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# ADVANCED OXIDATION PROCESSES FOR PESTICIDE DEGRADATION IN AQUEOUS MEDIA: A COMPARATIVE REVIEW

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***ABSTRACT:*** Pesticide contamination in aquatic environments poses a significant threat to ecosystems and public health due to the persistence and toxicity of these compounds. This review explores the degradation of pesticides in aqueous solutions using the heterogeneous photo-Fenton process under light irradiation, an advanced oxidation process (AOP). This review comprehensively examines the mechanism of action, which centers on generating hydroxyl radicals ($OH^{\bullet}$) under light irradiation. Key operational parameters, including catalyst dosage, pH, and light intensity, are evaluated for their influence on degradation efficiency. The study highlights the advantages of the heterogeneous system over its homogeneous counterpart, notably improved catalyst recovery, reduced iron sludge production, and greater reusability. Furthermore, widely used pesticides such as atrazine, imidacloprid, and chlorpyrifos are highlighted due to their environmental persistence and extensive agricultural application. The review synthesizes current literature on catalyst development, process optimization, and degradation mechanisms, particularly focusing on coated zeolite applications. This study intends to improve understanding of the heterogeneous photo-Fenton process and direct future research toward more effective and sustainable pesticide removal from contaminated water sources by consolidating experimental findings.

***KEYWORDS:*** *Heterogeneous photo-Fenton, Pesticide degradation, Advanced oxidation processes (AOPs), Water treatment*

## 1. INTRODUCTION

Pesticides are a category of chemicals utilized to eradicate, deter, or manage unwanted species, including insecticides (targeting insects), herbicides (targeting weeds), and fungicides (targeting fungi) [1]. The United States Code of Federal Regulations (CFR) defines a pesticide as any formulation or amalgamation of compounds designed to act as a plant regulator, defoliant, or desiccant [2].

The overuse of pesticides has concerned the scientific community because of its harmful impacts on human health, including the exacerbation of Parkinson's disease [3, 4]. This overuse also promotes prostate cancer and negatively impacts pulmonary function. It adversely affects the ecosystem by polluting its constituents (air, water, soil, and biota), leading to the demise of innumerable organisms. Pesticide pollution results in at least nine million premature fatalities globally each year [5]. Table 1 delineates the effects of pesticides on human health.

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Table 1. The impact of pesticides on human health

| Pesticide | Classification | Health Effects | Ref |
|---|---|---|---|
| **Chlorpyrifos** | Organophosphorus insecticide | Neurotoxicity;potential link to cancers (e.g., breast cancer) | [6] |
| **MLT** | Organophosphorus insecticide | Cholinesterase inhibition leading to respiratory problems, genotoxic effects (chromosomal/DNA damage), and liver toxicity | [7] |
| **Acetochlor** | Chloracetanilide herbicide | Developmental toxicity (e.g. low birth weight); elevated risk of colon, lung, pancreatic cancers | [8] |
| **HCB** | Organochlorine fungicide | Endocrine disruption (thyroid); porphyria; arthritis; liver abnormalities | [9] |
| **DDT, DDE** | Organochlorine insecticide | Endocrine disruption (diabetes, metabolic syndrome); neurotoxic and immunotoxic effects | [10] |
| **Endosulfan** | Organochlorine insecticide | Cardiotoxic and neurotoxic; reproductive toxicity; carcinogenic and teratogenic effects | [11] |
| **CBD** | Benzimidazole fungicide | Endocrine disruption (hormonal imbalance, fertility issues); carcinogenicity | [12] |
| **Carbofuran** | Carbamate insecticide | Reproductive toxicity (infertility); respiratory distress; endocrine disruption, and pancreatic damage | [13] |

| | | | |
|---|---|---|---|
| **Cypermethrin** | Pyrethroid | Immunosuppression; infertility, and neurotoxic effects | [14] |

It is estimated that just under 15% of applied pesticides achieve their intended objectives, while the remainder disperse into the environment, causing harm [15]. Furthermore, these substances are classified as persistent organic pollutants, which exhibit prolonged retention in aquatic environments and accumulate in biological organisms and sediments.

Although the goal is to increase agricultural productivity, it is clear that there are numerous negative effects on the environment and human health. According to their classifications and half-lives, each pesticide persists, accumulates, and is transported in soil and water for extended periods. These hazardous, poorly biodegradable, and water-soluble compounds can lead to significant environmental contamination through the infiltration of surface and groundwater. Agricultural proximity to water supplies results in pesticide contamination, posing significant dangers to human health upon ingestion [16].

Pesticides can be categorized based on their application and efficacy in eliminating organisms as follows: insecticides, herbicides, rodenticides, fungicides, molluscicides, bactericides, avicides, virucides, algicides, acaricides, and miticides [17]. Consequently, the elimination of pesticides from aqueous systems has emerged as a matter of considerable environmental importance in recent years. [18]. To address this challenging situation, advanced oxidation processes (AOPs) and both homogeneous and heterogeneous photochemical oxidation have demonstrated their efficacy [19].

## 2. PESTICIDE DEGRADATION PROCESSES

The degradation of intricate and persistent structures in pesticide compounds is exceedingly challenging. The degradation of pesticides in aquatic environments has garnered significant global attention. Multiple studies have emphasized two principal domains of pesticide degradation: The two principal domains of pesticide degradation are chemical degradation and adsorption [20]. Activated carbon serves as the principal element in specific adsorbent materials employed for the remediation of pesticide chemicals. [21]. The application of activated carbon to mitigate pesticide chemicals is, nonetheless, constrained by certain adverse factors. Included in this is the challenge of regeneration. Conventional treatment was insufficient to eliminate organic pollutants. Consequently, advanced oxidation processes (AOPs), which provide optimal efficiency, were employed to eliminate organic pollutants. (AOPs) are eco-friendly techniques for eliminating persistent organic pollutants. Various organic pollutants frequently found in aquatic ecosystems, such as dyes, pesticides, pharmaceutical residues, and industrial effluents, have been decomposed into more environmentally benign smaller molecules [22].

This paper offers a comprehensive and thorough analysis of the heterogeneous photo-Fenton process for the degradation of persistent pesticides in aquatic environments. This paper specifically examines the heterogeneous photo-Fenton system, emphasizing its advantages over the homogeneous system, such as improved catalyst recovery, reduced iron sludge production, and enhanced reusability, in contrast to previous reviews that offered a general overview of (AOPs).

This research meticulously examines key operational parameters, such as pH, catalyst dosage, and light intensity, and their impact on pesticide degradation efficiency. This paper emphasizes the development and utilization of coated zeolite-based catalysts. The materials

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possess a high surface area, exceptional adsorption characteristics, and stability that enhance the effectiveness and longevity of the active Fenton species.

The study encapsulates recent findings on catalyst design, process optimization, and catalyst deactivation, emphasizing novel bimetallic catalysts and materials responsive to visible light. It also suggests significant future research avenues, including the development of more durable and scalable catalysts, the investigation of degradation mechanisms, and assessments of long-term environmental and economic impacts.

