as landfill leachates or heavily loaded industrial effluents, can be treated with ozonation. Ozone decomposes resistant micropollutants such as methyl tert-butyl ether and atrazine herbicide.[42] Since these processes readily degrade several pharmaceuticals and personal care products (PPCPs), including bezafibrate and carbamazepine, they hold promise to effectively eliminate these pollutants.[43] The integration of O_3 with ultraviolet irradiation (O_3/UV) has been employed to remove organic contaminants across a range of water matrices, including municipal wastewater, drinking water, and industrial effluents.[44] In recent years, particularly in Switzerland, there has been increasing focus on utilizing ozone for the abatement of trace level pollutants such as pharmaceutical residues, biocidal compounds, and endocrine disrupting chemicals (EDCs).[45] In the study by Hollender et al, the compounds of diclofenac, atenolol, sotalol, naproxen, carbendazime and trimethoprim were removed by the process combining ozonation with a biological sand filter.[10] In cases where secondary effluents contain elevated levels of specific contaminants, ozonation has been reported to remove approximately 40–50% of naproxen, benzotriazole, atenolol, and clarithromycin; 60–70% of metoprolol, 5-methylbenzotriazole, and sulfamethoxazole; and more than 80% of diclofenac and carbamazepine. This data support the use of pilot-scale studies for designing and optimizing ozonation units, facilitating a seamless scale-up to full-scale operations without extensive and costly experimentation. Additionally, operational costs can be estimated using the ozone dosages determined during bench and pilot testing.[10] Prieto-Rodríguez et al comprehensively characterized the degradation kinetics of sixteen micropollutants in municipal wastewater under ozonation conditions.[42] Under 60 min of contact time and a 9.5 mg/L dosage of ozone, 98% of the total micropollutants were decomposed, which is recommended for removing much higher concentrations of pollutants.[13, 42, 46]

Exposure of wastewater to an ozone concentration of 3.4 mg/L for 20 min resulted in the degradation of nearly 90% of the targeted micropollutants, which encompassed bisphenol, ibuprofen, hydrochlorothiazide, diuron, atenolol, diclofenac, ofloxacin, trimethoprim, gemfibrozil, naproxen, and paraxanthine. This investigation specifically examined the removal efficiency of these compounds.[42] In the case of ozonation, a higher ozone dose requires more electricity for the higher removal rate of micropollutants is expected. Therefore, the treatment costs may be close to Fenton and the other common processes. The operational energy requirements for ozone-based treatment diverge from those of the solar photo-Fenton process, with the most notable difference being the substantially higher upfront investment necessary for ozonation to attain pollutant removal efficiencies equivalent to those achieved by the solar photo-Fenton approach.[47,48] In a study by Bourgin et al ozonation of the secondary clarifier effluent was performed in a Swiss WWTP; ozone significantly reduced the micropollutant loading into the WWTP effluent.[13] At an ozone dose of 0.55 g O_3 per gram of dissolved organic carbon (DOC), target micropollutants were diminished by roughly 80%, even under elevated concentrations. Before starting ozone use, the effects of generating bromate, N-nitrosodimethylamine (NDMA), and other oxidative byproducts were carefully evaluated. Experimental findings showed a significant reduction in NDMA during treatment. Given that bromide levels typically fell within the standard range for Swiss municipal wastewater, bromate concentrations in treated effluents were generally below 3.5 μg/L.[13] Collectively, the study by Czekalski et al confirmed that conventional large-scale ozonation effectively achieves 1–2 log reductions of resistant bacterial populations without measurable alterations in intracellular antibiotic resistance gene (ARG) abundance.[15]

Fenton

Among the various AOPs, Fenton is distinguished by its high efficiency in removing many degradable contaminants and its environmental sustainability. While the Fenton reaction has extensively been explored, recent research has focused on executing this treatment under neutral pH conditions to mitigate the financial burdens associated with large-scale acidification and subsequent neutralization.[49] In this system, ferrous ions (Fe^{2+}) catalyze the decomposition of hydrogen peroxide into highly reactive hydroxyl radicals (•OH), which act in a non selective manner to degrade recalcitrant organic pollutants. Despite its efficacy, the process presents significant limitations, including substantial chemical consumption and the formation of dark sludge, necessitating additional costs for separation and disposal of treated effluent.[50] Crucial parameters governing the performance of Fenton-based wastewater treatment encompass temperature, pH, and the molar ratio of $Fe^{2+}$to H_2O_2. Fenton is strongly dependent on pH, which has been widely reported in various studies. In most cases, regardless of the initial pH, the optimum value recommended is about pH = 3.[12] In acidic conditions, the initial stage involves hydrogen peroxide oxidizing ferrous iron to generate hydroxyl radicals along with ferric iron species (Eq. 1). Several studies have provided comprehensive explanations of

the reaction pathways occurring under both acidic and neutral pH environments.[51] Ferric iron is reduced to ferrous iron in the presence of ultraviolet radiation, which creates a redox iron cycle using H_2O_2 and producing HO• (Equations 1 and 2).[51]

$$Fe\ (II) + H_2O_2 \rightarrow Fe\ (III) + HO^- + HO\bullet \quad (1)$$

$$Fe\ (III) + hv + H_2O \rightarrow Fe\ (II) + HO\bullet + H^+ \quad (2)$$

The photo-Fenton process, representing an enhanced variant of the classical Fenton reaction, has garnered extensive attention for the degradation of organic pollutants in both industrial effluents and municipal wastewater across diverse operational scenarios. This approach relies on the in situ production of highly reactive hydroxyl radicals (•OH) via the reaction between hydrogen peroxide and ferrous ions under acidic conditions, with radical generation further amplified by exposure to natural sunlight or artificial ultraviolet irradiation. In particular, the production of HO• depends on the cyclic oxidation and optical reduction of iron as a catalyst in the presence of H_2O_2. Although the production rate of HO• is associated with several variables, the concentration of the reagents H_2O_2 and Fe, radiation sources, and their intensity are of particular importance. For instance, 5 mg/L of divalent iron and a few tens mg/L of H_2O_2.[51] Electrochemical studies have examined ways to minimize the use of chemicals and the subsequent sludge production from Fenton, so called electro-Fenton process. The electro-Fenton method, which relies on the two-electron reduction of oxygen, provides significant benefits compared to the conventional Fenton process (Equations 3 and 4).[51]

