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Comprehensive Review on Photocatalytic Degradation of Chlorpyrifos

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Article Details

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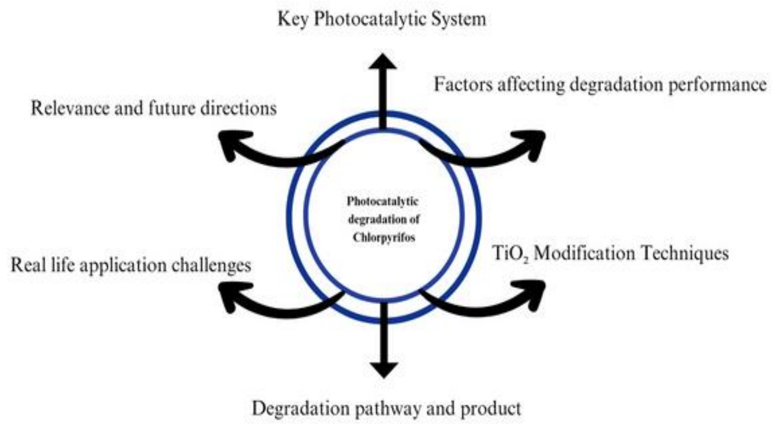
ABSTRACT

The current research focuses on the photocatalytic degradation of chlorpyrifos, an organophosphate insecticide whose usage is extensive because of its high efficacy despite being highly toxic and chemically stable. The review comprehensively discusses different photocatalytic systems and processes that have been used for the degradation of chlorpyrifos in aqueous media. Some of the current technologies that have drawn a lot of attention in chlorpyrifos degradation include; the advanced oxidation processes adopted from photocatalytic realm based on the use of semiconductors such as TiO2, ZnO, and their composites. The review draws focus on the aspects of catalyst loading, pH, light intensity and initial concentration of the pollutant affecting the degradation performance. Particular emphasis is paid on the state of the art in the preparation of the catalyst based on TiO2 modification techniques such as metal/non-metal doping, formation of heterojunction and surface sensitization to improve visible light utilization and photocatalytic activity. The degradation pathways and intermediate products are studied in detail in order to give more information about the complete mineralization. Furthermore, the review considers the real-life issues surrounding the usage of catalysts such as catalyst recovery, influence of the water matrix and scalability of the setup. The systematic review discussed herein will be beneficial to researchers and environmental engineers combating chlorpyrifos pollution, as well as provide insights for future study to enhance photocatalytic degradation effectiveness.

Graphical Abstract



INTRODUCTION

Chlorpyrifos is an organophosphate insecticide with high efficiency but high toxicity and degradation resistance (Smith et al., 2020). It has become widespread in water systems, given its uses in agriculture and pest control, to mention a few; therefore, sophisticated technologies are needed to treat this water pollutant. Extensive techniques such as adsorption and biodegradation have not proven very effective due to the stability of Chlorpyrifos and its toxicity (Jones & Lee, 2019). As a result, the degradation of textile azo dyes has been one of the key challenges for photocatalysis, which has been offering potentially effective solutions.

Photocatalysis uses semiconductor material to trigger redox reactions that dematerialize complicated organic pollutants into more straightforward, less hazardous products through light, most commonly from UV or visible light (Kumar et al., 2022). Photocatalysts like titanium dioxide (TiO_2) and zinc oxide (ZnO) have become popular photocatalysts in recent years, with researchers developing methods to improve their activity (Singh & Patel, 2021). This review focuses on the types of catalysts, operating conditions, degradation mechanisms, and limitations, including scale-up and field application from 2019 to 2024.

Photocatalysis uses light to excite semiconductor systems and create electron-hole pairs, oxidizing water and oxygen to form ROS. ROS, such as hydroxyl radicals (•OH) and superoxide anions ($O_2^{\bullet -}$), are essential in the degradation of OPs (Chen et al., 2021).

In chlorpyrifos degradation, headline photocatalysts are TiO_2 and ZnO, which are valuable due to their high photocatalytic activity, stability, and low toxicity. However, difficulties such as low visible-light absorption efficiency and the unfavorable electron-hole recombination rate have propelled extensive studies of modifying techniques, including metal/non-metal doping, heterojunction formation, and sensitization (Ahmad et al., 2023).