## 3. ADVANCED OXIDATION PROCESS

Oxidation is often an effective method for removing pesticides from water. The standard oxidation methods encompass chemical oxidation, biological oxidation, electrochemical oxidation, and moist oxidation [23]. The following discourse concerns Advanced Oxidation Processes (AOPs), which have garnered attention for their effectiveness in degrading pesticides in water or wastewater through the production of hydroxyl radicals (OH•) via ultraviolet irradiation catalysts and a combination of oxidants [24].

Recent breakthroughs have investigated various strategies for the breakdown of insecticides in aqueous solutions. For example, (AOPs) can attain up to 80% removal of atrazine when paired with ozonation and supplementary coagulants, such as aluminum sulfate [25]. Electrochemically enhanced oxidation processes (EAOPs) are a potential option that may efficiently destroy pesticides and vary conditions, including current density and electrode types [26]. Hybrid methodologies that combine cavitation and photocatalysis exhibit enhanced degradation efficiencies, indicating a possible synergistic effect in pesticide removal. [27]. Titanium dioxide has been highlighted for its effectiveness in eradicating methamidophos and acephate, attaining clearance rates ranging from 87.7 to 100 percent under experimental settings [25]. Current trends indicate that the integrated use of many techniques to improve the cleanup of pesticide-contaminated water is becoming more common [28, 29].

Several recent studies have investigated the removal of these pesticides from aqueous solutions using techniques such as filtration, coagulation, flocculation, sedimentation, adsorption, ion exchange, and distillation [30]. Biological processes, including aerobic and anaerobic therapies, are also recorded [31]. Most pesticides are non-biodegradable and biorefractory. For the cleanup of pesticide-contaminated water, (AOPs) and other, more effective technologies have been proposed because biological processes are not the best. By use of mineralization, these procedures aid in the removal of pesticides [32]. Figure 1 illustrates a schematic representation and classification of (AOPs).

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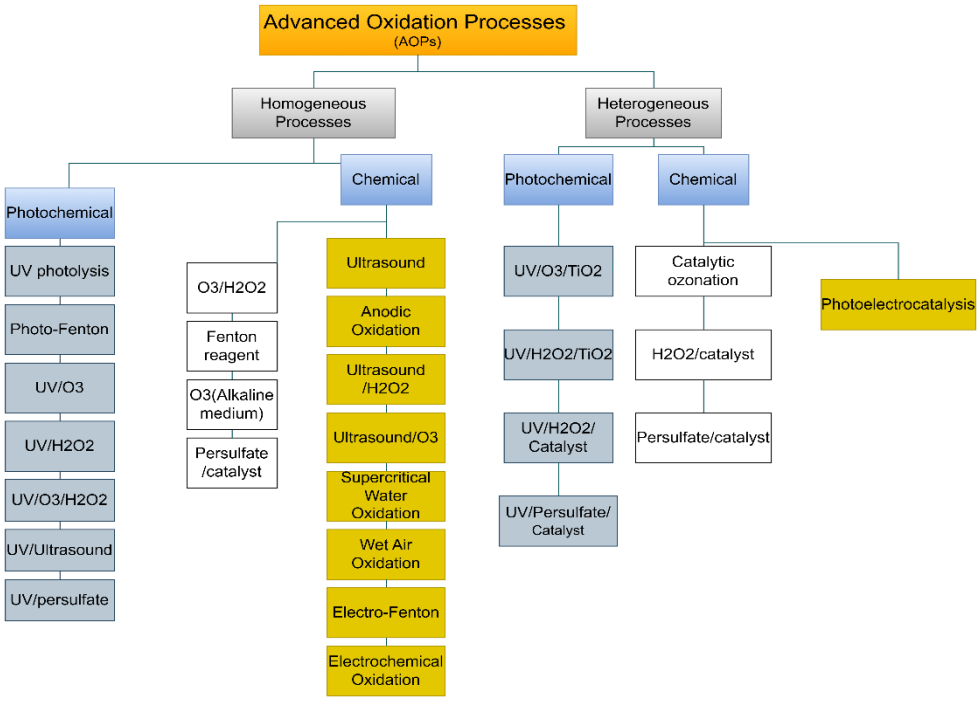


Fig. 1. Schematic representation and classification of different treatments based on advanced oxidation processes (AOPs).

In refractory wastewater treatment, Advanced Oxidation Processes (AOPs) are mostly employed to eradicate persistent organic contaminants. Author Tayyaba Jamil asserts that Advanced Oxidation Processes (AOPs) produce extremely reactive oxygen species that can decompose a range of organic molecules [33]. Traditional wastewater treatment technologies have a limited availability of reactive species, making them insufficient for the treatment of refractory wastewater [34]. However, a commonly referenced issue is the necessary control mechanisms for achieving optimal efficiency and effectiveness. The establishment of monitoring and feedback mechanisms enhances optimization, especially via the evaluation of chemical oxygen demand (COD) levels [15]. A significantly reduced (COD) level signifies that organic compounds have been considerably minimized or eliminated [2,17]. This facilitates the diversion of refractory wastewater to subsequent stages for further processing and treatment.

Photocatalytic degradation is an efficient method for treating wastewater contaminated with organic and inorganic compounds. Photocatalysis is considered one of the most efficient procedures for treating many types of wastewater, as it can totally eliminate contaminants at ambient temperature and atmospheric pressure [35]. Unlike traditional treatment methods, photocatalysis is an efficient and eco-friendly approach to converting pollutants into small, non-toxic molecules by emitting electromagnetic light [36].

### 3.1. Heterogenous and Homogeneous Processes

Advanced oxidation processes (AOPs) for water and wastewater treatment are broadly categorized into homogeneous and heterogeneous systems based on the physical state of the catalyst or active species relative to the aqueous phase [37]. In homogeneous AOPs, the catalysts (typically transition metal ions) or oxidants are fully dissolved in the bulk solution, ensuring uniform distribution and direct contact with target pollutants [38]. Conversely,

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heterogeneous AOPs utilize solid-state catalysts, such as metal oxides, supported catalytic materials, or immobilized photocatalysts, where the oxidative reactions occur primarily at the solid-liquid interface or on the catalyst surface [39]

The difference between these processes is in the site of radical formation and the following oxidation process. Highly reactive oxygen species (ROS) are produced directly in the bulk liquid phase in homogeneous systems like the classical Fenton process and the UV/$H_2O_2$ process, especially hydroxyl radicals ($OH^{\bullet}$). Therefore, high apparent reaction rates are obtained since the resistance of the phase boundaries is not present [40]. Heterogeneous processes on the other hand, such as photocatalysis ($TiO_2$-based) and heterogeneous Fenton-like systems, require the activation of oxidants or the generation of radicals on the surface of a solid catalyst [41]. Thus, the degradation efficiency of heterogeneous AOPs frequently will be controlled by adsorption-desorption phenomena and mass-transfer barriers at the interface.