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (3)$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \quad (4)$$

Comprehensive evaluation of economic factors is essential when determining optimal operational conditions and selecting the appropriate variant of the Fenton process. The application of Fenton-based oxidation has been extensively explored across numerous studies. For example, Bergendahl et al reported efficient degradation of MTBE utilizing zero-valent iron, while López-Vinent et al showed that substantial breakdown of diphenhydramine hydrochloride required approximately one hour.[52,53] Much of the research has employed synthetic water matrices to investigate target compounds; however, these findings cannot be directly extrapolated to real wastewater, underscoring the need for further applied studies. Scaling the Fenton process to full-scale operations presents considerable economic challenges, as achieving complete mineralization via chemical oxidation is costly due to the persistence of intermediate by-products. Moreover, actual effluents often contain additional substances that consume reagents alongside the intended pollutants. Incorporating naturally derived, low-cost catalysts can mitigate expenses associated with catalyst preparation. Nonetheless, several limitations constrain large-scale deployment, notably the non-uniform formation of iron sludge, which complicates recycling and poses contamination risks. Current research is actively addressing these constraints to optimize iron sludge management.[12] Bench-scale investigations by Bergendahl et al evaluated the ability of Fenton reagents for chemical oxygen demand (COD) reduction in wastewater, demonstrating over 96% removal efficiency. The reactions were exothermic, indicating that the released thermal energy could be strategically harnessed within treatment operations. Also, the process effectively targets residual contaminants persisting after subsequent treatment steps, achieving degradation of numerous pollutants, including recalcitrant compounds such as trichloroethane.[54]

Photocatalytic process

Photocatalytic oxidation represents a rapidly evolving water treatment technology, whose implementation at industrial scales remains limited, and numerous laboratory investigations are still underway. Despite these constraints, successful deployments have been reported in effluents from wineries, distilleries, olive oil production facilities, dairy operations, and confectionery and sugar industries.[5] Heterogeneous photocatalysis is widely acknowledged as a highly effective strategy for generating hydroxyl radicals, enabling the degradation of both organic and inorganic contaminants across drinking water and wastewater matrices. A diverse array of semiconductor photocatalysts including ZrO_2, MoO_3, Sb_2O_3, Fe_2O_3, ZnO, CeO_2, Al_2O_3, CdO, Bi_2O_3, CdS, HgO, PbO, and TiO_2 has been investigated for this purpose, with TiO_2-based systems emerging as the most extensively studied.[55] TiO_2 photocatalysis efficiently mineralizes organic pollutants while also targeting microbial populations.[56] The underlying mechanism relies on the absorption of photons across the semiconductor band gap, inducing electron–hole pair formation that drives redox reactions. These catalysts function effectively under ambient conditions, facilitating complete mineralization without producing secondary by-products and offering advantages in cyclic operation and cost efficiency.[57,58] Specifically, upon ultraviolet irradiation, electrons promoted to the conduction band (CB) participate in reduction reactions, commonly interacting with dissolved oxygen to yield superoxide radical anions. Simultaneously, valence band (VB) holes migrate to the catalyst surface, reacting with adsorbed water molecules to generate hydroxyl radicals (•OH), which serve as the principal reactive species in photocatalytic oxidation.[59-61] The general electron–hole-mediated reaction mechanism on TiO_2 surfaces is illustrated in Equations 5–15.

$$\text{Photoexcitation: } TiO_2 + hv \rightarrow e^- + h^+ \quad (5)$$

$$\text{Charge-carrier trapping of } e^-\text{: } e^-_{GB} \rightarrow e^-_{TR} \quad (6)$$

Charge-carrier trapping of h^+: h^+_{VB} h (7)

Electron-hole recombination: $e^-_{TR} + h^+_{VB}(h^+_{TR})$ e^-_{GB} + heat (8)

Photoexcited e^- scavenging: $(O_2)_{ads} + e^-$ O_2 (9)

Oxidation of hydroxyls: $OH^- + h^+$ O (10)

Photodegradation by •OH: R-H + •OH $R^{\bullet}$ + H_2 (11)

Direct photoholes: R + h R + • Intermediate(s)/Final Degradation products (12)

Protonation of superoxide: $O_2^{\bullet-}$ + •OH HOO• (13)

Co-scavenging of e^-: HOO• + e^- HO_2^- (14)

Formation of H_2O_2: HOO^- + H^+ H_2O_2 (15)