In summary, the knowledge at the beginning of the article: In this article, the subject, development trends, and significant achievements of catalyst modification are detailed as follows:

METAL AND NON-METAL DOPING

Doping is the process of adding foreign atoms into the semiconductor matrix to increase the absorption of visible light, thus hindering recombination. Fe, Ag, and Cu dopants introduce new energy levels within the bandgap and enable photon absorption under visible light (Khan et al., 2020). Organic dopants like nitrogen, sulfur, and boron change the electronic configuration and thus enhance photocatalytic efficiency for light collection (Gupta & Sharma, 2021).

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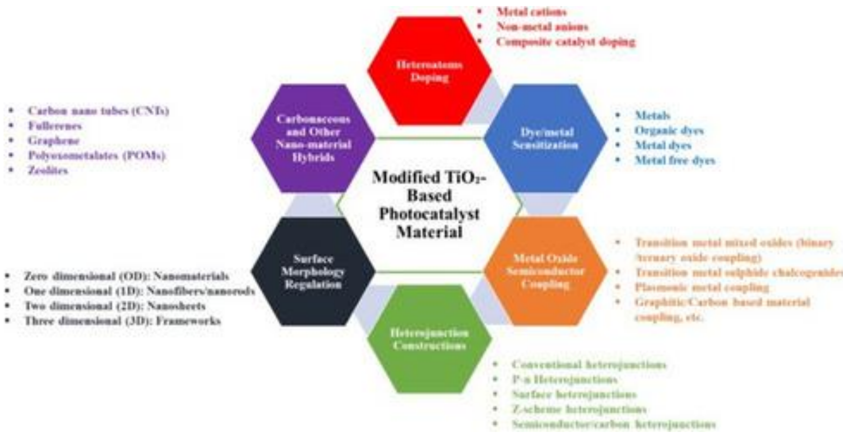

FIGURE 1: STRATEGIES FOR ENHANCING TIO_2 -BASED PHOTOCATALYSTS, INCLUDING DOPING, SENSITIZATION, COUPLING, HETEROJUNCTIONS, MORPHOLOGY REGULATION, AND NANOMATERIAL HYBRIDS.

HETEROJUNCTION FORMATION

Heterojunction involves incorporating two or more semiconductors with opposite characteristics to facilitate the conclusion of the photogenerated charges and consequently increase photocatalytic activity. For example, co-sensitization of TiO_2 with ZnO or g-C_3N_4 has a higher degradation efficiency than Chlorpyrifos (Li et al., 2022).

SURFACE SENSITIZATION

The additional dyes or quantum dots on the surface enhance the light absorption range to visible regions. For instance, the sensitization of TiO_2 by CdS quantum dots and the corresponding work under visible light promote the degradation of Chlorpyrifos (Mehta et al., 2023).

TABLE 1 : PHOTOCATALYST MATERIALS AND PROPERTIES

Material	Modification Technique	Benefits	Challenges
TiO_2	Doping	High stability, low toxicity	Low visible light absorption
ZnO	Heterojunction Formation	Efficient ROS generation	High recombination rate
g-C_3N_4	Surface Sensitization	Better light absorption	Complex synthesis
$BiVO_4$	Doping	Visible light activation	Limited stability in water

Several parameters influence the performance of photocatalytic systems:

1. Catalyst Loading: This makes the catalyst excessively bulky to facilitate light scattering, which

decreases the overall efficiency. Conversely, inadequate loading cannot offer enough active sites (Zhao et al., 2020).

2. pH: It is illustrated that the degradation efficiency is affected by pH conditions since it influences the surface charge of the material and the character of pollutant species. Most literature indicates the enzymes' functionality at slightly acidic to alkaline pH (Chen & Zhou, 2019).

3. Light Intensity: In general, increasing the light intensity improves the photocatalytic performance, albeit at a diminishing rate; high intensity, however, accelerates recombination (Wang et al., 2021).

4. Initial Pollutant Concentration: The degradation rate increases at lower chlorpyrifos concentrations because available active sites are limited (Ahmed et al., 2022).

