

Review

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Review

A Review of Various Advanced Oxidation Techniques for Pesticide Degradation for Practical Application in Aqueous Environments

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Abstract: Pesticides are chemicals used in agriculture, industry, and households to control pests and enhance crop yields but have emerged as pollutants in soil and water due to their presence in domestic and agricultural wastewater effluents. The World Health Organization (WHO) has identified the development of pesticide resistance as a significant threat to global public health. Consequently, removing pesticides in aqueous environments has gained considerable attention. Numerous methodologies, including biological, physical, and chemical methods, have been employed for their treatment. Among these methods, advanced oxidation processes (AOPs) have garnered particular interest due to their fast reaction rates and strong oxidizing abilities. This review focuses on various AOPs such as Fenton and Fenton-like oxidation, Ozonation, UV/H2O2 process, electrochemical oxidation, Photocatalytic oxidation, and UV/O3 process. The review analyzes and summarizes the current applications of these AOPs for treating pesticides in in aqueous environment. It also compares various AOPs treatment methods and discusses the challenges, the drawbacks, advantages, strategies for addressing these issues, and provides insights into the future prospects. Finally, propose potential strategies and areas of improvement for future research to enhance the efficiency and sustainability of AOPs in practical application.

Keywords: advanced oxidation process; aqueous environment; pesticides; wastewater treatment; Fenton process; ozonation; photocatalytic oxidation; electrochemical oxidation

1. Introduction

Pesticides play a crucial role in agriculture by protecting crops from pests, diseases, and weeds. They enhance food production and contribute to global food security. However, the widespread and often indiscriminate use of pesticides has led to their accumulation in the environment, presenting significant challenges and risks[1]. One key concern is the contamination of water sources, both surface water and groundwater, with pesticide residues. Pesticides can enter water bodies through runoff from agricultural fields, leaching from soil, and improper handling or disposal practices. This contamination poses a threat to aquatic ecosystems, drinking water supplies, and non-target organisms, including beneficial insects, birds, and mammals[2]. To address this issue, effective and environmentally-friendly pesticide treatment methods are essential. First and foremost, the removal of pesticide residues from water sources is necessary to safeguard human health. Consumption of

pesticide-contaminated water can lead to acute or chronic toxic effects, especially if the concentrations exceed regulatory limits[3]. Furthermore, the preservation of aquatic ecosystems is crucial. Pesticides can have detrimental effects on various aquatic organisms, such as fish, amphibians, and invertebrates. Even at low concentrations, these chemicals can disrupt reproductive systems, impair growth and development, and induce behavioral changes in aquatic life. By treating water sources contaminated with pesticides, we can help protect the balance and biodiversity of aquatic ecosystems[4].

The use of environmentally-friendly methods for pesticide treatment is vital to minimize the negative impact on the environment. Traditional treatment methods, such as activated carbon filtration or chemical precipitation, have limitations in terms of efficiency and selectivity. These methods may also generate harmful byproducts or require extensive post-treatment processes[3]. Emphasizing the importance of environmentally-friendly alternatives, advanced oxidation processes are gaining recognition. AOPs offer effective treatment solutions while considering environmental compatibility. By utilizing oxidation techniques like ozone, hydrogen peroxide, and UV radiation, AOPs can degrade pesticide residues and transform them into harmless byproducts. This approach minimizes the introduction of additional pollutants and promotes the sustainable management of pesticide-contaminated water sources[5]. Pesticide treatment plays a crucial role in protecting human health, preserving aquatic ecosystems, and ensuring environmental sustainability. With the increasing need for safer and more effective methods, the development and implementation of environmentally-friendly approaches, such as AOPs, are essential for addressing pesticide contamination and mitigating its adverse effects on ecosystems and society at large[6].

Advanced oxidation processes are a category of chemical treatment methods used to facilitate the degradation of organic contaminants in water and wastewater. AOPs employ the generation of highly reactive hydroxyl radicals (*OH) to oxidize and break down various organic compounds into harmless substances or lower toxicity intermediates[7]. In the context of pesticide treatment, AOPs offer a promising solution for the removal of pesticide residues from water sources. AOPs can effectively degrade and eliminate the pesticide residues[8, 9]. It involves the application of advanced oxidation techniques like ozone (O₃), hydrogen peroxide (H₂O₂), and ultraviolet (UV) radiation, either individually or in combination, to generate *OH radicals. These radicals possess strong oxidative power, enabling them to attack and break the chemical bonds of various organic compounds, including pesticide molecules [10]. The AOPs' potential lies in their ability to degrade a wide range of organic contaminants, including highly resistant pesticides. They can effectively transform complex pesticide structures into simpler and less toxic byproducts. By using AOPs, it becomes possible to treat water contaminated with different pesticide classes, such as herbicides, insecticides, and fungicides[5, 11]. Advanced oxidation processes (AOPs) offer advantages in terms of efficiency, selectivity, and environmental compatibility. They can be tailored to target specific pesticide compounds based on their reactivity and structure. Additionally, AOPs are capable of mineralizing pesticides into carbon dioxide (CO₂) and water (H₂O), reducing or eliminating the presence of potentially harmful byproducts[12]. The objective of this review is to explore and evaluate different types of Advanced Oxidation Processes in treating wastewater contaminated with pesticides. By analyzing existing studies and research findings, the review aims to compare the effectiveness of various advanced oxidation methods in terms of their efficiency, advantages, limitations, and applicability in the practical treatment of pesticide-contaminated wastewater, and suggestions for future research are proposed.

