

NANOPARTICLES FOR PHOTOCATALYTIC REMEDICATION OF PESTICIDE RESIDUES IN ENVIRONMENTAL SAMPLES

Abstract

Photocatalytic pesticide degradation using nanoparticles is a promising technique for remediating contaminated water and soil. Titanium dioxide, zinc oxide, and iron oxide nanoparticles can act as catalysts to accelerate the oxidation of organic pollutants by sunlight or artificial light sources. The process involves the formation of reactive oxygen species, such as hydroxyl radicals and superoxide anions, which can degrade pesticide molecules into innocuous byproducts like carbon dioxide and water. Photocatalytic pesticide degradation using nanoparticles has several advantages over traditional methods, including low cost, high efficiency, environmental friendliness, and low secondary pollution. However, there are some challenges and limitations that must be addressed, such as the nanoparticles' stability, recyclability, and toxicity, the impact of water quality parameters, and the scale-up and integration of the technology.

Keywords: Photocatalytic degradation, Pesticides, Organic Pollutants, Nanoparticles, hydroxyl radicals.

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I. INTRODUCTION

Although pesticides are frequently used in agriculture and other industries to manage pests and weeds, they also pose significant risks to the environment and human health. Pesticides have the potential to contaminate water sources, soil, crops, and aquatic ecosystems, as well as cause acute and chronic toxicity, endocrine disruption, carcinogenicity, and mutagenicity in humans and animals [1-5]. As a result, there is an urgent need to develop effective pesticide residue removal methods for water and soil. Photocatalysis, an advanced oxidation process that uses light energy to activate a semiconductor catalyst, such as titanium dioxide (TiO_2), and generate reactive oxygen species (ROS) that can oxidize organic pollutants into harmless products, is one of the promising pesticide degradation techniques. TiO_2 is a popular photocatalyst because of its low cost, high stability, nontoxicity, and high photocatalytic activity. However, TiO_2 has some drawbacks, including a large band gap that requires UV light to activate, a low quantum efficiency, and a high electron-hole recombination rate [6-8].

To overcome these limitations, various strategies for modifying TiO_2 nanoparticles (NPs) and improving their photocatalytic performance have been developed. Doping with metal or nonmetal elements, coupling with other semiconductors, loading with noble metals, and immobilization on various supports are examples of these. These changes can improve TiO_2 NPs' light absorption, charge separation, surface area, adsorption capacity, and catalytic activity [9].

In this review, we examined some recent studies on the use of TiO_2 NPs and their modified forms in photocatalysis for pesticide removal from water. We will also discuss the factors that influence pesticide photocatalytic degradation, such as pH, catalyst concentration, irradiation time, pesticide initial concentration, and the presence of other substances [11-14]. Photocatalysis is a method of using light to activate a substance (called a catalyst) that can accelerate a chemical reaction. Photocatalysis has numerous potential applications, including water purification, air purification, and energy conversion. One of the most promising applications of photocatalysis is pesticide decontamination using nanoparticles [15].

Using nanoparticles for photocatalytic pesticide degradation. Photocatalytic degradation is an advanced oxidation process that can effectively mineralize organic pollutants into harmless compounds by using semiconductors as catalysts such as TiO_2 , ZnO , CeO_2 , CdS , and WO_3 . This technique has a lot of potential for removing pesticides, which are widely used in agriculture but pose serious health and environmental risks [16].

TiO_2 and ZnO have garnered the most attention among semiconductors due to their high quantum efficiency, low cost, ease of synthesis, and environmental friendliness. They do, however, have some limitations, such as a small surface area, a high electron-hole recombination rate, and a limited light absorption range. As a result, many researchers have attempted to modify TiO_2 and ZnO using various methods, such as doping [17].

As an example, Zhu et al. recently developed a ZnO /reduced graphene oxide (rGO) nanocomposite for the photocatalytic destruction of the organophosphorus insecticide dimethoate using a hydrothermal approach. They discovered that the ZnO /rGO nanocomposite outperformed bare ZnO in terms of photodegradation rate and efficiency,

owing to the increased surface area, pore volume, charge transfer rate, and carrier transport caused by the presence of rGO [18].

Another study by Hadei et al. performed a systematic analysis of all studies that examined the photocatalytic degradation of pesticides utilizing TiO₂ nanoparticles (NPs) and ultraviolet (UV) irradiation and were published between 2009 and 2019. They found 53 active compounds for pesticides as well as 16 different forms of TiO₂ with an average photodegradation efficiency of 71%. They also discussed approaches to reduce the amount of energy required for this process, including the effects of experimental circumstances on photocatalytic activity and doping TiO₂ with metal and non-metal agents, inventive reactor designs, etc. [19-22].