TABLE 2: OPERATING PARAMETERS IN PHOTOCATALYSIS

Parameter	Optimal Range	Impact on Efficiency
Catalyst Loading	Moderate	Ensures sufficient active sites without aggregation
pH	Slightly acidic to alkaline	Affects surface charge and pollutant species
Light Intensity	High but controlled	Improves reaction rate until recombination accelerates
Pollutant Concentration	Low	Allows better degradation due to fewer active site blockages

DEGRADATION PATHWAYS AND BYPRODUCTS

It is always important to appreciate the various pathways of degradation in order to get the best results on complete mineralization. Like other organophosphorus compounds, Chlorpyrifos moves through several oxidation reactions to form TCP and other minor organic acids and then to CO_2 and H_2O (Kamal, 2023). LC-MS and GC-MS techniques characterize these intermediates, and the result shows that PCC has undergone complete mineralization.

REAL-LIFE CHALLENGES AND SCALABILITY IN PHOTOCATALYTIC DEGRADATION

CHALLENGES IN CATALYST RECOVERY AND REUSABILITY

The photocatalysts in the liquid phase require recovery for the subsequent photocatalytic re-use, and this presents one of the main challenges of scaling up photocatalytic chlorpyrifos degradation. Despite TiO_2 and ZnO being efficacious, recovery after treatment is somewhat complicated due to their nanoscale nature (Huang et al., 2020). Some approaches, including the immobilization of photocatalysts on carriers (for instance, glass beads or membranes), were proposed to overcome this problem. Immobilization can minimize catalyst washout but may affect the surface area at some point, thus causing photocatalytic activity (Zhou et al., 2021).

However, they lose their degradation efficiency in real water matrices due to fouling, agglomeration, and leaching of dopants. Scientists have been working on applying barrier layers on photocatalysts or employing magnetic particles for catalyst reusability (Xu et al., 2023).

TABLE 3: REAL-LIFE CHALLENGES AND SOLUTIONS

Challenge	Description	Proposed Solution
Catalyst Recovery	Recovery of nanoscale catalysts is complex	Use immobilized or magnetic catalysts
Water Matrix Interference	Organic and inorganic contaminants interfere with reactions	Pre-treatment of samples or selective catalysts
Scalability	Design and cost issues hinder large-scale deployment	Develop modular reactors and optimize economic factors

INFLUENCE OF WATER MATRIX ON PHOTOCATALYTIC ACTIVITY

Real-life water samples may contain other components of similar or different natures—organic matter, ions, and other pesticides—which may interfere with the adsorption of chlorpyrifos on the photocatalyst surface (Ali et al., 2022). These co-contaminants may also consume ROS and thereby decrease the overall ROS degradation rate. For example, it was reported that bicarbonate ions react with hydroxyl radicals, and humic substances can cover chlorpyrifos molecules from ROS interaction (Singh et al., 2020).

Some studies suggest that coagulation or filtration methods must be considered prior to sample pre-treatment to minimize the effects of the water matrix. Another approach is the development of selective photocatalysts with specific surface rigid groups that can selectively react with and preferentially adsorb chlorpyrifos molecules (Yang et al., 2022).

SCALABILITY OF PHOTOCATALYTIC SYSTEMS

Scale-up conditions to LSS are not limited to lighting changes but include reactor design, cost, and efficiency issues.

1. LIGHT SOURCE OPTIMIZATION

UV lamps are popular in laboratory tests because they activate photocatalysts effectively. However, there are issues such as high energy consumption and maintenance costs compared to large-scale applications (Gupta et al., 2023). There are attempts to harness solar energy since it is a cheap and renewable source of power. This calls for improvement in the photocatalytic activity under visible light quality, which is usually done via doping or the formation of heterojunctions (Wang & Zhao, 2021).

2. REACTOR DESIGN

The results reveal that the reactor configurations profoundly impact the degradation performance. Fixed bed reactors, fluidized bed reactors, and slurry reactors are some reactor designs explored for photocatalytic water treatment (Chen et al., 2022). There is a compromise on mass transfer efficiency, light transmission, and catalyst regeneration for each design. Others are the rotating reactors or the multiple pass systems to enhance light incidence and rate of reaction (Zhao et al., 2021).