2. Pesticides in Aqueous Environment

2.1. Sources of Pesticide Contamination in Aqueous Environment

Pesticide contamination in wastewater stems from various sources, primarily agricultural runoff and urban activities (Fig. 1). In agricultural settings, pesticides are widely used to protect crops from pests and diseases[13]. However, excess application or improper handling can lead to runoff during rainfall events, carrying pesticides into nearby water bodies or infiltrating groundwater.

Additionally, urban areas contribute to pesticide contamination through the use of lawn and garden pesticides, as well as pest control measures in households and public spaces (Fig. 2). Stormwater runoff from urban surfaces can transport these chemicals into sewage systems, further exacerbating contamination issues[14]. Furthermore, industrial activities such as manufacturing and chemical production may also contribute to pesticide pollution through improper disposal practices or accidental spills, adding to the complexity of managing pesticide contamination in wastewater systems. Efforts to mitigate pesticide pollution require a multifaceted approach, including improved agricultural practices, stricter regulations on pesticide use, and enhanced wastewater treatment methods to safeguard water quality and ecosystem health[13].

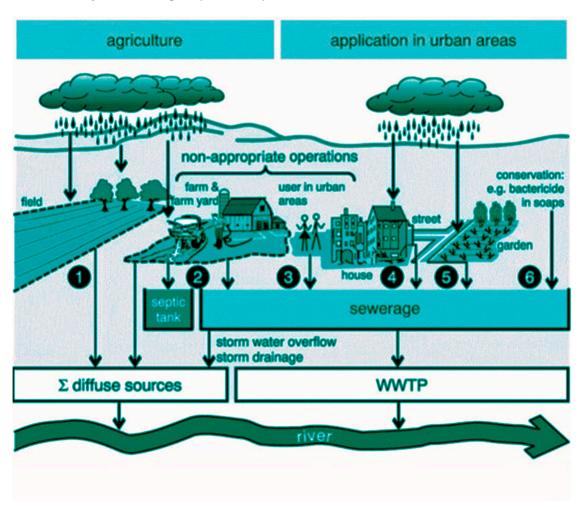


Figure 1. Important applications and major pathways for pesticide transport into surface waters. Field: spray drift during application, surface runoff and leaching with subsequent transport through drainage channels during rain events. Farm and Farmyard: improper operations (e.g., filling of sprayers, washing of measuring utilities, disposing of packing material, driving with seeping sprayers, cleaning of spraying equipment). These operations are done either at locations, which are drained to the sewerage, to the septic tank or into surface waters. Like for pesticide users in urban areas. Pesticides in building material: leaching during rain events. Applications on lawns, streets, road embankments: runoff during rain events.
Protection of materials: e.g. products containing antifouling ingredients that get into the sewerage (e.g. detergents, cosmetics).

Pesticide Contamination Sources

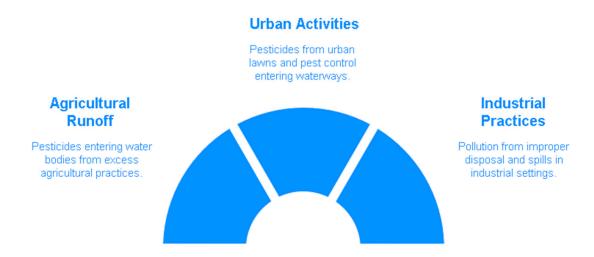


Figure 2. pesticide contamination sources.

2.2. Health and Environmental Impacts of Pesticide Pollution

Pesticide pollution presents significant health and environmental risks to both human populations and ecosystems (Fig. 3). Human health impacts arise from exposure pathways like consuming contaminated food and water, inhaling pesticide residues, and direct skin contact during agricultural activities. Chronic pesticide exposure is associated with various health issues, including cancer, reproductive disorders, and neurological ailments, with children and pregnant women being especially vulnerable[15]. Environmental consequences encompass soil, water, and air contamination, disrupting ecosystems, causing biodiversity loss, and affecting non-target organisms like beneficial insects and aquatic life through toxicity and habitat disturbances. Pesticides persist in the environment, leading to bioaccumulation and biomagnification, with long-term repercussions on ecosystems. The degradation of water quality due to pesticide runoff from agricultural areas and improper disposal practices threatens aquatic life, safe drinking water sources, and agricultural productivity by compromising essential water resources[16].

Pesticide Pollution Impacts

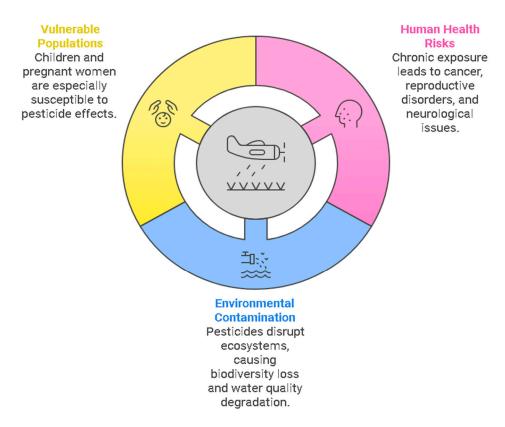


Figure 3. Pesticide pollution Impacts.