In addition, Singh et al.'s recent study investigated into the photocatalytic efficiency of ZrO₂@Ru and ZrO₂@Au nanostructures for the methyl parathion and diuron pesticides. Due to the development of Schottky barriers at the metal-semiconductor interface, which facilitated charge separation and transfer, they discovered that both nanostructures displayed remarkable photocatalytic activity when exposed to visible light [23].

These studies show that a promising and effective method for water purification is photocatalytic degradation of pesticides using nanoparticles. However, there are still some obstacles and knowledge gaps that need to be filled, including the analysis of economic and environmental feasibility as well as the optimization of catalyst characteristics, identification of intermediate products, and toxicity assessment [24].

Photocatalytic degradation is a method of breaking down organic pollutants in water by using light and a catalyst. The efficiency of photocatalytic degradation is affected by a number of factors, including the type and concentration of the catalyst, the wavelength and intensity of the light source, the pH and temperature of the water, the initial concentration and nature of the pollutants, and the presence of other substances that could interfere with the reaction. These variables can influence the rate and extent of degradation, as well as the formation of intermediate and by-products. As a result, it is critical to optimize these parameters for each individual photocatalytic degradation application [25-27].

These studies demonstrate that photocatalytic pesticide degradation using nanoparticles is a promising and efficient water purification technology. However, there are still some challenges and gaps to be addressed, such as catalyst optimization, identification of intermediate products and toxicity assessment, reactor scale-up and integration, and economic and environmental feasibility analysis [28].

II. OVERVIEW OF PHOTOCATALYSIS

Photocatalysis is a chemical process that accelerates reactions by using light and a photocatalyst. A photo catalyst is a solid material with the ability to absorb light and generate excited electrons and holes on its surface. These charge carriers can then interact with other molecules, causing them to oxidize or reduce. Photocatalysis has a wide range of applications, including water splitting, pollutant degradation, hydrogen production, and air purification [29].

Some of the principles of photocatalysis are:

- The photo catalyst should have a suitable band gap to absorb light of the desired wavelength and generate enough energy for the reaction.
- The photo catalyst should have a high surface area to increase the contact with the reactants and the light.
- The photo catalyst should have a good charge separation and transport ability to prevent recombination of the electrons and holes.
- The photo catalyst should be stable and resistant to corrosion, poisoning, or deactivation under the reaction conditions.
- Photocatalysis is a promising technique for solving energy and environmental problems, but it also faces some challenges, such as:
 - The low efficiency of light utilization and conversion due to reflection, scattering, or transmission losses.
 - The limited availability of suitable photo catalysts that can work under visible or solar light, which is more abundant than UV light.
 - The complex reaction mechanisms and kinetics that depend on various factors, such as pH, temperature, concentration, and catalyst loading.
 - The scale-up and integration of photocatalytic systems for practical applications.

Nanoparticles are ideal for use in photocatalytic processes due to their unique features. They have a high surface area to volume ratio, which enhances the number of active reactions sites. This can lead to higher photocatalytic activity and faster reaction rates. In addition, using nanoparticles can provide accurate mechanistic information regarding the photocatalytic process.

In doped, linked, capped, sensitized, and organic-inorganic nanocomposite semiconductor systems, nanoparticles can also be employed to increase the photocatalytic and/or optical properties of commonly used semiconductor materials. Core-shell nanoparticles, for example, with metals such as Au, Ag, Pt, Pd, Zn, Ni, and others as a core and metal oxide semiconductors such as ZnO, TiO₂, SiO₂, Cu₂O, Fe₂O₃, and SnO₂ as a shell have piqued the curiosity of many researchers [30].

Overall, the use of nanoparticles in photocatalytic processes has many advantages and has the potential to provide sustainable solutions to current environmental remediation problems.

Photocatalysis has many potential applications in environmental remediation, such as:

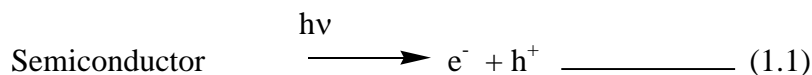
- Degradation of organic contaminants in wastewater, soil, and air. Photocatalytic materials can oxidize harmful substances like pesticides, dyes, pharmaceuticals, and volatile organic compounds (VOCs), converting them into harmless products like carbon dioxide and water.
- Reduction of greenhouse gases and air pollutants. Photocatalytic materials can also reduce carbon dioxide to produce fuels like methane or methanol, or reduce nitrogen oxides to produce nitrogen and oxygen. This can help mitigate climate change and improve air quality.