Although homogeneous AOPs have fast reaction rates and simple reactors, they have been found to have limitations in terms of operation, such as small range of optimum pH (usually acidic for iron-based systems) and production of secondary sludge containing metal complex ions that require expensive post-treatment separation. Heterogeneous AOPs have been proposed as a powerful alternative to address these shortcomings. The main advantage is that they allow for the recovery and re-use of the catalysts, resulting in less sludge production and continuous treatment processes. Additionally, heterogeneous catalysts may be more stable and have a wider pH range than homogeneous ones. In practice, however, some technical challenges like catalyst deactivation with time, possible leaching of active metals into effluent, and smaller surface-area-to-volume ratios have to be addressed for large-scale applications [42].

### 3.2. Heterogenous and Homogeneous Processes

Since its inception, the Photo-Fenton process—a sophisticated oxidation technique—has seen significant modification. The Fenton reaction, first elucidated by H.J.H. Fenton in 1894, involves the reaction of hydrogen peroxide ($H_2O_2$) with ferrous iron ($Fe^{2+}$) to produce hydroxyl radicals ($OH^{\bullet}$), potent oxidants capable of degrading organic pollutants [43, 44], as shown in Eq. (1) [45].

$$Fe^{+2} + H_2O_2 \rightarrow Fe^{+3} + OH^- + OH^{\bullet} \qquad (1)$$

The Photo-Fenton process enhances this reaction by incorporating ultraviolet (UV) or visible light, which accelerates the regeneration of $Fe^{2+}$ from $Fe^{3+}$, thereby increasing the production of hydroxyl radicals and improving the degradation efficiency of pollutants [44], as shown in Eq. (2) [46]. Figure 2 presents a schematic diagram of the photo-Fenton degradation process for organic pollutants using ferrites under visible light irradiation.

$$Fe^{+3} + H_2O_2 + hv \rightarrow Fe^{+2} + H^+ + OH^{\bullet} \qquad (2)$$

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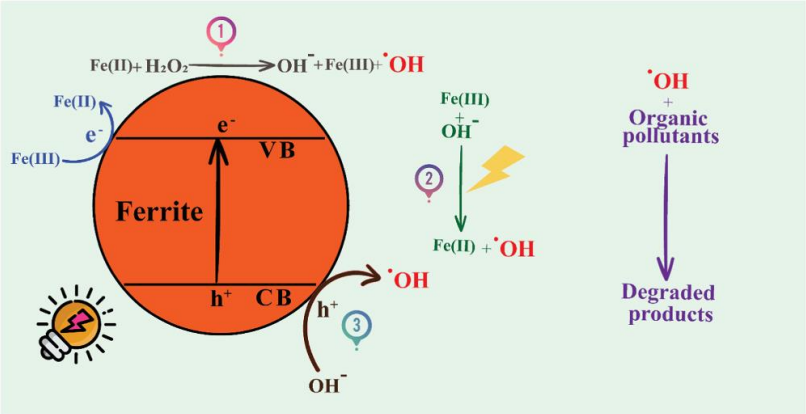


Fig. 2. Proposed mechanism for the photo-Fenton degradation of organic pollutants over ferrites under visible light.

As illustrated in Fig. 2, the photo-Fenton breakdown of organic pollutants by ferrites when exposed to visible light. The numbers 1–3 highlight three specific pathways leading to the generation of $OH^{\bullet}$ [47].

This method works best in acidic environments, usually with a pH of about 3. It can also use sunshine as an inexpensive light source, albeit it might degrade more slowly than artificial UV sources. The Photo-Fenton process has been modified over time for several uses, such as treating wastewater that contains pesticides, medications, and persistent organic pollutants. [48].

The procedure has been expanded to incorporate heterogeneous catalysts, like iron oxides and other mineral-based catalysts, which improve the process's overall efficiency by facilitating the reduction of $Fe^{+3}$ to $Fe^{+2}$ on the catalyst surface and enhancing the photo-generation of electron-hole pairs [49]. Additionally, the integration of the Photo-Fenton process with other advanced oxidation processes, such as ozonation and photocatalysis, has been explored to enhance the degradation of complex pollutants in industrial wastewaters [50].

Significant progress has been achieved in developing the photo-Fenton process, especially in terms of improving the advanced oxidation process's (AOP) efficacy and suitability for treating wastewater. Due to the limited catalytic activity and durability of conventional monometallic iron catalysts, research is being conducted on bimetallic systems like iron-copper, which provide better light absorption and charge mobility, hence improving wastewater pollutant degradation. Significant progress has been achieved in developing the photo-Fenton process, especially in terms of improving (AOP) efficacy and suitability for treating wastewater. Due to the limited catalytic activity and durability of conventional monometallic iron catalysts, research is being conducted on bimetallic systems like iron-copper, which provide better light absorption and charge mobility, hence improving wastewater pollutant degradation [51].

### 3.3. Parameters Affecting Pesticide Degradation by Photo-Oxidant

The breakdown of pesticides via photo-oxidation with a catalyst is affected by many aspects. The parameters encompass the physicochemical characteristics of the catalyst, the starting pesticide concentration, the solution's pH, the light's intensity and wavelength, and the catalyst dosage. Each aspect is essential for enhancing degradation efficiency and enabling the proper removal of pesticide pollutants from water.

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### *3.3.1 Initial Pesticide Concentration*

The initial concentration of pesticides is a crucial parameter. Elevated concentrations may necessitate extended degradation durations or increased catalyst dosages to attain complete breakdown [52]. The breakdown of permethrin, even at elevated concentrations (17,000 ppm), attained over 90% conversion within 8 hours utilizing $TiO_2$ under sun irradiation, demonstrating that substantial starting concentrations can be efficiently processed with suitable catalysts [53]. The investigation on mancozeb revealed optimal degradation at an initial concentration of 10 ppm, with around 90% degradation within 180 minutes using Ce-ZnO in natural sunlight [54]. The concurrent application of $TiO_2$ and Fe-zeolite for the degradation of imidacloprid demonstrated that initial concentrations of 100 mg/L may be nearly eliminated within 20 minutes, underscoring the significance of catalyst synergy and initial concentration in augmenting degradation rates [55]. These findings illustrate the importance of initial pesticide concentration in ascertaining the efficacy of photocatalytic breakdown processes.