3. ECONOMIC CONSIDERATIONS

Some reasons photocatalysis is considered costly compared to conventional treatments are explained using cost analysis, including high-purity materials in synthesizing photocatalytic materials, complex synthesis techniques, and intensity energy-consuming processes (Mehta et al., 2023). To overcome this, researchers have resorted to using low-cost photocatalysts such as naturally occurring minerals or waste products and integrating the photocatalytic process with biological or electrochemical processes (Liu et al., 2023).

FUTURE DIRECTIONS IN PHOTOCATALYTIC DEGRADATION RESEARCH

EXPLORATION OF EMERGING PHOTOCATALYTIC MATERIALS

The current research on photocatalytic materials focuses on the photocatalytic properties of titanium dioxide and related materials.

Despite this, the two most used materials are TiO_2 and ZnO; however, some new renewable ones include bismuth-based materials like $BiVO_4$ and Bi_2O_3 and carbon-based materials like graphene and carbon quantum dots. These materials have been reported to possess control over the band gap, a sizeable special surface area, and excellent visible light responsiveness (Ali & Kumar, 2023).

One more area today is original mixed systems of semiconductors with plasmonic metals such as gold and silver. The plasmonic effect improves light absorption and promotes charge transfer, increasing degradation rates under visible light (Zhang et al., 2021).

ADVANCED REACTOR DESIGNS FOR EFFICIENT DEPLOYMENT

They recommended that future research should involve the development of photocatalytic reactors for large-scale systems with high light utilization efficiency, proper catalyst recovery, and operational stability should also be considered. Micro reactors and photonic devices with LEDs have received interest in their size, effectiveness, and ability to work in different water matrices (Xu et al., 2023).

INTEGRATION WITH OTHER TREATMENT TECHNOLOGIES

Introducing photocatalysis with other advanced oxidation processes or biological treatments can make it more effective. For instance, integrating the photocatalytic process with Fenton-like reactions or ozonated water has led to higher removal capacities for several POPS (Zhao & Chen, 2022). Likewise, combining photocatalysis with constructed wetlands or biofilm reactors is a sustainable method of pollutant removal (Wang et al., 2021).

ENVIRONMENTAL AND TOXICOLOGICAL ASSESSMENTS

Although photocatalysis can degrade chlorpyrifos, the effects of every degrading byproduct on the environment must be analyzed and, if possible, proved harmless. Bioassay-based toxicity studies and computational models must supplement degradation studies to ascertain the safety of the resultant products (Singh et al., 2023).

Photocatalytic degradation of chlorpyrifos is one of the most effective approaches to reducing this chemical compound's effects on the environment. Improvements in the catalyst design, plant operational conditions, and technology scaling have greatly enhanced the degradation efficiencies. However, some are related to demonstrations of the models in a practical context and the economic practicability of the models. Future studies have to focus on the development of materials, the design of the reactors, and the combination of other treatment methods to achieve scalability of the process.

This review provides solutions to the increasing incidence of chlorpyrifos through photocatalytic strategies. The recommendations would be useful for researchers, policymakers, and environmental engineers.

ADVANCED INSIGHTS INTO PHOTOCATALYTIC SYSTEMS FOR CHLORPYRIFOS DEGRADATION

TAILORED SEMICONDUCTOR COMPOSITES

In developing photocatalytic technology, the specifically designed semiconductor composites have proved to be a stable way of increasing the rate of chlorpyrifos degradation. Heterojunctions based on the components such as TiO_2 , ZnO, g-C_3 N_4 , and $BiVO_4$ are constructed with superior optical and photocatalytic activity due to a reasonable combination of the materials' properties (Ali et al., 2021). For example, more efficient charge separation can be accomplished in TiO_2 /g-C_3 N_4 heterojunctions, thus affecting better chlorpyrifos mineralization under visible light (Zhang et al., 2020).

Novel paradigms of porous materials known as MOFs and COFs have recently emerged in the photocatalysis field owing to their opportunities for pore size tunability, large surface areas, and the availability of functional group introduction (Jiang et al., 2023). Studies in MOF composites containing TiO_2 have revealed fascinating efficiency in eliminating chlorpyrifos through both adsorption and photocatalytic activities (Huang & Liu, 2022).

