

Advanced Oxidation Process: Tearing Organic Pollutant

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Abstract

Pollutants are chemicals or materials that get into the natural environment and harm ecosystems and living things. The Advanced Oxidation Process (AOP) is an emerging technology for treating water contaminated with organic pollutants. AOPs are based on the generation of highly reactive hydroxyl radicals, which achieve the oxidation of robust organic compounds that resist degradation by traditional treatment processes. Hydroxyl radicals are produced in various ways, and AOPs include some of the methods that produce them. Fenton's reaction, photocatalysis, ozonation, and combinations such as UV/H₂O₂ systems or UV/TiO₂ are AOPs, and they are characterized by achieving the almost complete mineralization of the organic "parent" compound into harmless end products—principally, water and carbon dioxide—under quite mild conditions. This abstract presents the principles of operation of AOPs, their efficiencies in degrading various classes of organic contaminants, some key operational parameters, and some limitations. We also cover what appears to be an important trend: integrating AOP processes with traditional treatment systems. AOPs are versatile, scalable and can handle varying pollutant loads so are suitable for all water treatment needs. When combined with biological or physical methods they are more efficient, and research is focused on reducing energy consumption and operational costs. When combined with renewable energy like solar photocatalysis AOPs are also climate change mitigation and environmentally friendly solutions.

Keywords: Pollutants, Advanced Oxidation Process, Hydroxyl radicals, Organic contaminants, Traditional treatment system.

1. Introduction

Advanced Oxidation Processes (AOPs) is a group of chemical processes for the eradication of organic and inorganic contaminating chemicals in water and wastewater through in situ creation of strong, powerful reagents, predominantly hydroxyl radicals ($\bullet\text{OH}$), with high oxidative capacities. The radicals decompose complex and persistent chemicals into less complex, less toxic chemicals such as water and carbon dioxide. Examples of processes under AOPs include processes such as Fenton's reaction, ozonation, photocatalysis, and hybrid processes such as UV/H₂O₂ and electrochemical oxidation. Fundamentals of AOPs involve in-situ ROS (reliable oxidative species) creation via physicochemical and photochemical processes, initiation of secondary

redox processes, and pollutant mineralization. Scalability and integration with conventional processes is a dominant theme in studies, with a view towards efficiency improvement, minimizing consumption of energy, and sustainability. Emerging trends involve integration with emerging techniques such as integration with sound waves, membrane processes, and integration with hydrodynamic cavitation for efficiency and economy improvement [1-3]. Advanced Oxidation Processes (AOPs) play a critical role in wastewater treatment by effectively decomposing persistent and non-biodegradable toxins such as pharmaceutical residues, chemicals, and organic compounds. AOPs generate strong oxidative radicals, primarily hydroxyl radicals ($\bullet\text{OH}$),

which break down complex organic compounds into simpler, non-toxic substances like water and carbon dioxide. Recent studies have confirmed that AOPs, particularly hydrogen peroxide-based systems, significantly improve water quality, achieving a 93% reduction in contaminants in domestic wastewater treatment [4]. Hybrid AOPs, which combine traditional AOPs with membrane filtration or electrochemical oxidation, further enhance efficiency by accelerating reaction kinetics and ensuring complete pollutant mineralization [5]. Integrating inorganic membrane filtration with AOPs helps counteract membrane fouling, increasing operational lifespan and reducing costs [6]. AOPs also provide an environmentally friendly alternative to conventional treatment methods, making wastewater reuse a viable solution to address water scarcity. Their scalability and versatility make them essential for wastewater treatment in industries, pharmaceuticals, and urban areas. As research advances, AOPs are expected to become more cost-effective and energy-efficient, paving the way for sustainable wastewater management on a global scale [7].

2. Types of Advanced Oxidation Processes

2.1. Hydroxyl Radical - Based Processes

Hydroxyl radical-based processes serve as a basis for Advanced Oxidation Processes (AOPs) through efficient degradation of complex organic pollutants into less toxic compounds. Hydroxyl radicals ($\bullet\text{OH}$) are high reactivity species with capabilities to break down persistent water pollutants, and thus serve a key constituent in most AOP approaches. Certain processes include Fenton's reaction, electrochemical oxidation, ozonation, photocatalysis, and multi-method oxidation in hybrid AOPs with several processes in combination. Research confirms efficiency of hydroxyl radical-based AOPs in organic matter degradation through several approaches towards generating radicals, including hydrogen peroxide activation, catalysts, and ultrafine bubbles for oxidation [8]. There have been new catalysts designed for increased yield of hydroxyl radicals, with increased efficiency and durability in degradation in electrochemical AOPs [9]. Other studies present successful application of hydroxyl radical-based oxidation in decoloration of dye wastewater in textiles, with a considerable drop in

intensity [10]. All these advances pave the way for increased potential for application of hydroxyl radical-powered AOPs in detoxification in the environment, with a focus towards future application in sustainable wastewater management systems [11].