3. Overview of Different Advanced Oxidation Processes and Their Underlying Mechanisms of Wastewater Treatment

3.1. Fenton and Fenton-Like Process

Fenton's reaction relies on the use of hydrogen peroxide (H₂O₂) and a catalyst, typically iron (Fe), to generate hydroxyl radicals[17, 18]. The iron catalyst converts hydrogen peroxide to highly reactive hydroxyl radicals at a suitable pH[19]. These hydroxyl radicals can rapidly oxidize various organic pollutants, breaking them down into simpler and less harmful compounds. The underlying mechanism involves the reaction between iron catalyst and hydrogen peroxide, forming hydroxyl radicals via the Fenton reaction (Eq. 1.1)[18]. Building upon this fundamental mechanism, various advanced oxidation methods have been developed, such as photo-Fenton (PF), electro-Fenton (EF), photo electro-Fenton (PEF), and solar photo electro-Fenton (SPEF)[20-22]. These methodologies aim to enhance the circulation of Fe(III)/Fe(II) species and amplify the generation of hydroxyl radicals (*OH) to effectively degrade recalcitrant contaminants. The mechanisms underlying these advanced processes involve: 1) In-situ electro-generation of H₂O₂ through the two-electron reduction of molecular oxygen (O₂) on a carbonaceous cathode (Eq. 1.2); 2) Utilization of an electric field to facilitate the in-situ regeneration of Fe(II) species at the cathode (Eq. 1.3)[22]; 3) Accelerated conversion of Fe(III) to Fe(II) species via photocatalytic reactions, coupled with the decomposition of H₂O₂ to generate additional hydroxyl radicals (Eqs. 1.4~1.5)[20, 21].

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^-$$
 (1.1)

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$$
 (1.2)

$$Fe^{3+} + e^{-} \rightarrow Fe^{2+}$$
 (1.3)

$$Fe^{3+} + H_2O + hv \rightarrow Fe^{2+} + {}^{\bullet}OH + H^+$$
 (1.4)

$$H_2O_2 + hv \to 2 \, {}^{\bullet}OH$$
 (1.5)

The oxidation mechanism for the Fenton process is shown in Figure 4. Based on this principle, Fenton process has been widely used in various kinds of organic wastewater treatment. The degradation efficiency of organic pollutants in the Fenton process depends on operation parameters such as wastewater pH, concentration of Fenton reagent, and initial organic pollutants concentration, of which wastewater pH is a highly important parameter[19].

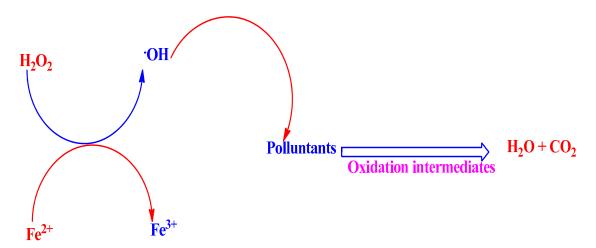


Figure 4. Reaction mechanism for the Fenton process.

3.2. Ozonation-Based Advanced Oxidation Process

Ozonation-based advanced oxidation processes (AOPs) primarily degrade and mineralize refractory contaminants through two main mechanisms: 1) Direct ozonation involves ozone reacting directly with target contaminants. This process encompasses redox reactions, cycloaddition reactions, electrophilic substitution reactions, and nucleophilic reactions[23]. 2) Another approach entails utilizing various physical or chemical methods to catalytically generate high redox potential reactive oxygen species (ROS) from ozone, notably hydroxyl radical (*0H)[25-28]. Indirect catalytic ozonation has emerged as the predominant approach for degrading and mineralizing refractory organic compounds. The synergetic effect between ozone and hydrogen peroxide has long been recognized and extensively explored by researchers for the mitigation of emerging contaminants, such as pesticides, dyes, endocrine disrupting chemicals (EDCs), pharmaceuticals, and personal care products (PPCPs)[29, 30]. This synergistic reaction between ozone and hydrogen peroxide generates powerful reactive oxygen species (ROS), particularly the hydroxyl radical (*0H) (Eq. 1.6), significantly enhancing the efficiency of removing various ozone-resistant pollutants.

$$H_2O_2 + O_3 \rightarrow {}^{\bullet}OH + {}^{\bullet}O_2^- + H^+ + O_2$$
 (1.6)

For example, Figure 5 shows the probable pathway of phenol degradation in the catalytic ozonation process over MgO/AC. Firstly, electrophilic hydroxyl radicals preferentially attack adjacent or para position of benzene ring in the reaction, and phenol is oxidized to the catechol or

hydroquinone. The hydroxyl radicals may also attack the 2 positions of p-benzoquinone, and generate 1, 2, 4-benzenetriol, 2, 5-dihydroxy-1, 4-benzoquinone and acetic acid. During the reaction, it was also speculated that there might be macromolecular substances such as acid anhydride or ester by MS analysis, and the specific formation process needs to be further studied. The final products of both these possible pathways are CO₂ and H₂O, as shown in Figure 6 [31].