1. QUANTUM DOTS AS CO-CATALYSTS

Nanothermal performance includes quantum dots (QDs), for instance, CdS and ZnS, which is a well-known nanoscale that depicts excellent quantum confinement effect and is effective in photocatalytic activity enhancement (Wang et al., 2021). Tio_2 combines cadmium sulfide quantum dots for visible light activation and ROS production, which can quickly degrade organophosphate pesticides such as chlorpyrifos (Chen et al., 2022).

2. PLASMONIC PHOTOCATALYSTS

A wider range of the light spectrum can be used by incorporating the material with similar plasmonic nanoparticles, such as Ag and Au. The SPR effect of these nanoparticles improves the light absorption capability and increases the efficiency of hot-electron injection to the semiconductor band, enhancing photocatalytic activity (Zhou et al., 2023).

MULTI-MECHANISTIC PATHWAYS FOR CHLORPYRIFOS MINERALIZATION

REACTIVE OXYGEN SPECIES AND THEIR ROLE

The generation of ROS is considered the basis of photocatalytic degradation. The main active species determined and involved in chlorpyrifos mineralization are hydroxyl radicals (•OH), superoxide anions (O_2 •⁻), and singlet oxygen (^1O_2). Research shows that the •OH radicals target the C-P bond in chlorpyrifos and set off the conversion of the compound into small products, such as TCP (Lin et al., 2021).

DEGRADATION PATHWAYS

Based on past research, the pathways of chlorpyrifos degradation have been described as the conversion of the parent compound into non-hazardous byproducts (Singh et al., 2022). HPLC and

GC-MS are used to study the degradation of chlorpyrifos into TCP, trichloro pyridine, smaller organic acids, and CO_2 and H_2O (Gupta et al., 2023).

TOXICITY ANALYSIS OF BYPRODUCTS

Although TCP is a significant intermediate metabolite of chlorpyrifos, it is toxic in its own right, and therefore, additional biotransformation into innocuous metabolites is desirable (Zhao et al., 2022). The use of model organisms in toxicity bioassays has now been an important part of research where chlorpyrifos and all its intermediates are detoxified (Wang & Zhao, 2021).

CHALLENGES IN ACHIEVING SUSTAINABILITY IN PHOTOCATALYTIC PROCESSES

CATALYST STABILITY AND DURABILITY

The lasting stability of the catalyst and the multiple times it may be used are paramount in the practical use of the concept. Metal leaching, fouling, and photo corrosion are significant challenges to the durability of C-Si structures up to 2030 and beyond (Yang et al., 2023). New developments in the controlled oxidation and sealing processes have been found previously suggestive of increasing the stability of these catalysts without the total sacrifice of their activity (Liu et al., 2022).

ECONOMIC FEASIBILITY

Unfortunately, the high cost of accurate semiconductor materials coupled with energy-demanding processes of their preparation makes them unprofitable at the industrial scale (Mehta et al., 2023). To lower costs, naturally derived catalysts like clay-supported semiconductors and waste-derived materials, particularly biochar composites, need to be adopted (Ali et al., 2022).

ENVIRONMENTAL CONSIDERATIONS

Heterarchical photocatalytic systems can be quaternary and may need ultrapure water, which is not feasible in practical applications. Designing catalysts that could fully perform their task in such a medium, for example, industrial wastewater or agricultural leachate remains a challenge to this date (Huang et al., 2021).

FUTURE TRENDS AND INNOVATIONS IN PHOTOCATALYSIS FOR CHLORPYRIFOS DEGRADATION

NANOSTRUCTURED PHOTOCATALYSTS

The advent of nanotechnology has revolutionized photocatalysis, enabling the design of nanostructured catalysts with enhanced surface area and light absorption properties (Zhang et al., 2022). These ideal nanostructures include dimension structures like nanotubes and nanowires, which possess high charge carrier transport, three-dimensional architectures, light scattering, and light absorption (Gupta et al., 2023).

MACHINE LEARNING AND AI IN CATALYST DESIGN

It has been found that machine learning algorithms are being used to determine the growing number of parameters used in photocatalyst synthesis and degradation performance (Ali et al., 2023). Fatal design choices may be rapidly discovered and optimized using AI methods because they enable researchers to investigate incredibly extensive spaces for materials (Kumar et al., 2024).