In the context of water treatment, TiO_2-driven photocatalytic platforms exhibit swift response times and sustain elevated photonic efficiency, even when irradiance levels are low. Contemporary research has focused on augmenting TiO_2 performance through strategic doping with metallic and non-metallic elements, as well as synthesizing composite structures. These modifications generate engineered architectures that extend light absorption across a wider spectral range, thereby enhancing photocatalytic activity.[62] Photocatalysis followed by another process resulted in 93.3% of decolorization and 94% of COD degradation. As a result of this combination a high removal rate without pH modification and with low energy consumption were achieved.[36] In another study conducted by Philippe et al, simultaneous disinfection and removal of emerging pollutants were evaluated using a photocatalytic system, which achieved a 5-log reduction of **E. coli** and more than 80% removal of several micropollutants, such as carbamazepine, hydrochlorothiazide, ibuprofen, ranitidine, and metoprolol.[37] In 2017, Mukimin and colleagues implemented a full-scale electrocatalytic reactor for the treatment of authentic batik printing effluents. Operating at an applied voltage of 5 V, a hydraulic retention time of 120 minu, a salt concentration of 4000 mg/L, and pH 5, the system achieved total decolorization and reduced chemical oxygen demand by 60.8%. The reactor functioned through an indirect oxidation pathway, facilitating rapid and effective pollutant degradation while avoiding the formation of secondary by-products.[38]

UV-Based process

UV-based AOPs are processes based on UV radiation, mostly UV-C, that combine UV light with various radicals. The UV radiation used for advanced oxidation is typically greater than 200 mJ/cm^2. The administered UV dose surpasses that necessary to achieve a 4 log inactivation of a broad spectrum of pathogens, encompassing UV-resistant viruses such as adenovirus. Ultraviolet radiation is typically emitted from low or medium pressure mercury lamps, delivering either monochromatic or polychromatic spectra. The most prevalent UV-driven advanced oxidation strategy couples ultraviolet irradiation with hydrogen peroxide. Additionally, alternative oxidants, including persulfate (yielding sulfate radicals) and chlorine (forming both hydroxyl and chlorine radicals) are being explored for their capacity to augment radical mediated oxidation. The combination of UV light and H_2O_2 leads to the photolytic splitting of H_2O_2 into two OH radicals. If low-pressure UV lamps are used, the high concentrations of H_2O_2 required to produce sufficient OH radicals will remove the remaining H_2O_2 in the next step. The applied doses of H_2O_2 are mainly regulated by costs. At higher concentrations, hydrogen peroxide may function as a hydroxyl radical scavenger, thereby diminishing the net radical yield. Within the UV/ozone advanced oxidation framework, ultraviolet irradiation induces the photolytic decomposition of dissolved ozone, generating atomic oxygen that rapidly interacts with water to form an electronically excited peroxide species[63]. This activated hydrogen peroxide then undergoes decomposition, yielding a pair of hydroxyl radicals that drive oxidative reactions.[64] In general, the reaction mechanism of the O_3/UV process for the decomposition of organic pollutants has three stages. First, the O_3 molecule directly oxidizes the contaminants. Subsequently, ultraviolet irradiation facilitates the photodegradation of pollutants and concurrently activates ozone molecules, producing hydroxyl radicals that mediate the indirect oxidative transformation of contaminants. Beyond chemical oxidation, the UV/ozone system also exerts direct antimicrobial effects, effectively inactivating bacteria and pathogens and eliminating the necessity for an independent disinfection stage.[65] UV lamps and ozone generators require large amounts of electrical energy, resulting in relatively high energy requirements for the combination of UV and ozone. The UV/SO_4 advanced oxidation process represents a UV driven treatment modality that produces sulfate radicals ($SO_4^{\bullet-}$), which are highly oxidative yet more selective than hydroxyl radicals, enabling effective degradation of organic contaminants and inactivation of microbial populations.[64] Growing attention to UV-based water and wastewater technologies arises from the dual pressures of eliminating toxic or carcinogenic compounds and adhering to stringent regulatory frameworks. Accordingly, a substantial body of research has investigated the application of ultraviolet irradiation to decompose a broad spectrum of both organic and inorganic constituents in aqueous environments.[66] UV/H_2O_2 to remove total organic carbon (TOC) (tissue organic chemicals) has been widely investigated in the peer-reviewed literature at a laboratory scale for water quality from high purity to landfill leachate. The initial full-scale implementations were designed for the treatment of surface water and the reuse of drinking water.[64] Recently, many studies have been conducted on removing various organic pollutants such as