2.1.1. Fenton and Photo-Fenton Processes

The Fenton and Photo-Fenton processes are widespread Advanced Oxidation Processes (AOPs) that generate hydroxyl radicals ($\bullet\text{OH}$) for organic pollutant degradation in wastewater. In the Fenton process, hydrogen peroxide (H_2O_2) and ferrous iron (Fe^{2+}) react to generate high-energy hydroxyl radicals. The process is effective in treating resistant industrial wastewater, with 99.99% COD and BOD removal under optimized conditions [12]. In the Photo-Fenton process, the Fenton reaction is augmented with ultraviolet (UV) radiation, regenerating Fe^{2+} from Fe^{3+} and improving radical yield and reaction efficiency. The process has been effective in decomposing food dyes in wastewater, with rapid photodegradation following first-order kinetics [13]. Electro-Fenton, with its incorporation of electrochemical oxidation for enhanced pollutant degradation [14], is researched to join these processes. All such processes have been considered environmentally friendly and cost-effective for treating industrial wastewater, with high efficiencies for complex pollutant removal.

2.1.2. Ozone-Based Oxidation

Ozone-based oxidation processes constitute a considerable subclass of Advanced Oxidation Processes (AOPs) in which ozone (O_3) is utilized as a powerful oxidant for organic and inorganic compound decomposition in effluents. Ozone can directly destroy contaminating compounds, and when blended with hydrogen peroxide (H_2O_2), ultraviolet (UV) radiation, or catalysts, it generates hydroxyl radicals ($\bullet\text{OH}$), and its overall effectiveness is enhanced. Studies have confirmed that ozonation-based AOPs can effectively decompose pharmaceutical residues and other persistent organic compounds and, for that reason, constitute a most promising technology for treating wastewater [15]. Ozonation plays a significant role in pollutant mineralization through its contribution to generating hydroxyl radicals, and many studies have considered its application in urban and industrial wastewater

[16]. One of the greatest impediments for ozonation-based AOPs is mass transfer and fairly high operational costs. However, when ozonation is blended with UV and catalysts, it has been proven to become efficient and cost-effective [17]. All these advances serve to reveal a growing role for ozonation-based oxidation in water purification and restoration processes in the environment.

2.1.3. UV/H₂O₂

The UV/H₂O₂ is a widespread Advanced Oxidation Process (AOP) utilizing ultraviolet (UV) radiation for hydrogen peroxide (H₂O₂) activation, producing powerful, active hydroxyl radicals (•OH). The radicals decompose organic matter, including drugs and cosmetics residues, in sewage and water treatment [18]. UV/H₂O₂ achieves high efficiency in pollutant degradation, with hydroxyl radicals contributing to decomposing complex organic compounds [18]. In addition, it is effective in transforming dissolved black carbon in water, with enhanced degradation capacity for organic compounds. While highly effective, its effectiveness can, nevertheless, vary with factors such as oxidant concentration, pH, and availability of natural organic matter. Widespread application in potable water treatment, reuse of wastewater, and purification of effluents in industries is a testimony to its function in modern-day environment purification.

2.1.4. Electrochemical Oxidation

Electrochemical Oxidation (EO) is one of the most significant Advanced Oxidation Processes (AOPs) generating in situ hydroxyl radicals (•OH) for degradation of persistent organic pollutant species. Electrochemical oxidation utilizes an electric current for enhancing oxidation at an anode, producing ROS, effectively decomposing complex contaminating species in wastewater. Electrochemical oxidation with boron-doped diamond (BDD) electrodes has become increasingly utilized for its effectiveness in oxidation through its high durability and ability for generating hydroxyl radicals [20]. Electrochemical oxidation in combination with other additional AOPs, such as Fenton and persulfate activation, have been utilized for enhancing pollutant removal efficiency [3]. Electrochemical oxidation has been utilized effectively for stormwater and industrial wastewater treatment, with significant contaminant removals in

terms of *Escherichia coli* and organic compounds [20]. With ongoing development, electrochemical oxidation is becoming increasingly a preferred environmentally friendly and scalable option for wastewater treatment.