- Production of clean and renewable energy. Photocatalytic materials can split water into hydrogen and oxygen, which can be used as fuels in fuel cells or combustion engines. Hydrogen is a promising energy carrier that does not emit any greenhouse gases or pollutants when used.

III. THE PHOTOCATALYSIS MECHANISM

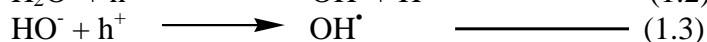
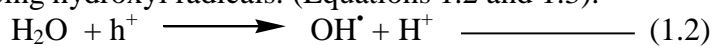
UV light activates a semiconductor photocatalyst in the photocatalytic process and creates a redox environment in the aqueous solution. Due to their electronic structure, which is characterized by a filled valence band and an empty conduction band, semiconductors serve as sensitizers for light-induced redox reactions [24]. The band gap is the measure of the energy disparity between the valence and conduction bands. The semiconductor photocatalyst absorbs photons with energies that are equal to or greater than its band gap or threshold energy E_g , which excites the occupied valence band electrons to the unoccupied conduction band, resulting in excited state conduction band electrons and positive holes in the valence band. To use these charge carriers in redox processes involving adsorbed species, recombination of these charge carriers must be successfully inhibited. Charge carriers can take several pathways, becoming stuck in shallow traps (ST) or deep traps (DT), or recombining non-radiatively or radiatively, releasing the input energy as heat. Finally, they can react with electron donors or acceptors adsorbed on the photocatalyst's surface [24]. Indeed, [26] demonstrated that every photoredox reaction happening at the particle surface is caused by trapped electrons and holes [31].

Semiconductors absorb light with an energy larger than or equal to the band gap energy (E_g), promoting an electron from the valence band to the conduction band, resulting in an electronic vacancy or hole (h^+) at the valence band edge. This hole can also be determined chemically. This hole can cause additional interfacial electron transfer or other chemical processes to an adsorbate, or it can diffuse into the bulk solvent with surface bound OH^- ions. The photogenerated electron is typically located at the conduction band edge, whereas the hole is located at the valence band edge. If the energies of the electron and hole do not match, deactivation of the catalyst via electron-hole recombination may be difficult. Unlike metals, semiconductors lack a continuum of interband states to aid in electron-hole pair recombination. This ensures that electron-hole pairs have a long enough lifetime to participate in interfacial electron transfer [32]. Thus, light excitation often produces an electron-hole pair poised at the conduction band and valence band margins (Equation 1.1).

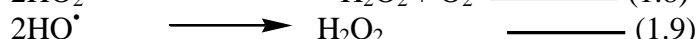
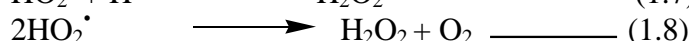
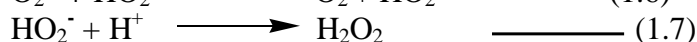
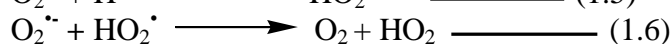


The photogenerated electron-hole pairs activate a sequence of redox processes in the aerated suspension of the semiconductor in contact with organic molecules, as outlined below.

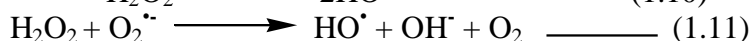
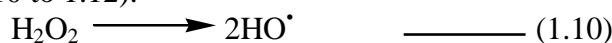
- The photogenerated holes oxidize adsorbed water molecules and hydroxyl ions, producing hydroxyl radicals. (Equations 1.2 and 1.3).



- Photogenerated electrons reduce dissolved oxygen to produce superoxide anion radicals (Equation 1.4), which in turn generate H₂O₂ via a series of redox processes (Equations 1.5 to 1.9).



- The photogenerated H₂O₂ undergoes further decomposition to yield hydroxyl radicals (Equations 1.10 to 1.12).



- Direct involvement of holes in oxidation reactions
- Formation and involvement of singlet oxygen species in oxidation.

These hydroxyl radicals OH and superoxide radicals O₂ are important species for pollution breakdown. **Figure 1** illustrates a visual representation of the numerous activities that occur on the lit surface of a photocatalyst.