### *3.3.2 pH of the Solution*

The pH of the solution markedly affects pesticide breakdown via photo-oxidation processes, as demonstrated by numerous research studies. The breakdown of pyrazosulfuron-ethyl was most efficient at neutral pH (7.0), but acidic circumstances (pH 3) enhanced the UV photo-Fenton treatment for chlorpyrifos, cypermethrin, and chlorothalonil, resulting in total degradation within one minute [56, 57]. Conversely, the degradation of atrazine was enhanced under neutral pH conditions during UV treatment, whereas acidic conditions favored the UV/$H_2O_2$ process [58], as illustrated in Fig.3. Both pesticides were considerably affected by the solution's pH, with maximum elimination efficiency attained at pH 9 for malathion and pH 3 for diazinon, as illustrated in Fig.4. The findings demonstrated that the extent of photolysis for malathion escalated with rising pH, whereas for diazinon, the extent of photolysis diminished with increasing pH. The initial occurrence occurs because $OH^{\bullet}$, at heightened concentrations, gradually capture the highly reactive $OH^{\bullet}$ species generated. The second event occurred because diazinon's degradation rate in acidic waters is faster than in other solutions; also, the molecular percentage of diazinon was greater at lower pH levels [59].

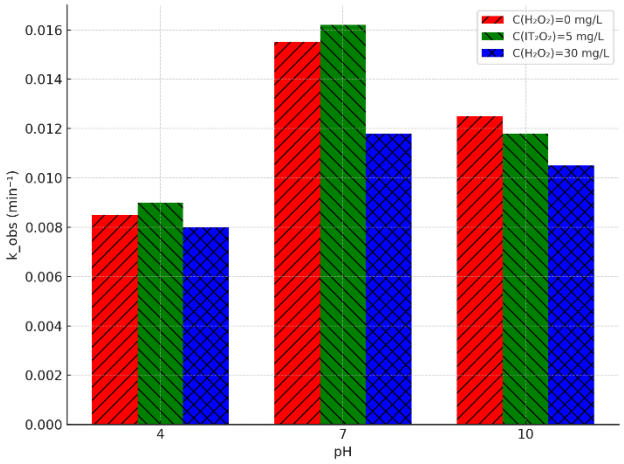


Fig. 3. Effect of solution pH on the pseudo-first-order reaction rate constants ($k_{obs}$) of ATZ during UV irradiation treatment under different $H_2O_2$ doses. Raw ATZ solution: 5 mg/L

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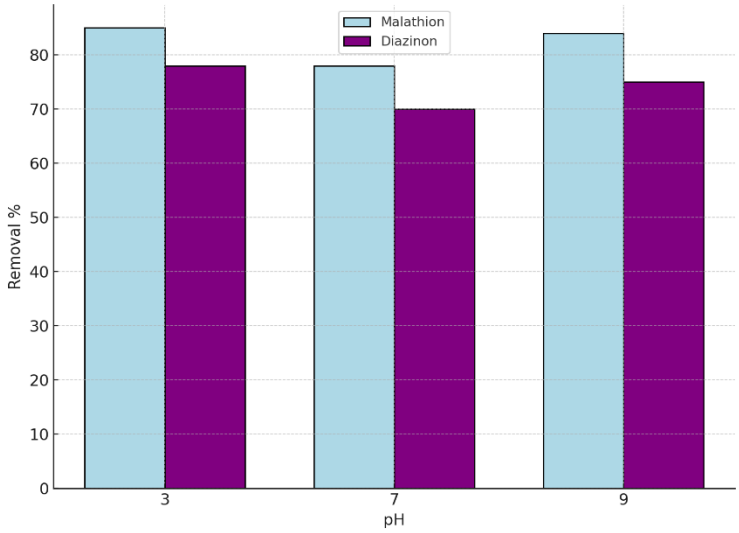


Fig. 4. the percentages of pesticide degradation at various pH levels following treatment with the UV/$H_2O_2$ process.

### *3.3.3 Light Intensity and Wavelength*

The intensity and wavelength of light substantially affect the breakdown of pesticides via photo-oxidation reactions. Research demonstrates that ultraviolet (UV) light, especially at certain wavelengths, improves the degrading efficacy of numerous pesticides. UV irradiation at 254 nm successfully degrades 2,4-Dichlorophenoxyacetic acid (2,4-D) within 5 minutes, achieving a 90% clearance rate when used in conjunction with hydrogen peroxide [60]. The photodegradation of herbicides such as terbuthylazine and isoproturon was more effective under UV light at 254 nm than at 365 nm, underscoring the significant influence of wavelength on the degradation process [61]. Moreover, the inclusion of catalysts like $TiO_2$ significantly enhances degradation rates across various wavelengths, with research indicating that photolysis at 306 nm exceeds that at 254 nm for specific pesticides [62].

Advanced oxidation technologies (AOTs) employing UV light, particularly at 254 nm wavelengths, have exhibited exceptional effectiveness in degrading pesticides such as Vydine, attaining up to 95% removal when integrated with photo-Fenton processes [63]. Solar-assisted techniques, including the solar Photo-Fenton reaction, efficiently break down pesticides such as dichlorvos; however, they may result in residual toxicity in the treated water [64].

A series of studies were performed with UV radiation at wavelengths of 254 nm (UV 254) and 350 nm (UV 350). A comparable group was run utilizing solar radiation occurring in March (Sol-Mar) and June (Sol-Jun). Experimental measures of pesticide concentration, total organic carbon mineralization, chemical oxygen demand, and biochemical oxygen demand were observed and documented in Fig 5 below. Results indicated that AOTs subjected to UV 254 irradiation or Sol-Jun solar radiation exhibited greater efficiency compared to those exposed to UV 350 or Sol-Mar irradiation. The elimination of pesticides using UV 254 and Sol-Jun was 50% and 32%, respectively, while the maximum Vydine elimination attained by UV 350 or Sol-Mar was 20%. The application of UV 254 in conjunction with photo-Fenton enhanced pesticide removal to over 95%. The photodegradation rates of Vydine in the presence of TiO2 were ranked as follows: UV 254 > Sol-Jun > Sol-Mar > UV 350 [63].

Optimizing light intensity and wavelength is crucial for improving the effectiveness of advanced oxidation processes in pesticide breakdown [65].

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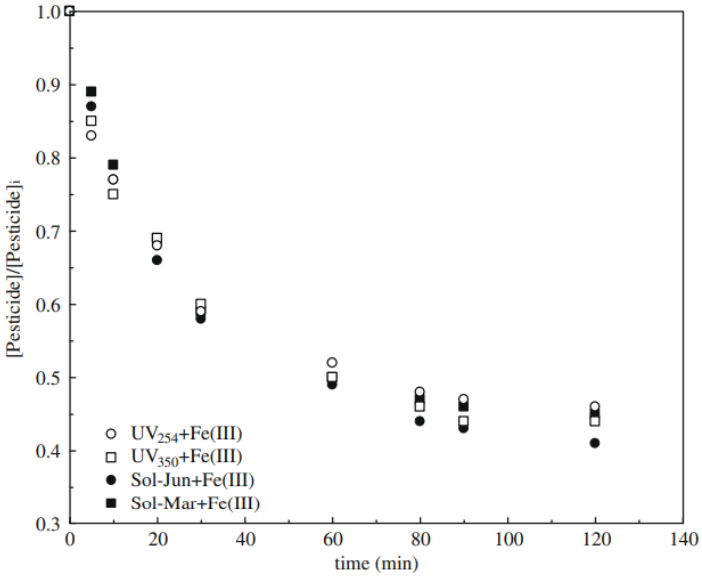


Fig. 5. Photo-degradation of Vydine by combining the UV/Fe(III) process using UV lamps and solar radiation. [Vydine]i = 25 mg/L, [Fe(III)] = 10 mg/L, initial pH = 4.6 ± 0.3, and T = 27 ± 1 C [63]

### *3.3.4 Catalyst Dosage*

Figure 6 illustrates the percentage of glyphosate degradation via heterogeneous photocatalysis in relation to the duration of visible light irradiation. The degradation was more pronounced with the cerium dioxide ($CeO_2$) catalyst than with zinc oxide (ZnO) and titanium dioxide ($TiO_2$). Following 90 minutes of irradiation, deterioration exhibited stability; $CeO_2$ attained 17% degradation, while ZnO and $TiO_2$ reached 6.8% and 6.4%, respectively.