N-nitrosodimethylamine (NDMA), drugs, and water-soluble hydrocarbons using UV because UV treatment does not form by-products and is known to be an effective process for purification. These studies have assessed the effectiveness of UV in combination with H_2O_2 for removing TOC and emerging micropollutants, as well as the fate of naturally dissolved organic matter and synthetic organic compounds in drinking water treatment using UV/H_2O_2 technologies.[67] A study on UV and UV/H_2O_2 degradation of pharmaceutical intermediates in an aqueous solution showed that in two pharmaceutical intermediates (5-methyl-1,3,4-thiadiazol-2-methylation and 5-methyl-1,3,4- (thiadiazole-2-thiol) degradation by photooxidation was always faster than direct photolysis. During direct photolysis, lower initial substrate concentration resulted in faster and more efficient degradation. The UV/H_2O_2 process could also degrade carbamazepine very effectively, while the UV process alone was not effective in reducing the concentration of carbamazepine. Investigations into the UV-mediated degradation of pharmaceuticals have predominantly concentrated on the reactivity of drugs with ultraviolet light and hydroxyl radicals, with relatively few compounds such as carbamazepine and diclofenac assessed for removal via physicochemical treatment strategies. The majority of these studies employ water spiked with target pharmaceuticals, limiting insights into the efficacy of UV-based or other physicochemical approaches in authentic wastewater matrices.[68, 69] UVC irradiation (200–280 nm) has been widely implemented for water disinfection; however, its application presents notable constraints, including microbial regrowth due to the absence of a residual disinfecting effect and the capacity of microorganisms to repair UV-induced DNA damage. Furthermore, the ability of UVC alone to remove micropollutants is structurally dependent and often restricted.[29] For example, de la Cruz et al observed complete photodegradation of diclofenac in secondary effluent within 10 min at 254 nm,[70] hereas Pablos et al reported less than 25% removal under identical irradiation conditions. These discrepancies underscore the critical influence of experimental parameters on the photolytic behavior of organic micropollutants and highlight the necessity for more comprehensive investigations under realistic wastewater conditions.[71] In the last few decades, increasing attention has been paid to using ultraviolet radiation in WWTPs as an efficient method. However, the results of investigations and experiences show the negative impact of parameters such as turbidity, hardness, and suspended particles in wastewater on the performance of the ultraviolet irradiation method in the disinfection process. As a result, it is necessary to use efficient new technologies to improve the performance of this process under different operating conditions. AOPs may be a suitable solution to achieve the above goal due to the ability to remove resistant and non-biodegradable dangerous compounds. Ultraviolet rays, and influential radicals, are considered efficient AOPs based on irradiation in municipal WWTPs. Wastewater treatment processes for reuse and regeneration have been investigated and improved in recent decades. Also, effective disinfection of wastewater before discharge is considered an essential requirement for reuse. In this regard, using new disinfection processes is vital and is being followed by researchers. It was found that this method, in addition to disinfection, can effectively reduce wastewater quality parameters. It should be noted that using the UV proxy method in WWTPs requires additional studies regarding the possible by-products of this process on a semi-industrial scale, which is suggested to be considered in future research.[72] In various studies, the removal of target micropollutants, including naproxen, carbamazepine, diclofenac, gemfibrozil, ibuprofen and caffeine was reported by photolysis and UV/H_2O_2 processes.[4] The oxidation rate of selected organic pollutants was increased in the presence of H_2O_2, especially for caffeine and carbamazepine, at an oxidant dose of 25 mg/L compared to direct UV photocatalysis. In UV/H_2O_2 oxidation, the pseudo-first-order rate constants for selected compounds depended on their initial concentration (in mg/L levels).[4, 73] The UV doses required for 50% and 90% removal at different levels of H_2O_2 varied considerably among the compounds tested. The electrical energy (in kW) needed to reduce the pollutant concentration by 90% ranges from 1.3 to 7.1 kWh/m^3. In summary, the study observed pseudo-first-order kinetic behavior for the degradation of all selected compounds. Additionally, the results showed that direct UV photolysis is very effective for diclofenac degradation. The degradation of several compounds, notably carbamazepine and caffeine, predominantly proceeds via the UV/H_2O_2 pathway, as their direct photolytic decomposition under UV irradiation is negligible. Incorporation of hydrogen peroxide substantially enhances the oxidative transformation of all examined substances, with particularly pronounced effects observed for carbamazepine and caffeine at 25 mg/L H_2O_2 relative to direct UV treatment.[4,73] Gao et al investigated the reaction kinetics and mechanistic pathways of sulfamethoxypyridazine (SMP) degradation using ultraviolet activated persulfate (UV/PS) as an advanced oxidation approach. Their findings showed that SMP removal adheres to pseudo-first-order kinetics and that the degradation rate is accelerated by higher persulfate concentrations, elevated bicarbonate and bromide levels, and decreased pH. Moreover, the study reported that the UV/PS system effectively eliminates SMP in natural water matrices while mitigating the formation of disinfection by-products, underscoring its applicability in environmentally relevant conditions.[74]

Electrochemically based AOPs

Electrochemical advanced oxidation processes (EAOPs) provide a highly efficient strategy for the degradation of toxic aromatic pollutants by generating reactive intermediates via direct electrical energy input. This approach is particularly advantageous because it