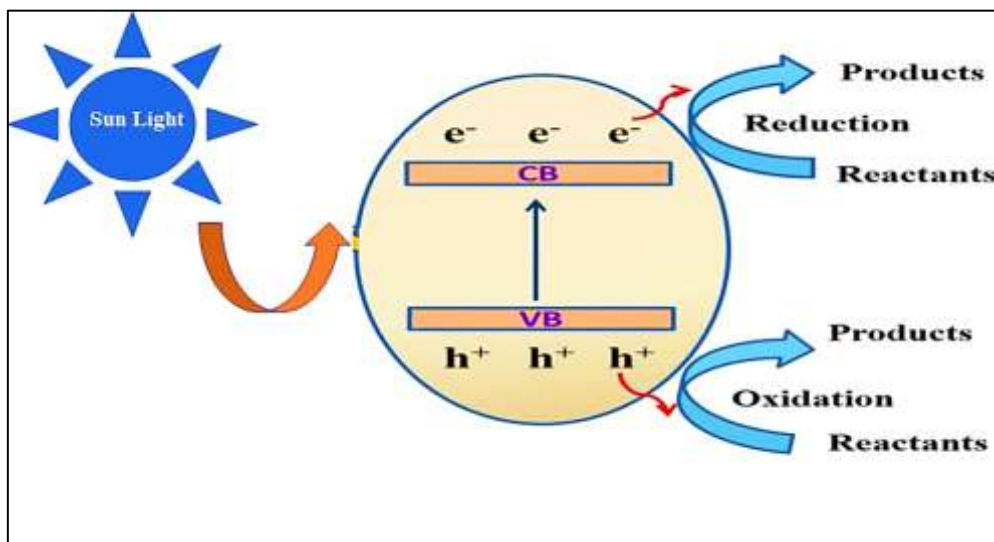


Figure 1: The process involved in a semiconductor upon band gap excitation

IV. CATALYSTS CHARACTERIZATION

Catalyst structural, physical, and chemical qualities are crucial for identifying the link between physicochemical properties and catalytic activity. Several approaches were employed to characterize the produced and doped catalysts. In this work, the following physicochemical characterisation approaches were used [28].

- 1. X-Ray Diffraction Studies:** In order to determine the crystallographic phase, degree of crystallinity, unit cell parameter, and crystallite size of the catalysts, X-Ray Diffraction (XRD) patterns were mostly used. Typically, high energy electrons are used to attack a target to produce X-rays. Commonly utilized X-ray sources include CuK α , CoK α , FeK α , and MoK α . The typical X-ray source is CuK α radiation, which has a wavelength of 0.154 nm and an energy of 8.04 keV. The incident monochromatized X-ray interacts with the atoms of a periodic lattice in the X-ray diffraction method. X-rays are constructively dispersed by atoms in an organized lattice in the directions suggested by Bragg's rule in Equation (4.1).

$$n\lambda = 2d \sin \theta \quad (4.1)$$

Where, d is the distance between two lattice planes, n is the order of reflection, λ is the X-ray wavelength, and θ is Bragg's angle. This law establishes a connection between the lattice spacing and diffraction angle in a crystalline sample and the wavelength of electromagnetic radiation. A diffraction pattern is the unique arrangement of the thousands of individual reflections that can be formed by crystal formations. Each reflection may have an index (hkl) assigned to it, indicating where it belongs in the diffraction pattern. The relationship between the pattern and the unit cell and crystalline lattice in the real space is reciprocal Fourier transformation.

- 2. Field Emission Scanning Electron Microscopy:** Using a Schottky electron gun and a Hitachi SU 70 FE-SEM, electron micrograph pictures were captured. The accelerating voltage range used for the measurements was 5–15 kV. On a surface covered with mounted carbon tape, powdered samples were dispersed equally. A can of air spray was used to remove the loose powdered sample.

With the use of a high-energy electron beam that scans the sample surface in a raster scan pattern, the Field Emission Scanning Electron Microscope (FE-SEM) creates images of the surface. The sample's surface topography, composition, and other characteristics, such as electrical conductivity, are revealed through the interactions between the sample's electrons and the atoms that make up its shells. These interactions result in signals. Secondary electrons (SE), backscattered electrons (BSE), characteristic X-rays, light (cathodoluminescence), specimen current, and transmitted electrons (STEM) are the several signal kinds that a FE-SEM can create. SE imaging is typically the most prevalent or standard detection technique. Because the spot size in a Field Emission SEM is smaller than in a typical SEM, it is able to provide images with an extremely high level of resolution, revealing features as fine as 1 to 5 nm.