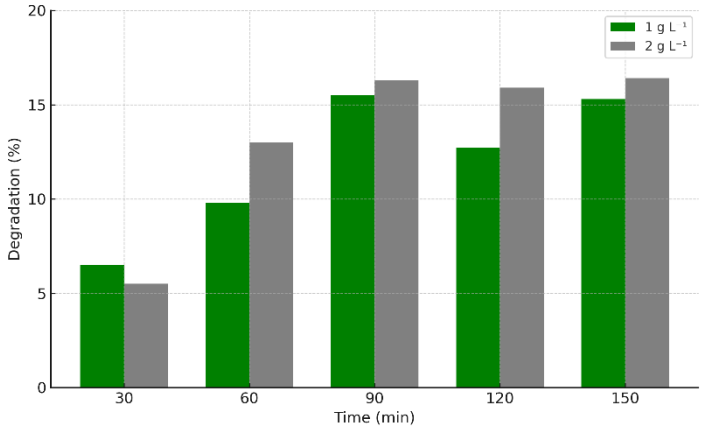


Fig. 6. Photocatalytic degradation kinetics of glyphosate using ZnO, $TiO_2$, and $CeO_2$ photocatalysts under visible light.

Figure 7 depicts the minor fluctuation in the glyphosate removal rate as the photocatalyst load diminishes. With an initial load of 2 g $L^{-1}$, degradation reached 17% after 90 minutes of irradiation, while a 1 g $L^{-1}$ photocatalyst load resulted in a degradation rate of 15% over the same duration. [66]. Wu et al. evaluated the impact of $CeO_2$ concentration on degradation efficiency and observed a decline in degradation with a reduction in catalyst load [36].

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Jiménez-Bautista et al. determined that a dosage of 34.8 g $L^{-1}$ of pellet-shaped $TiO_2$-kaolin composites was best for the full removal of pesticides across diverse water matrices [67].

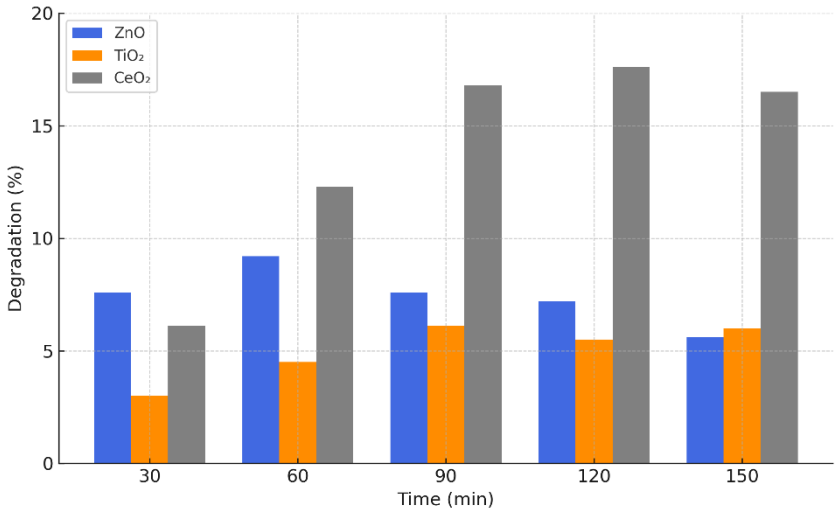


Fig. 7. Effect of $CeO_2$ photocatalyst dosage on the degradation kinetics of glyphosate [66]

### *3.3.5 Catalytic Reuse*

Recycling of catalysts in wastewater treatment is one determining factor of coming up with utilizing sustainable and eco-friendly methodologies. Catalysts such as iron oxides and modified zeolites demonstrate effective recovery and reuse with minimal loss of activity, indicating durability over successive reactions. The concurrent utilization of $TiO_2$ and Fe-coated zeolite in the degradation of imidacloprid resulted in a 1.4-fold increase in the reaction rate, indicating the synergistic effect of the catalyst combination [55]. Figure 8 depicts the percentage of activity following the reuse of the catalysts. Moreover, the integration of agricultural by-product catalysts enhances environmental sustainability and facilitates material recycling, hence minimizing waste [68].

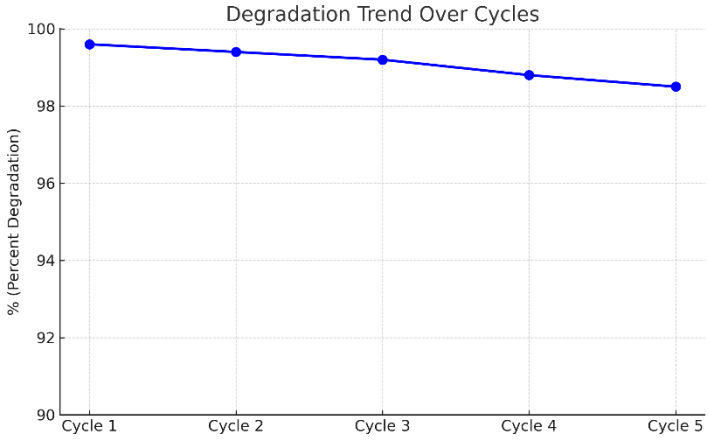


Fig. 8. Activity % after catalyst reuse [55]

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## 4. RECENT STUDIES OF DEGRADATION OF PESTICIDES THROUGH PHOTOCATALYSIS

Table 2 summarizes the findings of the research devoted to the photocatalytic degradation of organophosphate pesticides in the conditions of the application of different catalysts and different conditions of the reaction. These research works, which are mostly published in 2020 and above, focus on various parameters, like pesticide names, processes used, catalyst type, light sources, duration of reaction, and efficiency.

Some literature values resulted in the 100 percent degradation rate of all tested organophosphate pesticides. As an example, acephate was degraded 100% under visible light using RH-MCM-41/$Co_3O_4$. Also, azole pesticides were degraded 100% under wet peroxide oxidation $Fe_3O_4$-R400 with ambient conditions, pH: 5.0, catalyst: 0.5 g/L, and $H_2O_2$: 3-5 mg/L. In the same way, Chloridazon (CLZ) was also degraded with 99.98% percent of the amount by Photo-Fenton processes using ($FeSO_4$•$7H_2O$), a UV lamp (253.7 nm, 10-40°C at 60 min).