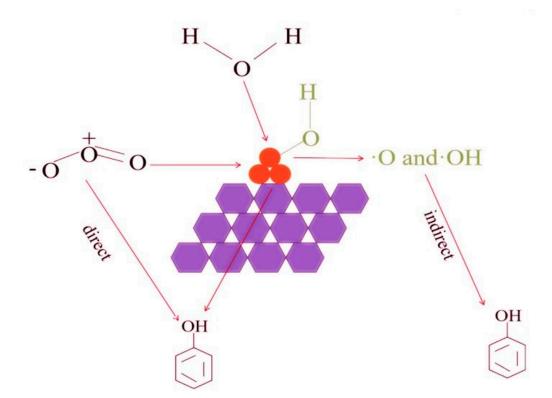


Figure 5. Mechanism of phenol degradation in catalytic ozonation.

Figure 6. The probable reaction pathway of Ozone degradation of Phenol (adapted with permission [31], Copyright 2020, Elsevier).

3.3. Photocatalysis

Photocatalysis involves the use of both a catalyst and light energy to generate highly reactive species that can degrade organic pollutants[32-34]. The catalyst, usually a semiconductor material such as titanium dioxide (TiO₂) or zinc oxide (ZnO), absorbs photons and creates electron-hole pairs. These charge carriers then participate in redox reactions, leading to the degradation of pollutants. The underlying mechanism includes the generation of hydroxyl radicals (*0H) through reactions between the catalyst and species like water or oxygen[34-36]. A prerequisite for initiating a photocatalytic reaction is that the energy imparted by photons onto the photocatalyst surpasses the energy gap (approximately 3.2 eV for titanium dioxide) between the valence band (VB) and the

conduction band (CB). Upon absorption of light energy equal to or exceeding 3.2 eV, electrons residing in the VB transition to the CB, resulting in the generation of photogenerated electrons (CB-e⁻) while leaving behind corresponding holes in the VB (VB-h⁺) (Eq. 1.7). In the presence of moisture in the ambient air, photogenerated electrons (CB-e⁻) and holes (VB-h⁺) interact with oxygen and water molecules, respectively. Photogenerated electrons (CB-e⁻) exhibit strong reducibility, facilitating the reduction of surface-bound oxygen molecules to superoxide free radicals (\bullet O_2^-), which subsequently undergo a cascade of reactions leading to the formation of hydroxyl radicals (\bullet OH) (Eqs. 1.8~1.10). Conversely, the VB holes (VB-h⁺) possess robust oxidation potential, enabling the oxidation of hydroxide ions (\bullet OH) (including those within water molecules) to generate free hydroxyl radicals (\bullet OH) simultaneously (Eqs. 1.11~1.12)[37, 38]. The hydroxyl radical (\bullet OH) emerges as the principal oxidant in the photocatalytic oxidative degradation of organic pollutants, owing to its formidable oxidation capabilities.

$$TiO_2 + hv \rightarrow e^- + TiO_2(h^+)$$
 (1.7)

$$nTiO_2(e^-) + O_2 \to nTiO_2 + \bullet O_2^-$$
 (1.8)

$$TiO_2(e^-) + O_2 + 2H_2O$$

$$\rightarrow TiO_2 + H_2O_2 + 2OH^-$$
(1.9)

$$TiO_2(e^-) + H_2O_2 \rightarrow TiO_2 + {}^{\bullet}OH + OH^-$$
 (1.10)

$$TiO_2(h^+) + H_2O \rightarrow TiO_2 + H^+ + {}^{\bullet}OH$$
 (1.11)

$$TiO_2(h^+) + OH^- \to TiO_2 + {}^{\bullet}OH$$
 (1.12)

When exposed to radiation, photocatalysts become activated, generating highly reactive photo-induced charge carriers that interact with pollutants, as depicted in Figure 7. This process allows for the efficient removal of pollutants at ambient temperature and pressure, offering a solution to the high energy consumption typically associated with conventional methods.

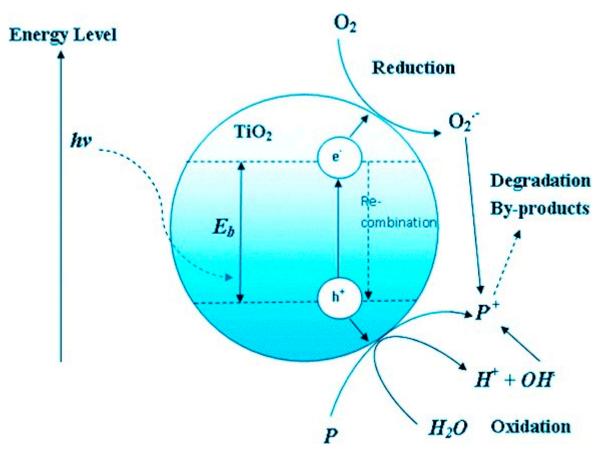


Figure 7. Photocatalytic mechanism.