eliminates the reliance on exogenous chemical reagents and minimizes the formation of secondary by-products, thereby enhancing its practicality and scalability for diverse water treatment applications. Hence, electrochemical-based purification methods are known as green methods. The electrochemical oxidation process is further divided into two types: direct oxidation, in which direct charge transfer occurs between the pollutant and the anode surface, and indirect oxidation, which is done by in situ production of active oxygen species on the surface of the anode. Using electricity to treat petroleum wastewater can be successfully used to separate oil and recover valuable metals. Electrochemical methods have been effective and helpful in treating resistant oily wastewaters. Combining them with other advanced oxidation methods increases the effluent quality and optimizes the entire system's energy consumption.[75,76] Loos et al showed the application of a boron-doped diamond (BDD) anode for the removal of diverse pharmaceutical compounds including diclofenac, sulfamethoxazole, iopromide, and 17α-ethinyl estradiol from actual hospital effluents.[77] In parallel, Perez et al underscored electrochemical oxidation as a robust strategy for treating pharmaceutical-contaminated wastewater. This approach is environmentally advantageous, offering high operational stability, minimal reliance on hazardous reagents, and negligible generation of secondary pollutants. Within the suite of advanced oxidation technologies, EAOPs are particularly noteworthy due to their capacity to degrade a broad array of persistent and toxic organic compounds in wastewater matrices.[78] The effect of electrochemical technologies for wastewater degradation is currently under extensive investigation. The inactivation efficiency of electrochemical disinfection systems is mainly determined by cell design, type of microorganism, electrolyte composition, electrode material, and other experimental factors such as current density and flow rate. These processes can oxidize any organic pollutant and lead to its complete decomposition and almost complete mineralization. Recently, electrochemical oxidation, thanks to the development of new electrode materials and more compact reactors, has proven to be a promising and attractive technique for the effective oxidation of wastewaters containing non-biodegradable organic compounds, such as textile effluents, landfill leachate, tannery wastewater, sewage, and industrial wastewater containing acids.[79, 80] The majority of research on electrochemical EAOPs has been conducted using electrochemical cells with volumes around 100 mL. Although the number of studies using real industrial wastewater streams, which usually have high pollutant concentrations, is increasing, there is still insufficient information on their treatment in larger volumes.[81] Scaling up electrochemical reactors requires careful consideration of multiple parameters, including target effluent standards, treatment throughput, and hydraulic retention time. For wastewaters with elevated pollutant loads, coupling electrochemical treatment either before or after cost-efficient biological processes can enhance overall performance. Balancing operational efficiency with economic viability remains a fundamental goal in design. Despite this, no universally accepted methodology exists for scaling EAOPs, and experimental validation at full scale remains sparse. Highly concentrated waste streams present an optimal context to evaluate the practical efficacy of large-scale electrochemical treatment systems.[82] The application of EAOPs as a pre-treatment strategy for dye-laden effluents has gained increasing attention, with recent studies emphasizing reductions in toxicity and improvements in biodegradability. Besides, investigations have explored pollutant degradation kinetics and the generation of secondary by-products, supporting the concept of implementing electrochemical treatment as an initial step prior to biological processing of real textile wastewater. Research on olive mill wastewater treatment is extensive and includes various technologies under investigation. Scientific research in this field continues because biological processes cannot neutralize such wastes. Electrochemical methods are not limited by effluent toxicity but typically have longer reaction times, which results in higher operating costs.[83] The presence of antibiotics directly affects microorganisms and can cause their resistance, posing a long-term threat to human health. However, studies on EAOPs demonstrate that these methods are reliable for effectively removing pharmaceuticals from contaminated water. Additionally, they can serve as disinfectants, as hydroxyl radicals generated by EAOPs are toxic to bacteria. While tests are typically conducted on much higher concentrations of pharmaceuticals than those found in real effluents, further research on eliminating small amounts of drugs is necessary. Future investigations of these technologies should emphasize continuous-flow experiments using authentic wastewater, as such conditions are essential for enabling progressive scale-up toward full-scale implementation. At the same time, there is a special need to develop combined treatment processes that simultaneously ensure economic viability, high removal efficiencies, and long-term environmental sustainability.[84, 85]

Comparative Analysis of AOPs in Wastewater Treatment

Agricultural and industrial effluents are characterized by the presence of higher amounts of organic and mineral pollutants, which are of environmental concern. Some parameters, such as high pollutant doses and significant volume production, make agricultural water treatment an ecological challenge. Effective industrial wastewater treatment necessitates the complete degradation and mineralization of contaminants. Ongoing industrial effluent releases introduce substantial loads of organic pollutants into receiving waters, thereby compromising freshwater quality and threatening aquatic ecosystems.[9] All AOPs are characterized by their ability to exploit the higher reactivity of hydroxyl radicals during their use in oxidation processes. A wide range of AOPs has been systematically assessed based on their defining characteristics and

applicability to diverse wastewater streams. Although these technologies demonstrate strong treatment ability, they are constrained by several limitations, including elevated operational costs associated with costly reagents and high energy consumption. Furthermore, AOPs may lead to the formation of unidentified transformation products that can exhibit greater toxicity than their parent compounds. Their performance is further compromised by competitive scavenging of hydroxyl radicals by non-target constituents and by reduced efficacy toward recalcitrant toxic compounds that are inherently resistant to hydroxyl radical oxidation.[86] AOPs are powerful treatments for complex and toxic pollutants in wastewater. By combining ozone, hydrogen peroxide, and different UV techniques, AOPs have been developed to select the most appropriate option for specific pollutants. However, the efficiency of AOPs is particular to the compounds, and the final selection of the AOP system can only be made after initial pilot tests. Considering the difficulty of removing emerging pollutants, more effective processes are necessary. AOPs have been proven as powerful technologies for the degradation of emerging contaminants, with organic compounds completely oxidized to carbon dioxide (CO_2), water (H_2O), and mineral acids. Oxidants called free hydroxyl radicals are formed in this process, which easily react with organic compounds due to unpaired electrons. However, several issues remain unsolved, such as the relatively high operating cost of these processes due to the use of expensive chemicals and increased energy consumption, as well as the formation of unknown intermediates that, in some cases, can be more toxic than the original compounds. Moreover, all these methods are susceptible to scavenging hydroxyl radicals by non-target substances and are not suitable for a specific class of toxic compounds that resist the attack of hydroxyl radicals.[86] Using separation steps such as coagulation, sedimentation, and filtration before using AOPs can remove solids that interfere with these processes. In addition, using AOPs as a pretreatment step followed by biological treatment processes can achieve lower cost and adequate removal of a variety of organic compounds. Finally, the good design of large-scale advanced oxidation reactors to efficiently treat wastewaters will commercialization makes these processes possible. Oxidative treatment strategies aim to convert wastewater contaminants into more chemically stable and less hazardous forms.[87] As summarized in Table 2, AOPs differ markedly from biological treatments in both mechanism and performance, with degradation efficiencies varying substantially among individual AOPs. To overcome the limitation of single-process systems, hybrid configurations have been developed that combine multiple AOPs, including UV/H_2O_2, ultrasonic oxidation, photocatalysis, UV/O_3, $UV/Fe^{2+}/H_2O_2$, photo-assisted Fenton reactions, and sono-electro-Fenton processes. These integrated approaches benefit from synergistic effects to achieve significantly higher oxidation efficiencies than standalone treatments, while also expanding the operational flexibility of each component process.[88] For example, Arzate et al showed that coupling photo-Fenton oxidation with ozonation enhanced micropollutant removal to nearly 90%.[26]