A large variety of catalysts were utilized—different types of catalysts. The conditions of reaction were varied, and the sources of light were visible light, UV light, sunlight, and LED light. They varied from seconds to hours; they were also performed at different dosages of catalysts and concentrations of pesticides. Table 2 contains the data on the degradation of different pesticides, e.g., Alpha-Cypermethrin, Atrazine, Imidacloprid, Azole Pesticides, Chloridazon (CLZ), 2,4-D Herbicide, Sulfoxaflor glyphosate, known as N-(phosphonomethyl)glycine, Pyridaben (spider pesticide), pesticide, Acetop-20 (herbicide), Atlantes insecticide, Chlorpyrifos (CPF), Malathion, Imidacloprid (IMI), Carbaryl (CB), Clomazone (CLO), and Acephate.

Table 2. Comparison of various catalysts for the removal of pesticides from aqueous solutions: A literature review.

| Pollutant (Type) | AOP Process | Catalyst | Notable Conditions (light source, etc.) | Efficiency | Ref. |
|---|---|---|---|---|---|
| **Alpha-Cypermethrin (insecticide)** | Photocatalytic degradation | ZSM-5 zeolite/$TiO_2$ hybrid catalyst | Initial conc.: 160 mg/L; UV (ambient laboratory light) | 90% removal | [69] |
| **Atrazine (herbicide)** | Photocatalytic degradation | Cu-doped ZnO (Cu–ZnO) | Sunlight irradiation | 83.9% removal | [70] |
| **Imidacloprid (insecticide)** | Photocatalytic ozonation | $TiO_2$ + Fe-exchanged zeolite (dual catalyst) | UV intensity ~250 W/m²; $O_3$ dosage 100 mg/h; Initial conc. 100 mg/L | >99% removal | [55] |

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|---|---|---|---|---|---|
| **Azole fungicides (mixture)** | Catalytic wet peroxide oxidation | $Fe_3O_4$ (magnetite) on biochar ("$Fe_3O_4$–R400") | Ambient conditions: pH 5.0; Catalyst 0.5 g/L; $H_2O_2$ 3–5 mg/L | 100% removal | [71] |
| **Chlorpyrifos (CPF) (insecticide)** | Photocatalysis | nHAP@CFGO/ZnO nanorod composite | Visible light; pH 3.5; 60 min reaction | 97.0% removal (60 min) | [72] |
| **Chloridazon (CLZ) (herbicide)** | Photo-Fenton process | Homogeneous $FeSO_4 \cdot 7H_2O$ ($Fe^{2+}$ source) | UV-C lamp 254 nm, 10 W, 40°C, 60 min | 99.98% removal (60 min) | [73] |
| **2,4-D (herbicide)** | Electro-Fenton process | $PbO_2$ anode + Fe/SBA-15 (heterogeneous Fenton) | pH 5; Fe/SBA-15 catalyst 1.25 g/L; 2,4-D 30 mg/L initial | 99.85% removal | [74] |
| **Sulfoxaflor (insecticide)** | Photocatalytic ozonation | $TiO_2$ + Fe-zeolite (combined catalysts) | UV lamps 254 nm; ~18 min treatment for full breakdown | ~100% (nearly complete in 18 min) | [75] |
| **Glyphosate (herbicide)** | Photocatalytic degradation | $CeO_2$ vs. ZnO vs. $TiO_2$ (comparison) | Visible light; Catalyst dose 2 g/L; 90 min irradiation | $CeO_2$: ~17%; ZnO: 6.8%; $TiO_2$: 6.4% | [66] |
| **Pyridaben (acaricide), Acetochlor-20 (herbicide), Atlantes (insecticide)** | Photo-Fenton (sunlight) | $H_2O_2$ (Fenton reagent) | Direct sunlight; 40 min exposure | Pyridaben 97%; Acetochlor-20 90.2%; Atlantes 86.3% | [76] |
| **Chlorpyrifos (CPF) (insecticide)** | Photocatalytic degradation | $Dy_2EuSbO_7$/ZnBiDyO$_4$ (novel composite) | Visible light; 156 min reaction | 98.78% removal | [77] |

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| | | | | | |
|---|---|---|---|---|---|
| **Malathion (insecticide)** | Ion-exchange (adsorption) process | Zeolites: Mordenite, Ferrierite, ZSM-5, USY | No light (adsorption only); Contact time 8 h | ~88–91% removal (varies by zeolite; USY best at 90.9%) | [78] |
| **Imidacloprid (insecticide)** | Photocatalytic degradation | Nano-ZnO particles | UV (254 nm) or sunlight; 60 min | 95% removal (60 min) | [79] |
| **Carbaryl (insecticide)** | Photocatalytic degradation | ZnO nanorods vs. commercial ZnO | UV vs. solar vs. visible light; 60 min | ZnO-nanorods: ~98% (UV), ~100% (solar), 68% (visible); ZnO-commercial: 87% (UV/solar combined), 22% (visible) | [80] |
| **Clomazone (CLO) (herbicide)** | Photocatalysis (suspended) | $TiO_2$–ZSM-5 composites (P25 and TNT forms) | Osram Vitalux 300 W lamp (UV/Vis); 180 min | P25-$TiO_2$/ZSM-5: 86.7% removal; TNT-$TiO_2$/ZSM-5: 68.6% removal (180 min) | [81] |
| **Acephate (insecticide)** | Photocatalytic degradation | RH-MCM-41/$Co_3O_4$ (silica mesoporous + $Co_3O_4$) | Visible light; 0.25 g/L catalyst; Initial conc. 50 mg/L; pH 8; 40 min | 100% removal (40 min) | [82] |

### 4.1. Heterogenous and Homogeneous Processes

Though all the studies reviewed in Table 1 confirm the potential of photocatalytic advanced oxidation processes (AOPs) in pesticide removal, a critical and comparative evaluation demonstrates that there is a wide variation in the performances and operational viability of the different methods and their scientific merits. The apparent uniformity of the reported removal efficiencies often hides significant differences in the reusability of catalysts, selectivity, and real-world applicability to environmental conditions. The removal efficiency of various systems was over 99 percent, especially the systems that used homogeneous photo-

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Fenton reactions or hybridized catalyst systems. As an example, the use of $FeSO_47H_2O$ in the presence of UV-C light resulted in the almost complete loss of chloridazon [75], and integrated $TiO_2$/Fe-zeolite catalysts with ozonation produced equally high efficiencies against imidacloprid [56]. However, these results are commonly produced in a strictly controlled laboratory environment, and little evidence of performance reproducibility in various water matrices is available. In comparison, the performance range of the cerium oxide ($CeO_2$) based systems was wider, where the degradation efficiencies were reported to be as low as 17% to full removal based on the type of pesticide, light source, and the structure of the catalyst [67, 84]. This disparity indicates that designing the composition and structure of catalysts is important to specific target compounds. Figure 9 summarizes various results from the literature concerning the time and efficiency of different catalysts used for removing pesticides from water.