2.2. Non-Radical Based Process

Non-radical based Advanced Oxidation Processes (AOPs) introduce a new mechanism for contaminant degradation free of sulfate (SO₄•⁻) and hydroxyl (•OH) radicals. These processes include processes such as direct electron transfer, singlet oxygen (¹O₂) oxidation, and surface-bound activation of oxidants, and occur predominantly in a non-radical mechanism. Non-radical AOPs have become a significant alternative in consideration of their selectivity, less water matrix compounds' interference, and less energetic requirements compared with radical-based AOPs [21]. Persulfate (PS) and peroxymonosulfate (PMS) have been demonstrated in experiments to have the capability of being activated with transition metal catalysts and carbon-based catalysts for producing singlet oxygen, selectively attacking electron-abundant pollutants with minimum secondary pollution. Besides, metal-free catalysts such as nitrogen-doped carbon have recently been demonstrated to effectively enable contaminant degradation through electron transfer reaction [22]. Non-radical AOPs have an additional value in complex water matrices in which traditional radical-based processes are hindered with an issue of scavenging, and thus represent a new technology for selective oxidation and environmentally friendly water purification.

2.2.1. Persulfate and Peroxy Mono Sulphate Activation

Persulfate (PS) and peroxymonosulfate (PMS) activation are well-studied non-radical based Advanced Oxidation Processes (AOPs) that effectively degrade organic pollutants via processes including high-valent metal oxidation, singlet oxygen (¹O₂) formation, and direct electron transfer. Unlike processes with radicals, non-radical processes exhibit increased selectivity and enhanced stability in complex aquatic environments, and can therefore effectively be applied in processes for wastewater treatment processes. Recent work depicts that many catalysts, including metal oxides, transition metal

sulfides, and metal-organic frameworks (MOFs), stimulate PMS activation for generating reactive species including singlet oxygen and high-valent metals including Fe(IV) and Co(IV), and stimulate pollutant degradation [23]. Transition metal sulfides (e.g., CoS, FeS, CuS) with multi-faceted activation performance have been discovered through studies, with a range of prevalent dominant reactive species in each system. High-valent metal production during persulfate activation have been discovered to boost selectivity and oxidation efficiency [24]. All these observations present increased potential for PS and PMS activation in processes for water purification and restoration in the environment.

2.2.2. Catalytic Wet Air Oxidation

Catalytic Wet Air Oxidation (CWAO) is a non-radical mechanism Advanced Oxidation Process (AOP) utilizing high temperature and high pressure oxygen or air and a catalyst for degradation of organic contaminants in wastewater. Unlike radical mechanism-based oxidation processes, CWAO utilizes a non-radical route through oxygen transfer reaction, generating selective oxidation and contaminant mineralization. It effectively treats refractory organic compounds such as phenol and sewage sludge, with transition metal oxides, noble metal, and metal-organic frameworks (MOFs) utilized for catalysts in enhancing oxidation efficiency [25]. According to research, CWAO effectively reduces operational temperatures and pressures when utilizing homogenous and heterogeneous catalysts such as Cu- and Mo-based materials [26]. Besides, its integration with membrane-based processes has been effective in improving micropollutant removal [27]. As research continues, CWAO increasingly becomes an environmentally friendly and cost-effective alternative for wastewater treatment, with development focused towards improving catalysts' stability and efficiency in terms of energy consumption.

2.3. Hybrid AOPs

Hybrid Advanced Oxidation Processes (AOPs) involve combining two or more AOPs, or combining them with traditional treatment processes, in an attempt to maximize pollutant degradation efficiency. Hybrid processes utilize synergistic

effects between two or more oxidation processes, enhancing reaction kinetics, mineralization efficiency, and energy efficiency. Hybrid AOPs have been effective in treating persistent contaminants such as pharmaceutical residues, industrial effluents, and organic micropollutants [5]. Typical examples of hybrid AOPs include processes such as UV/H₂O₂/O₃, sonochemical oxidation, and electrochemical Fenton processes, and have proven to exhibit high performance compared to individual single AOP processes [28]. In addition, technoeconomic analysis has proven that hybrid AOPs, such as UV/Fenton and UV/electro-Fenton, exhibit cost-effective wastewater treatment with high pollutant efficiency. With ongoing development, hybrid AOPs are increasingly becoming subjects of investigation for full-scale operations, with a view to optimizing operational factors and combining them with current infrastructure in treatment processes.