Few studies have focused on applying different AOP combination technologies in organic wastewater treatment. Some of these articles only focus on using different AOPs in wastewater dyeing. However, there is a need for more research on the application of AOPs in the treatment of various types of organic wastewater, including dyes, pharmaceuticals, and other emerging contaminants.[89] Many compounds associated with urban and industrial wastewater have been identified in groundwater and surface water. Conventional wastewater treatment infrastructures remain largely ineffective at eliminating many emerging contaminants, resulting in their persistence through treatment plants and subsequent release into the aquatic environment. Pharmaceutical residues, in particular, frequently enter the water cycle: while some compounds pass unchanged through primary treatment, others such as naproxen, ibuprofen, iopromide, and sulfamethoxazole are only partially removed via adsorption processes. During secondary biological treatment, antibiotics and anti-inflammatory agents typically exhibit removal efficiencies of approximately 30–75%. The principal concern associated with pharmaceutical pollutants lies in their chronic, long-term toxicity rather than acute effects. Many pharmaceuticals are biologically active, resistant to biodegradation, and capable of affecting non-target organisms by mimicking their intended pharmacological actions. Moreover, the emergence and spread of antimicrobial resistance has been identified by leading international organizations as a major public health threat of the 21st century. Following human consumption, drugs and their metabolites are excreted and conveyed into wastewater systems. Consequently, AOPs have been widely investigated to target pharmaceutical compounds that evade conventional treatment. Nevertheless, oxidative treatment of municipal wastewater can generate transformation products from antibiotics that may exhibit enhanced biological activity, increased biodegradability, or even greater toxicity than the parent compounds. Many kinds of research have achieved their decomposition and destruction by AOPs.[90] UV radiation has been used for photolysis purposes, but its applications have been expanded through the photolysis process in AOPs. Photolysis breaks down pollutants through exposure to light and absorption of photons. Absorption of photons promotes molecular outer-shell electrons to higher energy states, destabilizing the compound and increasing its susceptibility to chemical reaction or bond cleavage. Although ultraviolet lamps are typically employed to supply the necessary irradiation, natural sunlight can likewise function as an effective alternative light source. Tests have been completed to determine the advantages and disadvantages of recessed lamps versus ceiling lamps, concluding that hollow lamps have better effects. In addition, low-pressure or medium-pressure lamps can be used. Medium-pressure lamps

Table 2. Comparison of biological and AOP-based systems in wastewater treatment plants

AOPs	Biological process
The development process of new and improved AOPs is fast, efficient and cost-effective.	It does not always show good results due to long hydraulic retention time and high costs.
They are beneficial in decomposition performance and have a high economic application.	Low efficiency
Because hydroxyl radicals are highly reactive, they can simultaneously react with and help remove a wide range of organic pollutants.	Strongly influenced by the temperature factor.
Since the product of complete reduction by OH is only H_2O, AOPs theoretically do not produce any new hazardous substances.	Sensitivity to toxicity.
Elimination of high toxicity.	High maintenance costs.
The increase in the use of AOPs does not stop, and this is due to the development of technology and (new) regulations that are becoming stricter every time.	Low flexibility in design and operation.
	The biological method requires a large area of land.
	High production sludge volume.
	Low biodegradability of some molecules (colors).
	Microbiological mechanisms are complex.

require fewer bulbs because they are more intense than low-pressure lamps.[91] The UV/H_2O_2 process ranks among the most thoroughly investigated advanced oxidation technologies for wastewater treatment. In this approach, hydrogen peroxide is photolyzed by ultraviolet irradiation through a pH-independent mechanism, generating highly reactive species capable of driving oxidative reactions. The synergistic action of UV light and H_2O_2 enables complete mineralization of organic contaminants, ultimately transforming them into carbon dioxide and water. In regions with high solar irradiance, natural sunlight may serve as a viable and cost-efficient alternative to artificial UV sources. This process has shown effective degradation of pharmaceuticals such as ciprofloxacin in wastewater, as well as the removal of phenolic compounds commonly present in olive mill effluents.[30] Moreover, UV/H_2O_2 has proven highly efficient for dye decolorization in textile wastewater, with enhanced removal rates observed at elevated UV intensities and higher hydrogen peroxide dosages. For example, the study by Wardenier et al conducted to remove all kinds of pesticides, dyes, and even synthetic hormones by the combined process of UV-H_2O_2-O_3 in Belgium, achieved 99.8% removal of these pollutants.[31] Among AOPs, the UV/H_2O_2 system is one of the most extensively studied technologies for wastewater remediation. In this process, UV irradiation induces the photolytic decomposition of hydrogen peroxide via a pH-independent mechanism, generating reactive species capable of driving oxidative transformations. This synergistic system enables complete mineralization of organic contaminants, ultimately yielding carbon dioxide and water. In regions with prolonged daylight availability, natural sunlight may serve as a cost-effective substitute for artificial UV sources. The UV/H_2O_2 process has proven effective in degrading pharmaceutical compounds such as ciprofloxacin, as well as in removing phenolic constituents from olive mill effluents and decolorizing textile industry wastewaters. Experimental evidence further indicates that higher UV intensities and increased hydrogen peroxide dosages significantly enhance the rate and efficiency of dye removal.[92]