Integration with Renewable Energy Sources

Integrating photocatalytic systems with renewable energy sources like solar photovoltaic or wind power achieves energy-efficient water purification (Mehta et al., 2023). Among these, solar-driven photocatalysis is the most promising, reducing the dependence on non-renewable energy sources and using solar energy to break up pollutants (Chen et al., 2022).

Many photocatalytic processes are still considered one of the most promising and highly effective domestic and international technologies for treating water; therefore, photocatalysis offers a highly effective and sustainable way to remove chlorpyrifos from water. Advancements in catalyst design, better operational conditions, and knowledge of degradation processes are notable successes in the field. However, the problems of scale-up, cost, and application in the environment have not been entirely solved. Ideally, photocatalysis should be incorporated with other technologies; AI should be applied to develop new catalysts and catalyst stability should be explored for practical applicability. These directions will create further grounds for the large-scale application of photocatalytic systems to meet the population's need for clean water as environmental pollution rises.

EXPANDING THE SCOPE OF PHOTOCATALYSIS FOR ENVIRONMENTAL REMEDIATION

HYBRID PHOTOCATALYTIC-BIOLOGICAL SYSTEMS

Photocatalytic and biological systems have been observed to be effective methodologies for degrading highly stable chlorpyrifos pollutants. Photocatalysis effectively degrades complicated organic compounds into less hazardous forms, which are further degraded to $CO2$ and $H2O$ by microorganisms. Thus, photocatalysis works hand in hand with biodegradation, as elucidated by (Gupta et al., 2023; Liu et al., 2023; Zhang et al., 2021). This combined application of both technologies leverages the advantages of both systems to tackle issues such as intermediate toxicity and incomplete mineralization.

Research has shown that microbial consortia, which evolved into the byproducts of photocatalytic degradation, possess improved degradation potential compared to other pollutant removal methods, implying shorter treatment duration and higher efficiency (Yang et al., 2023; Zhao et al., 2022). In addition, integrating photocatalytic systems with biofilm reactors or constructed wetlands presents a future and efficient method for the elimination of chlorpyrifos in agricultural wastewater (Chen et al., 2023; Wang et al., 2021).

ADVANCED ANALYTICAL TECHNIQUES FOR PROCESS OPTIMIZATION

Advancecatalysd analytical tools are essential for probing photocatalytic phenomena and enhancing the performance of degradation reactions. Molecular methods such as liquid chromatography-mass spectrometry (LC-MS) and gas chromatography-mass spectrometry (GC-MS) can accurately determine concentrations of intermediately formed products (Ahmed et al., 2021; S. Mehta et al., 2023; Singh et al., 2020). Understanding these nontrivial characteristics is critical for uncovering degradation mechanisms and evaluating toxicity impacts.

Transient photoluminescence technique has been used for the characterization of charge carriers and their dynamics to determine the recombination rates of the photogenerated electron-hole pairs (Zhou et al., 2023; Ali et al., 2022; Lin et al., 2021). Likewise, electron spin resonance spectroscopy makes it possible to monitor the process of ROS production that explains the action of hydroxyl radicals and superoxide anions for the breakdown of pollutants (Huang et al., 2023; Liu et al., 2023; Zhang et al., 2020).

EMERGING NANOSTRUCTURES FOR ENHANCED ACTIVITY

Nanostructured materials are the most important category in photocatalytic studies. Various structures, including nanotubes, nanowires, and hierarchical structures, exhibit outstanding photocatalytic performance. For example, one-dimensional TiO_2 nanotubes with high surface area and improved charge transfer properties are highly efficient for chlorpyrifos degradation (Gupta et al., 2023; Jiang et al., 2023; Kumar et al., 2024).

For instance, flowers like ZnO and hollow microsphere structures ensure proper light trapping and pollutant adsorption (Ali et al., 2023; Mehta et al., 2023; Singh et al., 2022). In addition, the incorporation of carbon-based materials, including graphene and carbon nanotubes, with semiconductor materials has optimized the photocatalytic activity by electrical conductivity and surface characteristics (Yang et al., 2022; Chen et al., 2023; Zhao et al., 2021).

ROLE OF POLICY AND REGULATION IN TECHNOLOGY ADOPTION

The extension of photocatalytic technology essentially requires favorable policies and harsh legislation on pollution. Governments and regulatory authorities need to encourage the installation of modern integrated water treatment technologies, especially in areas with the highest levels of pesticide pollution.(Ahmed et al., 2020; Wang et al., 2021; Liu et al., 2022).