3.4. UV/H₂O₂ Process

UV/ H_2O_2 has demonstrated efficacy in degrading macromolecular organic pollutants in water, leading to the formation of smaller molecule organic species[39, 40]. This process exhibits notable removal efficiency towards fluorescent compounds, substances containing benzene rings, or those with double bonds owing to the formation of high redox potential hydroxyl radical (Eq. 1.13)[39, 41]. The UV/ H_2O_2 process employs three main degradation mechanisms: Firstly, hydrogen peroxide's strong oxidizing properties enable direct oxidation of organic compounds in water. Secondly, UV irradiation initiates molecular bond dissociation, leading to the breakdown of organic pollutants. Thirdly, under UV irradiation, hydrogen peroxide undergoes photolysis, generating hydroxyl radicals ($^{\bullet}OH$) that are instrumental in oxidizing and decomposing organic pollutants. This oxidation facilitated by hydroxyl radicals constitutes the primary reaction pathway in the UV/ H_2O_2 process.

$$H_2O_2 + hv \ (\lambda = 250 \sim 254 \ nm) \rightarrow 2 \ ^{\circ}OH$$
 (1.13)

Hydroxyl radicals (·OH) initiate their attack on the carbaryl molecule, causing the disruption of chemical bonds within carbaryl. This reaction can also result in the hydroxylation of the carbaryl molecule, incorporating hydroxyl groups (OH-) into its structure. As a consequence, subsequent reactions may lead to the breakdown of the carbaryl ring, fragmenting the compound into smaller components and generating intermediate compounds. These intermediates, including hydroxylated carbaryl derivatives and other by-products, are formed throughout the degradation process[42]. Further oxidation and decomposition reactions, facilitated by hydroxyl radicals (·OH), proceed to break down complex structures into simpler, more readily mineralized compounds. The degradation sequence progresses until complete mineralization of carbaryl is achieved, yielding non-toxic inorganic end products such as carbon dioxide (CO₂) and water. The monitoring of by-products formed during the degradation process remains essential to validate the efficiency and safety of the

treatment[42]. In Figure 8, the assessment of carbaryl elimination utilizing UV and UV/H₂O₂ processes was explored. It became evident that the use of UV alone without H₂O₂ for carbaryl removal exhibited minimal effectiveness. Conversely, the combination of UV irradiation with H₂O₂ significantly hastened the elimination process, resulting in complete degradation within 75 minutes, attributed to the heightened generation of hydroxyl radicals facilitated by H₂O₂. The postulated pathway mechanism was based on the analysis of aromatic intermediates, carboxylic acids, and anions through GC-MS and IC techniques. Key indicators supporting carbaryl decomposition by UV/H₂O₂ included variations in dissolved oxygen levels, pH, acidity concentrations, and formaldehyde presence. The results underscore that carbaryl pesticides are effectively degraded through UV and UV/H₂O₂ processes, highlighting the potential of this approach for pesticide removal in drinking water and wastewater treatment applications.

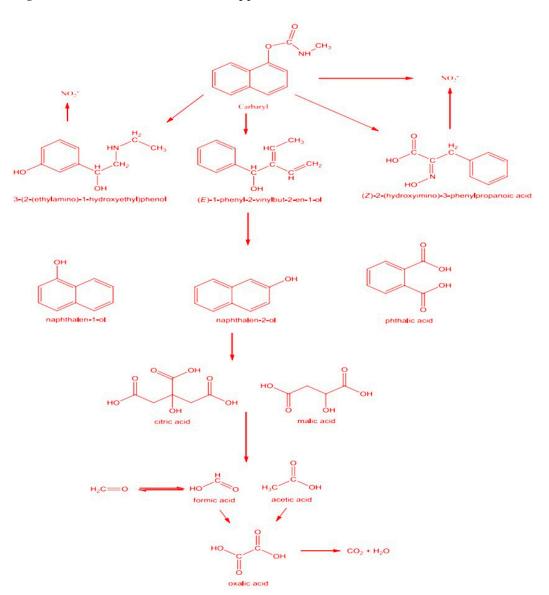


Figure 8. Suggested degradation mechanism of carbaryl with UV/H₂O₂-process (adapted with permission [42],Copyright 2020, Copyright 2020, Elsevier).

3.5. UV/O₃ Process

The UV/O₃ process represents an advanced photochemical oxidation method where ozone and ultraviolet radiation are introduced simultaneously. This approach capitalizes on ozone's oxidative properties and ultraviolet light's photolytic capabilities, utilizing the active species generated from ozone decomposition under ultraviolet light to oxidize organic matter. Glaze et al. outlined the

synergistic mechanisms between ultraviolet light and ozone, (Eq. 1.14~17)[43]. Ozone (O₃) undergoes photolysis under UV radiation, resulting in the production of hydrogen peroxide (H₂O₂). Subsequently, hydrogen peroxide reacts with ozone to generate hydroxyl radicals (*0H), a process known as the peroxone process. Additionally, hydrogen peroxide can independently produce hydroxyl radicals (*0H) under UV radiation.

$$O_3 + OH^- \rightarrow {}^{\bullet}OH \tag{1.14}$$

$$O_3 + H_2O \xrightarrow{hv} H_2O_2$$
 (1.15)

$$O_3 + H_2 O_2 \rightarrow {}^{\bullet}OH$$
 (1.16)

$$H_2O_2 \stackrel{hv}{\rightarrow} {}^{\bullet}OH$$
 (1.17)

In the combination of ultraviolet and ozone, another active species, HO_2 •, is generated, which significantly contributes to the degradation of organic pollutants in water[44]. An outstanding advantage of this combined process is its ability to promote the indirect reaction of ozone and facilitate the transformation of organic compounds from ground state molecules to active species. This creates favorable conditions for the oxidation of organic compounds, thereby enhancing their degradation efficiency.