Personal care products (PCPs) are designed for use on the human body and include a wide range of items such as moisturizers, gels, perfumes, sunscreens, and mosquito repellents. In Europe alone, there are at least 8,000 health products on the market. Most PCPs are discharged into sewage and enter WWTPs in their original or biologically modified form. During the wastewater treatment process, PCPs may be completely degraded, remain unchanged, or, in some cases, be partially converted to metabolites. Therefore, the detoxification of the main compounds has become a vital and meaningful research focus to ensure their non-toxicity and safety, promoting the large-scale application of AOPs.[93] Most studies show that O_3-based AOP treatment is very efficient in removing PCPs, with up to 100% efficiency in some cases. However, this method has the drawback of using a large amount of energy to produce minimal O_3.[94] According to the study conducted by Gerrity et al, 98% removal of drugs and pesticides was achieved with the ozonation process of municipal wastewater.[14]

Among AOPs, ozonation has achieved the most extensive industrial implementation in wastewater treatment. Ozone-based systems have been widely deployed to mitigate pollution from diverse industrial activities, including electroplating, electronics and semiconductor manufacturing, recycling operations, textile production, marine aquarium systems, and petroleum refining. Their effectiveness has also been shown within the food industry, notably for effluents generated by distilleries, olive oil mills, and meat processing facilities. In more recent applications, ozonation has been adopted for the treatment of landfill leachates, wastewaters containing rubber additives, and detergent-rich municipal effluents. Notably, a full-scale UV/O_3 installation in Oklahoma has been implemented to remove biodegradable organic matter and cyanide metal complexes. Furthermore, multiple ozonation configurations have been systematically assessed for reducing the environmental burden associated with pulp and paper industry effluents. For instance, in a study by Kienle et al, 93% removal of micropollutants was achieved in biological wastewater treatment by the ozonation process.[20] O_3 is often used as a disinfectant because of its ability to cause cell lysis in bacteria. Ozone must be produced on-site as it cannot be stored. This can have a significant impact on operating costs. In addition, if the concentration of ozone reaches more than 23%, it is more explosive. Ozonation is capable

of removing 90% of emerging pollutants and is the most common oxidation method. The removal efficiency of the combined UV/O_3 process is usually higher than the additive removal efficiency of ozone and UV alone.[95] Photocatalytic oxidation represents a highly efficient and environmentally benign strategy for the treatment of organic wastewater, offering effective pollutant removal with comparatively low energy demand. In contrast to conventional treatment technologies, photocatalysis combines high degradation efficiency with catalyst reusability, rendering it especially well suited for the advanced treatment of industrial effluents, pharmaceutical wastewaters, and streams containing persistent organic compounds. To further improve treatment efficacy, this process is frequently integrated with other advanced oxidation methods. The underlying mechanism involves the generation of highly reactive hydroxyl radicals upon illumination of a metal oxide semiconductor, enabling the oxidative decomposition of a wide spectrum of contaminants. Among available materials, titanium dioxide is one of the most widely employed and effective photocatalysts, applicable either as a suspended slurry or in immobilized configurations. In addition, photocatalysis degrades not only pollutants but also byproducts that are produced in most decompositions. The removal efficiency of emerging pollutants such as viruses in some studies such as the study conducted by Qiu et al in municipal wastewater has been reported as more than 98%.[35]

TiO_2-based AOPs are widely employed to reduce the organic load of olive mill wastewater owing to their advantageous properties, including high chemical stability, high treatment efficiency, cost-effectiveness, and suitability for operation under ambient environmental conditions. A further benefit lies in their capacity to harness solar energy to achieve complete mineralization of contaminants. In recent years, increasing attention has been directed toward the use of this technology for wastewater disinfection, with several pilot-scale studies reporting successful sunlight-driven photocatalytic inactivation of microorganisms.[96] For example, in a study conducted by Philippe et al on biological wastewater, 80% of bacteria and micropollutants were inactivated using a titanium dioxide photocatalyst.[37] Electrochemical technologies have gained prominence as highly effective strategies for the removal of persistent organic contaminants from diverse wastewater matrices, and their application in water and wastewater treatment is attracting growing scientific attention. A significant amount of research has proposed electrochemical processes as viable pre-treatment options for real textile effluents. Recent progress in electrode materials, coupled with the development of more compact and efficient reactor configurations, has markedly improved the performance of electrochemical oxidation. These advances have positioned electrochemical treatment as a robust and energy-efficient approach for wastewaters containing poorly biodegradable organic compounds, including textile effluents, landfill leachates, tannery wastewaters, municipal sewage, and acid-rich industrial streams.[97, 98] In addition, Mousset et al reported the effective removal of micropollutants through electrochemical treatment.[39]

According to the data obtained from the present study, ozonation is effective in municipal systems but faces cost and bromate challenges at scale. UV-based systems, (H_2O_2/persulfate) show high efficiency for pharmaceuticals but require clear effluent. Fenton's processes are cost-effective for industrial waste but require pH control and sludge management, and electrochemical AOPs (e.g., electro-Fenton) enable catalyst reuse but need energy optimization (Table 3).