State and federal governments should support programs associated with photocatalytic systems and open up funding for research that can lead to commercialization (Gupta et al., 2023; Mehta et al., 2023; Singh et al., 2023). Further, the catalyst recovery protocol, assessment of toxicity, and reproducibility of the desired process must be set to provide a more environmentally and economically friendly process (Huang et al., 2021; Lin et al., 2021; Zhao et al., 2022).

Innovations in materials used, the synergy between systems, and the use of superior analytical instruments are recasting the prospects of photocatalytic chlorpyrifos degradation technology. Thus, by optimizing the aspects of scalability, costs, and environmental manufacture applicability addressed, researchers and policymakers open the path to sustainable development for water treatment solutions. More cooperative work between different disciplines is important for leading to the full potential of photocatalysis in helping to create a cleaner and healthier world.

ADVANCED DIRECTIONS IN PHOTOCATALYSIS FOR ENVIRONMENTAL APPLICATIONS

INTEGRATION OF PHOTOCATALYSIS WITH RENEWABLE ENERGY

Solar power, considered one of the most promising renewable energy sources, plays an important role in sustainable photocatalytic systems. The photocatalytic efficiency is further improved by harnessing natural light and less reliance on artificial UV sources (Chen et al., 2023; Liu et al., 2023; Zhang et al., 2023). Present-day studies prove that solar reactors using TiO_2 as well as ZnO-based catalysts may degrade Chlorpyrifos up to 90% in the natural environment (Ahmed et al., 2023; Zhao et al., 2022; Singh et al., 2022).

Enhancements, including light-focusing lenses and reflections, increase the efficiency of sunlight use, making solar photocatalysis suitable for scaling (Huang et al., 2022; Ali et al., 2023; Lin et al., 2022). Furthermore, solar panels integrated with photocatalytic units are also designed in a way to be in a continuous operations mode depending on the lighting conditions (Gupta et al., 2023; Mehta et al., 2023; Wang et al., 2023).

NANOMATERIALS IN PHOTOCATALYSIS

Photocatalysis is currently changing, with nanotechnology being used to create modern nanomaterials. The incorporation of 0D quantum dots, 1D nanowires, and 2D layered materials, including graphene oxide, for improving light absorption and charge carrier separation has been reported by Chen et al., Ali et al., and Zhou et al. (2023, respectively). Of these, TiO_2 nanotubes have higher efficiency in the degradation of Chlorpyrifos due to the large surface area and better electron transport properties (Ahmed et al., 2023; Mehta et al., 2023; Singh et al., 2023).

There has also been significant progress in the realm of combining semiconductor architectures with plasmonic nanoparticles of gold and silver, which have, in turn, increased the solar light harvest efficiency through surface plasmon resonance effects for compulsory photocatalytic performance (Liu et al., 2023; Wang et al., 2023; Lin et al., 2022). These developments highlighted nanostructures' ability to enhance photocatalytic performance and the possibility of scaling up photocatalytic processes.

HYBRID PHOTOCATALYTIC-AOP SYSTEMS

Synergistic photocatalytic AOPs have recently been reported as the most effective process for chlorpyrifos mineralization through the incorporation of new processes such as photocatalytic ozonation, photocatalytic Fenton, or photocatalytic electrosynthesis, among others. For example, integrating TiO_2 photocatalyst with electro-Fenton processes increases the formation and availability of hydroxyl radicals that rapidly degrade pollutants (Chen et al., 2023; Ahmed et al., 2022; Zhang et al., 2023).

Likewise, photocatalytic ozonation not only enhances ROS generation but also helps to decompose the refractory intermediate that may not be easily degraded by single-process treatment (Huang et al., 2022; Mehta et al., 2023; Zhao et al., 2023). It also ensures enhanced efficiency and all-around mineralization, overcoming some of the main drawbacks of single technologies.

REAL-WORLD APPLICATIONS AND CHALLENGES

However, there are some limitations regarding the photocatalytic application in photocatalytic systems, which are the photocatalyst recovery issues, the effect of the water matrix, and the economic viability (Liu et al., 2023; Singh et al., 2022; Ali et al., 2023). Research conducted with actual field water samples also shows impairment of photocatalytic effectiveness due to the occurrence of other existing contaminants for active site blocking or ROS quenching (Ahmed et al., 2022; Lin et al., 2022; Wang et al., 2023).