3.6. Electrochemical Oxidation

Electrochemical oxidation involves the application of electrical energy to drive the oxidation of pollutants in an aqueous solution, resulting in their breakdown into less harmful substances. In AOPs, reactive species, primarily hydroxyl radicals (•OH), are generated, which are powerful oxidizers capable of decomposing a wide range of organic contaminants [45]. Figure 9 illustrates the mechanism of electrochemical degradation of organic pollutants using both non-active and active anodes.

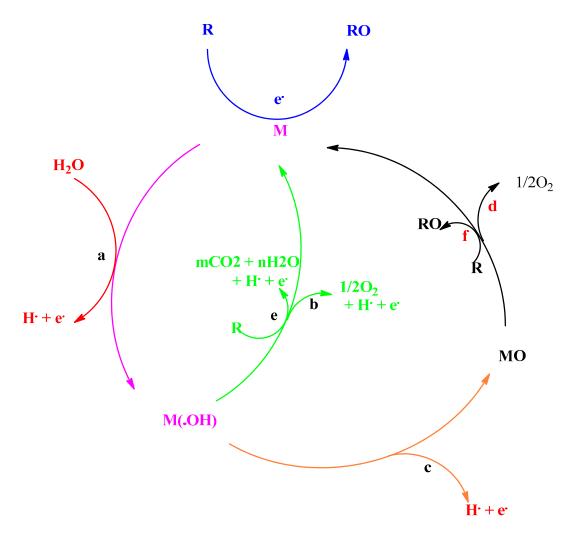


Figure 9. Mechanism diagram of electrochemical degradation organic pollutants on non-active (reactions a, b and e) and active anodes (reactions a, c, d and f); The blue line indicates the direct oxidation; (a) generation of hydroxyl radicals, •OH, (b) oxygen evolution based on •OH, (c) formation of the higher metal oxide, MO, (d) oxygen evolution base on chemical decomposition of MO, (e) electrochemical combustion of the organic compound via •OH, (f) electrochemical conversion of the organic compound.

4. Advantages and Limitations of Advanced Oxidation Processes in the Dechlorination of Pesticide Pollutants

Table 1. Comparisons of different AOPs based on their advantages and limitations in the Dechlorination of Pesticide Pollutants.

Advanced Oxidation Process (AOPs)	Advantages	Limitations	References
Photocatalysis	- Broad applicability: Photocatalysis can effectively degrade a wide range of pesticides, including various chemical classes High degradation efficiency: The generation of highly reactive hydroxyl radicals (OH) through photocatalysis	 Catalyst selectivity: Not all pesticides can be efficiently degraded by photocatalysis, as the process's effectiveness depends on the pesticide's adsorption and reaction properties. Light dependency: Photocatalytic reactions require a light source, preferably 	[46, 47]

pesticide degradation. - Regeneration of catalyst: Catalyst materials like TiO2 or reused, leading to cost savings.

enables efficient and complete ultraviolet (UV) radiation. This dependency may limit operation under certain conditions and increase energy consumption. ZnO can be regenerated and - Catalyst recovery and recycling challenges: Separating the catalyst from the treated water or waste stream can be challenging, affecting the overall efficiency and practicality of photocatalysis.

Ozonation

process

Fenton process

- Wide pesticide applicability: Ozone is highly reactive and effective in degrading various pesticide classes, including herbicides, insecticides, and fungicides.
- Rapid reaction kinetics: Ozonation offers fast reaction rates, resulting in relatively quick degradation of pesticides.
 - No chemical byproduct formation: Ozone decomposes into oxygen, or additional chemical pollutants.
 - Effective for complex matrices: Fenton's reaction can efficiently degrade pesticides even in complex matrices like wastewater or soil samples, where other treatments may encounter difficulties.
- Wide pH range: The Fenton reaction can operate under a wide pH range, allowing flexibility in treating different environmental conditions. - High reactivity: Fenton's reaction generates highly
- reactive hydroxyl radicals, leading to rapid and effective degradation of pesticides.
 - Efficient in acidic conditions (pH 3-4).
- Cost-effective compared to other AOPs

- Limited persistence: Ozone has a short half-life and readily decomposes. Therefore, its effective contact time with the pesticide may be limited and require continuous ozone generation for sustained degradation.

- Selectivity: While ozone can degrade many pesticides, there may be variations in reactivity, and some pesticides might require longer contact times or higher ozone concentrations.

- Off-gas management: The leaving no harmful residues removal and treatment of ozonerich off-gases can be challenging, requiring appropriate air pollution control measures.
 - Catalyst limitations: Selecting the proper iron catalyst and maintaining its activity is crucial. Iron catalysts may lose efficiency over time due to precipitation, fouling, or other factors, necessitating replacement or regeneration.
 - Hydrogen peroxide requirement: The Fenton's reaction relies on the addition of hydrogen peroxide, which can be costly and pose safety concerns in large-scale applications. - pH adjustment: Fenton's
 - reaction often requires pH adjustment to initiate the reaction. This step adds complexity to the process and might limit its application in some scenarios.

[48, 49]

[50]

 UV/H_2O_2

Sonochemical

degradation

 - UV/H₂O₂ is effective in degrading many pesticide classes and complex mixtures.