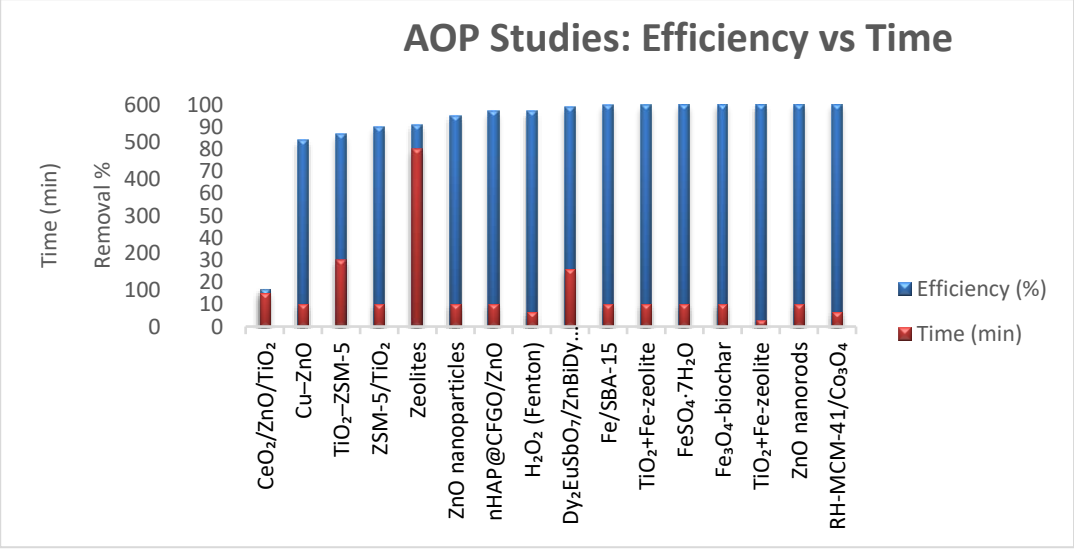


Fig. 9. Comparative performance of different photocatalysts in terms of pesticide removal efficiency and reaction time.

A distinct trend that can be identified is that various catalysts seem to be selective to different classes of pesticides. Conventional metal oxide photocatalysts (including $TiO_2$ and ZnO) were more effective in the breakdown of non-polar chlorinated pesticides, including chlorpyrifos and carbaryl [74, 82], whereas activities of the $CeO_2$ catalysts were better with the polar pesticides glyphosate and acephate [67, 84]. Nevertheless, these selectivities are only explored in a systematic way infrequently, and few works explain the physicochemical reasoning behind this sort of interaction. Additionally, inconsistencies exist in the performance of similar catalyst systems when compared, as some systems that should perform similarly do not; for example, one study shows that ZnO performs well while another indicates that it performs poorly. This discrepancy suggests that crucial parameters such as surface area, crystal phase, and synthesis method are either not reported or inadequately controlled, which weakens the generalization of results. A conclusive impact on degradation results is also provided by operational parameters. Homogeneous Fenton reactions, although very reactive, need precise pH control (pH = 3) and usually lead to the formation of sludge, thus making them less sustainable in continuous treatment applications [75, 76]. More robust and reusable heterogeneous systems, e.g. $TiO_2$ or $CeO_2$, can be UV or visible light activated, and their performance in natural sunlight can vary significantly. Moreover, there are limited studies that address the longevity of catalysts, their deactivation resistance, or their ability to be regenerated.

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As an illustration, the reusability of the $TiO_2$-kaolin composites is better in the pelletized form. [68], The majority of studies continue to use fresh catalysts, and the problem of metal leaching, especially in iron and cerium catalysts, is still not well addressed. A major limitation across the reviewed literature is the sparse consideration of degradation by products and long-term ecotoxicological impacts. Few studies include total organic carbon (TOC) analyses, mineralization rates, or identification of transformation products, despite frequently reporting high degradation percentages. This lack of mechanistic investigation makes it difficult to ascertain whether apparent pesticide degradation equates to detoxification or merely the conversion into equally hazardous intermediates. Moreover, toxicity assays and environmental safety assessments are generally absent, particularly in works focused solely on kinetic performance.

There also remains a noticeable absence of standardization in experimental setups. Variations in pH, catalyst dosage, initial pesticide concentration, and light intensity between studies hinder direct comparison and synthesis. This fracturing requires standardized benchmarking procedures that can facilitate significant comparison between systems. Additionally, field-scale validation is critically lacking. Most studies remain at the batch laboratory scale, with little to no data from pilot or continuous-flow reactors that reflect real-world operating conditions.

Considering these observations, it becomes evident that while photocatalytic AOPs hold enormous potential, the current body of literature is skewed toward efficiency metrics without equally rigorous attention to environmental relevance, mechanistic clarity, or scalability. Future research must move beyond percentage removal figures to embrace integrated evaluations that simultaneously address degradation efficiency, mineralization, toxicity, and catalyst lifecycle. Without this holistic approach, the transition of AOPs from laboratory innovation to practical water treatment solutions will remain limited.

Table 3. Identified Knowledge Gaps and Research Needs in Photocatalytic AOP Studies

| Knowledge Gap | Implications for Research and Application |
|---|---|
| **Absence of defined testing conditions (e.g., pH, light intensity, catalyst dosage)** | Limits the ability to compare studies or replicate findings across different systems |
| **Minimal reporting on total organic carbon (TOC) and mineralization data** | Obscures whether degradation results in full detoxification or harmful intermediate formation |
| **Insufficient studies on catalyst aging, reusability, and regeneration** | Raise concerns about long-term economic and operational feasibility |
| **Limited understanding of transformation products (TPs) and byproduct toxicity** | May result in unknown environmental or health risks despite apparent pollutant removal |
| **Rare inclusion of real-world water matrices or pilot-scale systems** | Laboratory results may not translate effectively into practical applications |

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# 5. $CeO_2$-BASED CATALYSTS IN ADVANCED OXIDATION PROCESSES

Recently, nanoceria ($CeO_2$) has attracted considerable interest as one of the most promising candidates widely used in the fields of photocatalysis [83], cytochrome acceleration [84], antioxidants [85], superoxide scavengers [86], etc. All these applications originate from the intrinsic properties of $CeO_2$, such as the presence of rich oxygen vacancies within crystal defects and the unique ability of reversible valence state switching between $Ce^{+4}$ and $Ce^{+3}$ [87, 88]. Moreover, $CeO_2$ possesses ideal biocompatibility and redox couple similar to natural enzymes, so it could be used as a highly active enzyme mimic [89, 90].