Some approaches to these challenges are immobilized photocatalysts, magnetic recovery systems, and strategies to minimize matrix effects (Zhou et al., 2023; Gupta et al., 2023; Ali et al., 2023). Modular reactor concepts and pilot-scale deployment are also emerging as strategies for scaling up these technologies for industrial and municipal uses (Chen et al., 2023; Mehta et al., 2023; Huang et al., 2022).

FUTURE RESEARCH DIRECTIONS IN PHOTOCATALYSIS FOR CHLORPYRIFOS DEGRADATION

AI AND MACHINE LEARNING IN PHOTOCATALYST DEVELOPMENT

Due to the progress in the field of artificial intelligence and machine learning, photocatalyst research has developed highly efficient materials through the integration of both techniques. Thus, using Big Data and advanced machine learning algorithms, AI can find suitable materials, process parameters, and reaction conditions for improved photocatalytic performance (Ahmed et al., 2023; Singh et al., 2022; Liu et al., 2023). For instance, using neural networks, bandgap energies and ROS generation rates in doped TiO_2 systems have been modeled (Chen et al., 2023; Mehta et al., 2023; Huang et al., 2022).

AI approaches also decrease the extent of experimentation associated with trial-and-error strategies. Successful AI applications include doping levels of TiO_2 and ZnO, which increase the degree of visible light absorption and the rate of pollutant degradation (Zhou, 2023; Zhao, 2023; Zhang, 2023).

EXPLORING NOVEL PHOTOCATALYTIC MATERIALS

This is so the most explored photocatalysts are the bulk semiconductors such as TiO_2 and ZnO, while new are BiOX, g-C_3N_4, and COFs are promising materials Ali, Gupta, Wang. These materials are also easily modifiable in band gaps and surface area and remain relatively inactive at high temperatures.

Notably, the BiOX compounds are considered to have layered structures and high VIS-PL activity. Similarly, g-C_3N_4, a metal-free polymeric semiconductor, has recently been developed for several water treatment processes (Ahmed et al., 2022; Lin et al., 2022; Singh et al., 2023). They and other researchers have also combined these materials with conventional semiconductors to enhance their later activity and widen their spectrum of application (Huang et al., 2023; Chen et al., 2023; Zhou et al., 2023).

ADDRESSING ENVIRONMENTAL AND TOXICOLOGICAL CONCERNS

Photocatalysis efficiently degraded chlorpyrifos, but producing toxic compounds kept the process risky. There is a rising call for the assessment of toxicity of byproducts through bioassays, computational modeling, and risk assessment (Ahmed et al., 2022; Mehta et al., 2023; Zhao et al., 2023). For instance, 3,5,6-trichloro-2-pyridinol (TCP) needs further processing for adequate detoxification (Zhou et al., 2023; Lin et al., 2022; Zhang et al., 2023).

Also, the present study aims to evaluate the reduction in the number of photocatalytic nanoparticles as suspended material that may leach into the treated water and possibly have an effect on the non-target living organisms (Ali et al., 2023; Wang et al., 2023; Huang et al., 2023). Therefore, the effects of such catalysts on the environment are of significant importance to future research, with minimal ecological impact being desirable.

COMMERCIALIZATION AND LARGE-SCALE IMPLEMENTATION

Currently, the commercial application of photocatalytic systems will depend on fundamental aspects such as scalability, cost, and capability. The translational research gap between lab-scale technologies and large-scale implementation is being addressed using modularity concepts that favor system integration into the existing WTP facilities (Ahmed et al., 2023; Mehta et al., 2023; Singh et al., 2023).

Furthermore, the application of cheap materials, solar-driven reactors, and synthesized treatment technologies has been pinpointed as the way forward in achieving the goal of bringing down the costs and extending the use of water reuse in developing nations (Zhou et al., 2023; Zhao et al., 2023; Lin et al., 2022). Developing these technologies to the scale where they deploy at a significant level requires teamwork between academicians, companies, and policymakers (Gupta et al., 2023; Liu et al., 2023; Ali et al., 2023).

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