- It offers relatively fast reaction rates and can achieve high degradation efficiencies.
 - The process can be easily controlled by adjusting the dosages of UV light and hydrogen peroxide.
- No sludge production, and H_2O_2 decomposes into water and oxygen.

Efficiency: Sonochemical degradation can achieve high levels of pollutant degradation due to the intense cavitation and localized hotspots created by ultrasound waves.
Versatility: It can be applied to a wide range of pollutants, including organic compounds, pesticides, and pharmaceuticals.
Green process: Sonochemical

pharmaceuticals.
- Green process: Sonochemical degradation is generally considered a green process as it operates at ambient temperatures and pressures, reducing energy consumption.

Selectivity: Electrochemical oxidation allows for selective degradation of specific pollutants, depending on the choice of electrode material and operating conditions.
 Continuous operation: It

- Continuous operation: It enables continuous pollutant

Electrochemical removal as long as a sufficient oxidation supply of electricity is available.

- Easy control: Parameters such as current density and electrode potential can be adjusted to optimize the degradation process.
- No chemical addition is needed.

- UV/H₂O₂ requires a sufficient supply of hydrogen peroxide, which can add to the operational costs.

 The presence of certain water constituents can inhibit or compete with the reaction, reducing overall efficiency.

 UV/H₂O₂ may not be suitable for treating large volumes of water due to the limited penetration depth of UV light.

- Energy-intensive: Sonochemical degradation requires high power ultrasound waves, making it an energy-intensive process.

including organic compounds, pesticides, and pharmaceuticals.

- Green process: Sonochemical degradation is generally considered a green process as

 Electrode fouling: Fouling of the electrodes can occur during the electrochemical oxidation process, reducing its efficiency.

Limited applicability:
 Electrochemical oxidation may
 not be suitable for certain types
 of pollutants that are less
 amenable to oxidation or require
 specific reaction pathways.

 Cost: The cost associated with electrical power consumption, electrode maintenance, and system setup can be a limitation. [51]

[52]

[5, 53]

- Versatility: Advanced oxidation with peroxides can effectively degrade a wide range of organic pollutants, including hard-to-treat compounds. - Simplicity: Peroxide-based AOPs often have Advanced straightforward reactor oxidation with designs, making them easier peroxides to implement and operate. In certain cases, the reactions involving peroxides can be initiated by natural light rather than requiring

additional energy sources.

 Cost: The use of peroxides in AOPs can contribute to higher operational costs due to the procurement and handling of reagents.

compounds.
- Simplicity: Peroxide-based
 AOPs often have
 straightforward reactor
 designs, making them easier
 to implement and operate.
- No need for external energy: - pH sensitivity: The effectiveness

:- pH sensitivity: The effectiveness of peroxide-based AOPs can be pH-dependent, and optimizing the reaction conditions may be necessary to achieve optimal degradation efficiency. [54, 55]

5. Studies on Pesticide Treatment in Aqueous Environment Using AOPs

Table 2. A categorization of the studies based on the type of pesticide, AOP utilized, and their key findings.

Studies	Type of pesticides	AOP utilized	Key findings
The Efficiency of Advanced	Wide range of	Ozonation, UV/H2O2,	AOPs efficiently degrade
Oxidation Processes for the	pesticides	Fenton processes	pesticides, reducing their
Removal of Pesticides from			concentration below
Water			regulatory limits
Comparative Study of	Various pesticides	Ozone, UV, AOPs	AOPs involving peroxides
Pesticide Degradation by		involving peroxides	show higher degradation
Ozone, UV, and Advanced		(e.g., UV/H ₂ O ₂)	rates than individual ozone
Oxidation Processes			or UV treatment
Application of Advanced	Various pesticides	Electro-Fenton,	AOPs can effectively
Oxidation Processes for		photocatalysis, and	remove pesticides from soil,
Removing Pesticides from		Sono-oxidation	with some methods
Soil			showing higher efficiency
			than others
Advanced Oxidation	Pesticide containing	UV, ozone, UV/O3	AOPs effectively degrade
Processes for the Treatment	wastewater	process	pesticides in wastewater,

of Pesticide containing			highlighting their potential
Wastewater			as a treatment option
Process Optimization and	Various pesticides	Not specified	The study focuses on the
Kinetics of Pesticide			optimization and kinetics of
Degradation by Advanced			pesticide degradation,
Oxidation Processes			providing insights into
			effective AOP application
			for pesticide treatment
Advanced Oxidation	Various pesticides	Photocatalysis,	AOPs showed promising
Processes for Degradation		ozonation, Fenton	results for pesticide
of Pesticides in Water		processes	removal, with effectiveness
			varying based on pesticide
			type, initial concentration,
			and reaction conditions
Pesticide Degradation by	Various pesticides	Ozonation, Fenton	AOPs effectively degraded a
Advanced Oxidation		processes, UV	wide range of pesticides,
Processes		radiation	reducing their
			concentrations to acceptable
			levels. Optimal degradation
			efficiency required careful
			optimization of AOP
			parameters
Evaluation of AOPs for	Various pesticides	Photocatalysis,	AOPs demonstrated
Pesticide Removal in Water:		ozonation, electrolysis	significant potential for
A Critical Review			pesticide treatment, but
			further research was needed
			to optimize their
			effectiveness. Reaction
			conditions and catalyst

selection played a crucial role in determining AOP efficiency Advanced Oxidation Various pesticides Photocatalysis, Fenton AOPs efficiently removed Processes for the processes, ozonation pesticides, but the choice of Degradation of Pesticides in process depended on the Aqueous Environment: A specific pesticide and water Review characteristics. Understanding degradation mechanisms and optimizing operating conditions were essential Evaluation of Advanced Various pesticides Ozonation, UV/H2O2, AOPs effectively degraded Oxidation Processes for photocatalysis pesticides, reducing their Mitigating the concentrations to Environmental Impact of environmentally safe levels. Pesticides Reaction time, pH, initial pesticide concentration, and catalyst selection were critical factors for optimizing AOP efficiency