2.3.1. AOPs Combined with Biological Treatment

The combination of Biological and Advanced Oxidation Processes (AOPs) has been an effective method towards persistent pollutant degradation in effluents. Electrochemical oxidation and Fenton processes, for example, serve as a pre-treatment for decomposing complex organic pollutants into less complex, biodegradable intermediates, whose degradation is then facilitated through increased effectiveness in a successive biological treatment [29]. Research confirms that a combination of AOPs with biological processes maximizes pharmaceutical pollutant mineralization, with over 90% efficiency in optimized experiments [30]. The combination of processes has, in addition, proven effective in PPCPs and pharmaceuticals' removal in effluents and toxicity reduction towards microbial communities [29]. Research in abattoir effluent treatment confirms that AOPs can serve as an additional supplementary form of treatment for increased biodegradability preceding a biological treatment. Optimizing operational factors and developing

2.3.2. AOPs Integrated with Membrane Filtration

Hybridization of membrane filtration with Advanced Oxidation Processes (AOPs) is a promising strategy for wastewater treatment, with the potential to

enhance pollutant degradation and membrane performance. Fenton oxidation, ozonation, and persulfate activation are a few AOPs coupled with membranes to reduce fouling, extend membrane lifespan, and improve contaminant removal efficiency. Research highlights that inorganic membrane filtration coupled with AOPs effectively degrades recalcitrant organic pollutants and inhibits membrane contamination [31]. Hybrid Fenton oxidation and ultrafiltration have also been demonstrated to eliminate paracetamol and reduce the accumulation of chemical residues [32]. In produced water treatment, oxidation-membrane hybrid technologies demonstrate improved fouling inhibition and water quality improvement [33]. While research is ongoing, efforts are directed towards optimizing membrane material and introducing cost-effective AOPs for large-scale wastewater treatment solutions.

3. Mechanism of Organic Pollutant Degradation

Advanced Oxidation Processes (AOPs) degrade organic pollutants by generating highly reactive species such as hydroxyl radicals ($\bullet\text{OH}$), sulfate radicals ($\text{SO}_4^{\bullet-}$), and singlet oxygen ($^1\text{O}_2$). The reactive species non-selectively attack organic molecules, breaking them down into smaller, more biodegradable compounds, and ultimately leading to complete mineralization into CO_2 and H_2O . Research highlights that catalysts, such as cobalt-anchored biochar, enable peroxymonosulfate (PMS) activation, enhancing efficient pollutant degradation [6]. Persulfate-based AOPs are also influenced by natural organic matter, which can either enhance or inhibit degradation efficiency [34]. Copper-based catalysts have also been extensively studied for activating AOPs through processes such as photocatalysis and Fenton-like reactions [35]. These degradation mechanisms allow for the optimization of AOPs for wastewater treatment and environmental remediation.

3.1. Generation of Hydroxyl Radicals (OH)

Hydroxyl radicals ($\bullet\text{OH}$) are the main reactive species in advanced oxidation processes (AOPs) with high oxidation potential for organic pollutants degradation. The generation of $\bullet\text{OH}$ can be achieved through various methods, such as through

electrochemical oxidation, catalytic activation and ultrafine bubble. Heterogeneous catalysts are known to promote the formation of hydroxyl radicals in electrochemical advanced oxidation processes (AOPs), significantly improving the efficiency of contaminant degradation [9]. Ultrafine bubbles have also been utilized to improve hydroxyl radical production, which is essential for degrading textile dyes [10]. It also allows for in-situ activation of hydrogen peroxide in electrochemical AOPs to expedite the generation of $\bullet\text{OH}$ [36]. Disambiguation and enhancement of these generation pathways is vital towards improving AOP performance in wastewater treatment applications.

3.2. Oxidation pathway of Organic Pollutants

Advanced Oxidation Processes (AOPs) for the treatment of organic pollutants rely on multiple degradation mechanisms, which involve radical-mediated oxidation, reactions with singlet oxygen, and direct electron transfer. Although Hydroxyl radicals ($\bullet\text{OH}$) and sulfate radicals ($\text{SO}_4^{\bullet-}$) mainly degrade complicated organic compounds into smaller, more degradable intermediates and finally mineralize into CO_2 and H_2O , it has been recently reported that the MnCe-based catalysts enhance the oxidative efficiency via the synergistic effect of radical and surface catalytic mechanisms [37]. Moreover, the oxidation of singlet oxygen ($^1\text{O}_2$) has been observed as a selective mechanism for the degradation of contaminants, especially pharmaceuticals and personal care products. Photocatalytic and Fenton-like processes have also been evidenced to target the pollution by oxidative cleavage, hydroxylation, and decarboxylation pathway, as such contamination control models [35]. These pathways can be harnessed to optimize the use of AOP in wastewater, sludge treatment and environmental reclamation.