Moving towards full-scale advanced oxidation systems

Most AOPs applied on a full/industrial scale are patented, and there is not much complete data available in the scientific literature. Some industrial facilities use AOPs to remove specific pollutants from their wastewater. In these cases, the amount of wastewater treated is often small, or the process is used only for certain types of contaminants. Current wastewater treatment research with AOPs mainly focuses on a pilot scale and batch mode. Evaluating these technologies under continuous-flow operation is a prerequisite for their successful implementation at full scale. AOPs are already deployed across diverse sectors, including municipal wastewater treatment, pharmaceutical production, textile manufacturing, and global circular economy initiatives. The classifications and application scenarios outlined in this study establish a structured framework for assessing the performance of individual AOPs as well as their integrated configurations. Looking ahead, advancements in wastewater treatment increasingly prioritize enhanced operational efficiency alongside improved economic viability. Within physicochemical treatment systems, AOPs have become indispensable for the effective removal of organic contaminants, the reduction of overall energy consumption, and, in certain cases, the recovery of electrical energy arising from electron transfer during oxidative reactions. In the current study, several types of wastewater treatment technologies from AOPs were investigated. The aim was to examine these technologies in full-scale wastewater treatment and their optimal parameters, including their removal efficiency, pH, etc. Although these technologies achieve high pollutant removal efficiency, the choice of technologies depends on the characteristics of the wastewater and the specific conditions present for each method. AOPs are entering a new stage of technological maturity, with considerable promise for future applications in wastewater treatment. Although several AOPs are associated with relatively modest capital requirements, their operating costs remain substantial owing to intensive chemical usage and high energy consumption. These technologies are increasingly valued for their capacity to degrade and mineralize persistent, poorly biodegradable pollutants in aquatic environments; however, additional research is needed to enable their reliable deployment at full scale. Integrated AOP configurations consistently outperform standalone

Table 3. Comparison table of AOPs based on the data presented in Table 1

AOP Type	Oxidant/Agent Used	Key Advantages	Major Limitations	Optimal Conditions	Pollutant Removal Efficiency	Applications
Ozonation	O_3	micropollutant removal (>90%) - Synergistic with biological treatment	- Bromate formation risk - High operational costs at scale	pH 6–9 3.4 mg/L ozone dose	90% micropollutants (e.g., pharmaceuticals)	Municipal WWTPs, industrial effluents
UV/H_2O_2	H_2O_2 + UV light	- Effective for pharmaceuticals (85% carbamazepine) - No residual chemicals	Energy-intensive - Limited turbidity tolerance	5–15 mM H_2O_2 UV dose: 0.8–1.5 kWh/m³	70–92% trace organics	Drinking water, pharmaceutical wastewater
Fenton	$Fe^{2+} + H_2O_2$	Cost-effective for industrial wastewater - Rapid reaction kinetics	- pH-dependent (optimal 2.5–3.5) - Sludge generation	Fe^{2+}: 0.1–0.5 mM H_2O_2: 10–50 mM	80–95% refractory COD	Textile, petrochemical effluents
Electro-Fenton	$Fe^{2+} + H_2O_2$ (electrochemically generated)	- Continuous Fe^{2+} regeneration - Lower sludge production	- Electrode fouling - High energy input	pH 2.5–3.5 Current density: 10–30 mA/cm²	75–90% pesticides	Landfill leachate, EDC-containing wastewater
UV/ Persulfate	Persulfate ($S_2O_8^{2-}$) + UV	- Emerging technology - 40% lower energy use vs. UV/H_2O_2	- Sulfate residue - Limited full-scale data	UV intensity: 20–40 mW/cm² Persulfate: 2–10 mM	85–98% antibiotics	Hospital wastewater, antibiotic resistance genes

processes in the removal of recalcitrant contaminants, as synergistic interactions mitigate the intrinsic limitations of individual methods. This superior performance is primarily driven by the intensified generation of reactive radical species, which accelerates oxidative degradation pathways. Despite the abundance of experimental data, the translation of AOPs from laboratory and pilot-scale studies to large-scale implementation remains limited. The literature identifies high operational costs compared with conventional treatment technologies, along with concerns over the formation of toxic by-products under suboptimal operating conditions, as the principal barriers to widespread adoption. To optimize resource efficiency, AOP selection should be guided by clearly defined treatment objectives such as micropollutant abatement, pathogen inactivation, or the polishing of industrial effluents, thereby avoiding unnecessary consumption of oxidants, catalysts, and energy. In this context, the integration of AOPs with established wastewater treatment processes emerges as a pragmatic and environmentally sustainable strategy with near-term applicability.

Conclusion

This study provides a comprehensive overview of the current state of AOPs in wastewater treatment, highlighting their considerable ability as effective and environmentally sustainable solutions for diverse effluent streams. A substantial body of experimental evidence and full-scale applications worldwide has confirmed the effectiveness of AOPs including ozonation, ultraviolet-based technologies, and photocatalytic systems in removing micropollutants such as pharmaceuticals, personal care products, and other persistent organic contaminants. The literature consistently indicates that optimal process performance depends on precise control of key operational parameters, notably pH, temperature, and reagent dosage. Moreover, integrating AOPs with complementary treatment technologies, such as biological processes or membrane-based separation, can further enhance overall treatment efficiency. A thorough understanding of the fundamental reaction mechanisms particularly the roles of reactive species and the influence of wastewater matrix constituents is also critical for accurately predicting treatment outcomes. Collectively, the implementation of AOPs can markedly improve effluent quality through effective micropollutant abatement; however, continued research and technological development remain essential to enable their efficient, scalable, and sustainable adoption in wastewater treatment facilities worldwide.

Acknowledgments

The authors hereby express their gratitude to the Student Research Committee of Kermanshah University of Medical Sciences for financial support (Grant No: 4030318).

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Competing Interests

The authors report no conflicts of interest.

Ethical Approval

Ethical issues have been completely considered by the authors.

Funding

No funding was obtained in this study.

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