6. Factors Influencing Pesticide Degradation in Aqueous Environment

The efficiency of AOPs is strongly influenced by the pH of the reaction medium, with different pesticides showing varying degradation rates at different pH levels. Optimization and adjustment of pH to suit the specific AOPs and pesticide are crucial for maximum efficiency[9, 56]. Temperature is another critical factor affecting AOPs efficiency, as higher temperatures generally enhance reaction rates by increasing kinetic energy. However, extremes in temperature can impact the stability of catalysts or reactants, necessitating the maintenance of an appropriate temperature range[7, 57]. Catalysts play a key role in AOPs by improving reaction rates and selectivity. The selection of suitable catalysts compatible with both the pesticide and AOPs system significantly influences overall efficiency. Furthermore, the duration of AOP treatment, initial pesticide concentration, and the presence of other substances in the matrix can all affect degradation efficiency[56, 58]. Optimizing reaction time, considering initial pesticide concentrations, and understanding the impact of coexisting substances are essential for effective pesticide degradation processes. It is worth noting

that the impact and optimal conditions of these factors can vary depending on the specific pesticide, AOPs method, and environmental conditions. Therefore, conducting preliminary investigations and optimization studies considering these factors is crucial to ensure effective pesticide treatment using AOPs.

7. The Current Challenges and Limitations Faced in the Application of AOPs for Pesticide Treatment in Aqueous Environment and Future Directions

The implementation of AOPs for pesticide remediation presents several noteworthy challenges and limitations. To begin with, the diverse chemical compositions of pesticides lead to varying degradation rates and pathways when exposed to AOPs. This variability complicates the development of effective treatment methods, requiring tailored strategies for individual pesticides, thereby augmenting the intricacy and cost of the treatment process[59]. AOPs often rely on high-energy sources like UV radiation, ozone, or hydrogen peroxide, which can be demanding in terms of resources and expenses, especially when considering large-scale applications. The generation of potentially harmful by-products during AOP treatment raises alarming concerns regarding water quality and environmental repercussions, compelling the necessity of thorough monitoring and mitigation measures. The efficacy of AOPs is susceptible to water quality factors such as pH, temperature, and the presence of assorted organic and inorganic components, further complicating their practical implementation in real-world treatment scenarios[60].

The application of AOPs for pesticide treatment is an evolving field that offers promising future directions. One key direction is the development of more efficient and cost-effective AOPs tailored specifically for different types of pesticides. Future research efforts may focus on enhancing the selectivity and effectiveness of AOPs to target a wider range of pesticides with improved degradation rates and pathways. There is a growing emphasis on developing integrated treatment approaches that combine AOPs with other innovative technologies to enhance pesticide removal efficiency while minimizing the formation of harmful by-products. Moreover, future directions in AOPs for pesticide treatment may involve the optimization of operating conditions, such as pH, temperature, and reactor design, to ensure consistently high treatment performance and scalability from lab-scale to field-scale applications. Continuous advancements in AOPs technology, including the use of alternative energy sources and novel catalyst materials, can further enhance the sustainability and practicality of AOPs for pesticide treatment[61].

8. Conclusion

Advanced Oxidation Processes have proven highly effective in degrading diverse pesticides, consistently reducing their concentrations below regulatory limits. Among tested methods, UV/H₂O₂ and UV/O₃ systems demonstrated superior degradation rates compared to standalone ozone or UV treatments. Comparative studies of AOPs, such as UV, ozone, and the combined UV/O₃ approach revealed that hybrid methods outperform individual techniques, emphasizing the value of synergistic oxidation strategies. Key operational parameters, including pH, temperature, reaction duration, initial pesticide concentration, and catalyst choice, significantly influence degradation efficiency. These factors exhibit variable impacts depending on pesticide properties and reaction conditions, underscoring the need for meticulous optimization of AOP parameters to maximize performance.

While AOPs offer notable advantages, such as broad applicability, rapid kinetics, high degradation efficiency, and catalyst reusability, challenges persist. Limitations include reliance on light sources, treatment selectivity, transient effects, catalyst constraints, and operational costs. Addressing these drawbacks is critical for scalable and sustainable implementation. Future research should prioritize three areas: (1) Catalyst Innovation: Developing selective, stable catalysts through novel materials (e.g., nanostructured composites, catalytic coatings) and mechanistic studies on pesticide-catalyst interactions. (2) Parameter Optimization: Investigating how pH, oxidant

concentration, irradiation intensity, and sequential/simultaneous treatment modes affect degradation pathways and by-product formation. (3) Sustainability Enhancements: Reducing energy consumption and costs while improving long-term efficacy for real-world wastewater treatment scenarios.

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