3.3. Kinetic of Pollutant Degradation

Factors such as the composition of the catalyst, concentration of the oxidant, the time of the reaction and the structure of the pollutant affect the kinetics of its degradation (in Advanced Oxidation Processes, AOPs). The reaction kinetic models of organic contaminants degradation rate by the different kinetic models (pseudo-first-order, pseudo-second-order, and bimolecular) were proposed. Kinetic

studies of perovskite-based catalysts for oxidation of pollutants, e.g., Acid Orange II, fit a pseudo-second-order kinetic model, and degradation efficiency of 97% is reached under optimum conditions. PS-based AOPs are also efficient in degrading chlorpyrifos, exhibiting high reaction rate constants, highlighting the strong pollutants degradation capabilities of sulfate and hydroxyl radicals. Nanoconfined catalytic systems reduce oxidation activation energy by improving electron transfer and mass transport, which contributes to a reaction rate increase of 3-order magnitudes. Aromatic compound removal via AOPs has been shown to follow first order reaction kinetics, making elucidation of kinetic mechanisms during treatment critical for wastewater treatment optimization.

4. Challenges and Limitations of AOPs

4.1. High Energy Consumption

One of the big challenges associated with AOPs is their energy consumption (e.g. in UV irradiation, electrochemical oxidation, and plasma-based treatments). On the other hand, energy-hungry methods like UV/H₂O₂ and electro-Fenton oxidation need a lot of energy to produce hydroxyl radical, which are expensive for large-scale use [3]. Ghime and Ghosh (2020) state that recent studies have focused on optimum operational conditions, incorporation of renewable energy sources, and hybrid AOPs to improve energy efficiency. Future studies will focus on enhancing catalyst efficiency and reactor design for reductively-coupled processes to reduce energy requirements without sacrificing the efficacy of pollutant degradation.

4.2. Formation of Toxic Byproducts

The unintentional production of hazardous byproducts during the breakdown of organic pollutants is one of the major problems with Advanced Oxidation Processes (AOPs). Chlorine-based AOPs can produce disinfection byproducts (DBPs), including as chlorinated and brominated chemicals, which can be harmful to the environment and human health. Research has indicated that endocrine-disrupting chemicals and pharmaceuticals are examples of emergent organic micropollutants (EOMPs) that function as precursors for the creation of DBP, potentially increasing the toxicity of treated water. To provide safe and efficient water

purification, managing these harmful byproducts calls for process optimization, sophisticated monitoring systems, and integration with other treatment methods.

4.3. Cost Effectiveness and Scalability

The affordability and evolutionary possibilities of Advanced Oxidation Processes (AOPs) are main barriers to their general use. The use of these methods on a large scale is hindered by the high costs of both - capital and operational associated with energy-intensive technology. Some of these technologies are among the most energy-demanding in the industry as they use a lot of electricity such as ozone treatment, electrochemical oxidation, and UV-based AOPs. To boot, the requirement for specific reagents and catalysts for a number of processes pushes up the cost. Reportedly, the sustainable approach can be encouraged by producing affordable catalysts, incorporating renewable energy sources, and adjusting process parameters. More demands for modularity and flexibility can only be met with a rise in the range of the technology as acute issues such as differences in water quality, reactor design constraints, and maintenance requirements are likely to arise in the future.

Conclusion

Advanced Oxidation Processes (AOPs) are identified as the most effective and flexible way of cleaning water contaminated with persistent organic pollutants. AOPs are powerful breakdown agents, it helps those highly reactive radicals (especially hydroxyl radicals) to be created. This leads to the degradation of the complex pollutants that end up as harmless products such as water and carbon dioxide. The different AOPs, such as Fenton's reaction, photocatalysis, ozonation, and hybrid systems, have shown remarkable efficiency in the removal of the pollutant in all kinds of industries and households. Despite being very useful, AOPs can face the following challenges such as high energy consumption and toxic by-product formation, leading to rising costs, hence making it difficult to introduce them on a large scale. But with a continuous experiment, the project focuses on the development of the energy-efficient catalysts, and attempt to merge the AOPs with biological and membrane-based treatment systems to secure the sustainability and

cost-effectiveness. Forthcoming innovations, for example, the use of renewable energy resources and the development of catalytic materials will enhance the preparation of AOPs for the treatment of wastewater globally. AOPs as an applied technology can be expected to make water treatment services superior to the existing quality of life and environment on a global scale through dealing with the current limitations and the process optimization.

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