One of the most important features of $CeO_2$-based catalysts is that they are stable and can be recycled. Numerous reports have demonstrated low catalyst deactivation and leaching after a number of cycles, particularly when supported in zeolite frameworks or immobilized in composites.

## 5.1. Characteristics of Y Zeolite

Y zeolite belongs to the faujasite family and is distinguished by its thermal stability and a Si/Al atomic ratio of 1-1.5 that makes it structurally robust and a catalyst **[91]**. The zeolite has a three-dimensional porous channel system with 12-oxygen ring openings and supercages that allow molecular diffusion **[92]**. New developments have seen the creation of hierarchically structured Y zeolites that contain mesoporosity and microporous structures, improving their reactions with large molecules **[93]**. Also, titanium (Ti) is reported to increase the catalytic activity of Y zeolites, especially in the epoxidation of cycloalkenes, since the Ti species has a tetrahedral structure within the zeolite structure. In addition, additional mesoporous Y zeolites have been prepared, and the ratio of pore volume is also reasonable in the petroleum refining and petrochemical reactions. Generally, Y zeolites are multipurpose in nature and can be applied in a wide variety of catalytic reactions**.**

As a rule, the source of zeolites may be split into natural and synthetic zeolites. Generally, natural zeolites are inexpensive and readily available, but they contain minerals, metals, quartz, and other impurities. Synthetic zeolites are usually made and utilized to achieve high uniformity, purity, and large surface area of zeolites. The properties of zeolite could be modified by varying the conditions of synthesis, such as temperature, ratio of raw materials, time of reaction, activation process, and aging time [94, 95].

## 5.2 $CeO_2$ on Y Zeolite as a Catalyst

The support was Y zeolite, on which a homogeneous $CeO_2$ catalyst was deposited. It was selected because of its big pore diameter and high-silicon-to-aluminum proportion that makes it a special support medium of desorption and diffusion in the catalytic test [96]. The properties of Y zeolite might enable this substance to become useful in the area of catalysis [97].

The recent research work has identified the possibility of using cerium oxide ($CeO_2$) in combination with zeolites, especially USY zeolite, to increase the effectiveness of pesticide degradation. The oxidation ability of $CeO_2$ and the acidic sites of zeolite have a synergistic effect enhancing the catalytic degradation of chlorinated volatile organic compounds (CVOCs), which can be applied to pesticide degradation processes [98]. Moreover, $CeO_2$-ZnO nanocomposites have proved to be very effective in the degradation of organophosphorus insecticides such as endosulfan and dimethoate, and the optimum conditions of synthesis have been shown to improve their catalytic performance [99]. Moreover, modified zeolite-supported biofilms have also been considered, with the zeolite acting as a support but also to increase microbial activity and biodiversity and thus to increase the rate of biodegradation of such

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pesticides as MCPA and glyphosate [100]. All these results are indicative that the combination of $CeO_2$ with zeolites can play a major role in enhancing the performance of pesticide remediation technologies [101].

## 6. CURRENT CHALLENGES AND PRACTICAL LIMITATIONS

Recently, nanoceria ($CeO_2$) has attracted considerable interest as one of the most promising Although there has been an increased success of Advanced Oxidation Processes AOPs in pesticide degradation at the laboratory level, there exist certain practical and scientific drawbacks that have inhibited the further application of AOPs. One of the main problems is catalyst stability, as many reported systems cannot demonstrate long-term activity in repeated experiments or real water matrices. There is also a problem of scalability, as the synthesis of nanocomposites or doped photocatalysts is expensive and complex, in particular, in rural or decentralized settings.

In addition, the solar-powered or outdoor treatment units cannot be used in many systems due to the reliance on UV or controlled artificial light. There are very few studies that present a complete toxicity evaluation of the degradation by product or measure the level of mineralization using TOC or LC-MS/MS. Such ignorance is dangerous to environmental safety since removal efficiency does not always imply complete detoxification.

Finally, the absence of standardized experimental conditions, in particular, the light intensity, catalyst dosage, and pH, does not allow comparing the studies, and it does not allow developing universal design protocols. To overcome these shortcomings, it is important to change the direction of the research by emphasizing the integrated performance of degradation, such as stability, safety, cost, and real-world adaptability.

## 7. CONCLUSION

The review has critically analyzed the use of the heterogeneous photo-Fenton process in the degradation of persistent and toxic pesticides in water. The evidence provided is convincing of the fact that this advanced oxidation process (AOP) is a very effective and promising technology in terms of reducing the serious environmental and health hazards that pesticide contamination poses.

The oxidative degradation of a wide range of recalcitrant pesticide molecules is achieved through the core mechanism, which is based on the light-accelerated formation of highly reactive hydroxyl radicals (OH) via the catalysis of hydrogen peroxide by a solid catalyst. Key operation variables such as the dosage of catalyst, initial pH, concentration of $H_2O_2$, and light intensity/wavelength have severe impacts on the efficiency of degradation and need to be optimized each time with respect to a particular system. The heterogeneous method has significant benefits over homogeneous photo-Fenton, mainly because of better catalyst recovery, reduced iron sludge production, and increased catalyst reuse, which also makes the process more sustainable and potentially applicable in practice. The review also showed the degradation of commonly used and environmentally persistent pesticides, including atrazine, imidacloprid, and chlorpyrifos, which indicated that the process can be applied to difficult pollutants. Much attention was given to the synthesis and activity of coated zeolite catalysts that exploit the high surface area, adsorptive capacity, and stability of the zeolite scaffold to host and promote the activity of the active Fenton species (usually iron or other metals), and frequently to better efficiency and stability.

This review complements the fundamental understanding of the heterogeneous photo-Fenton process by summarizing the current understanding of the catalyst design, process

optimization and the mechanism of degradation. It indicates that despite the great improvement, there are still problems, especially with respect to catalyst long-term stability and leaching under different conditions, the possible generation of toxic transformation products that have to be closely monitored, and the scale-up of reactor designs to address the issues in practical water treatment. In conclusion, this review provides a focused summary of the existing progress of the heterogeneous photo-Fenton process as a method of pesticide degradation with particular attention to coated zeolite-based catalysts. The paper is a valuable reference to develop a sustainable and efficient water treatment technology that summarizes essential knowledge about operations and identifies future research directions such as catalyst stability, visible-light responsiveness, and scalability.

The priorities of future research ought to be

- Developing strong, highly active, and visible-light-responsive catalysts, and specifically focusing on developing new coatings and supports, zeolites in particular.
- Clarifying specific degradation pathways and intermediate toxicity of a greater variety of pesticides.
- Coming up with effective, scalable reactor systems that will be applicable in different water matrices.
- Undertaking full cost-effectiveness and lifecycle studies to determine practical feasibility.

To sum up, the heterogeneous photo-Fenton technology is a critical and developing technology, especially when it uses new catalyst systems such as coated zeolites. Further research and development of the solutions to the challenges identified have great potential for making this process a more efficient, sustainable, and practical solution to protect the water resources against pollution by pesticides.

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