One of the most used methods for determining the shape and size of the catalysts is field emission scanning electron microscopy (FE-SEM). FE-SEM will offer information on the chemical composition close to the surface in addition to topographical data like optical microscopes. Instead of using light, FE-SEM uses electrons to produce enlarged pictures. It provides more magnified 3-D images than an optical microscope. The numerous ways that primary electron beam interactions with catalysts happen in an electron microscope. Back scattered electrons and secondary electrons are collected by a detector in the scanning electron microscope to create the image.

- 3. Energy Dispersive X-ray Analysis (EDX):** Dispersive Energy The technique used to determine the elemental makeup of the samples is called X-ray analysis. The substance being studied determines the energy of the X-ray that is released when it interacts with an electron beam. Each element in the sample can be visualized by moving the electron beam across the material. In EDX, which operates at liquid nitrogen temperature, lithium drifted silicon is utilized as the detector. Depending on the energy of the incoming X-rays, the detector will produce photoelectron when the X-rays hit it. This produces electron-hole pairs, which in turn provide the current pulses as the signal. Since X-rays are also produced when electrons contact with samples during FE-SEM analysis, EDX is always conducted in conjunction with FE-SEM analysis. The samples' EDX spectra were captured using a JEOL Model JED-2300 equipment.
- 4. High Resolution Transmission Electron Microscopy:** For determining the size of nanoparticles, high resolution transmission electron microscopy (HR-TEM) has been widely used. A tungsten anode, an accelerating anode, and a beam aperture control make up the electron cannon. At the point where it reaches the specimen, an electron lens system concentrates the electron beam, which has an extremely tiny cross section. In order to form a picture on a fluorescent screen and capture it on film, the transmitted electrons must first pass through another set of electronic optics. Transmitted electrons, including unscattered, elastically and inelastically scattered electrons, are used in HR-TEM. High resolution and reduced chromatic aberration are produced when high energy electrons (200 keV or more) are used.

Using a JEOL TEM-3010 electron microscope run at a 300 keV accelerating voltage, high resolution transmission electron microscopic (HR-TEM) pictures were captured. The catalysts were dissolved in isopropanol using sonication to prepare the samples for HR-TEM examination, then they were deposited on a copper grid.

- 5. Ultraviolet - Visible Diffuse Reflectance Spectroscopy:** ultraviolet - diffuse visibility for the identification and characterization of metal ion coordination and its presence in the frame work or extra-frame work location of metal-containing molecular sieves and doped semiconductors, reflectance spectroscopy (UV-DRS) is recognized to be a very sensitive and practical approach. It focuses on the investigation of electronic transitions between atomic, ionic, or molecular orbitals or bands in the gaseous, liquid, and solid states. This method is based on the way a powdered sample reflects light in the visible and ultraviolet (UV) ranges. DRS-UV-Vis spectra can be used to study a catalyst's bulk and surface properties.
- 6. Fourier Transform Infrared Spectroscopy:** A multidisciplinary analytical method known as Fourier Transform Infrared Spectroscopy (FT-IR) provides information about a material's structural specifics. It can also be utilized to confirm surface properties like acidity and isomorphous substitution by other material constituents. In FT-IR, electromagnetic radiation in the infrared part of the spectrum is absorbed, changing the vibrational energy of molecules as a result.. It is an effective and powerful method for locating organic compounds with strong charge separation and polar chemical bonds, such as OH, NH, or CH. The IR spectra can be thought of as the fingerprints of the functional groups because each one has a distinct vibrational energy. Using the KBr pellet approach, the IR spectra of uncalcined and calcined materials were captured on an FT-IR

spectrometer (Nicolet Avatar 360). A pellet was created using a hydraulic press utilizing a combination made up of around 10 mg of the sample and 70 mg of spectral grade KBr. This pellet was utilized to record the infrared spectra between 4000 and 400 cm^{-1} by being scanned 50 times at a resolution of 4 cm^{-1} .

V. NANOPARTICLES FOR PESTICIDE RESIDUES REMOVAL

Pesticides are commonly used in agriculture to protect crops from pests and illnesses, but they can also leave hazardous residues on fruits and vegetables, posing a health risk to consumers.

One answer could be nanoparticles, which are tiny particles with diameters ranging from 1 to 100 nanometers. Nanoparticles have unique features that make them appropriate for a variety of applications such as medication delivery, catalysis, and environmental cleanup. Some nanoparticles, in particular, have the ability to bind to pesticide molecules and remove them off fruit and vegetable surfaces [30].

Researchers, for example, have created magnetic nanoparticles coated with a polymer that can selectively capture organophosphorus pesticides, which are among the most widely used and toxic pesticides. The nanoparticles can be sprayed or dipped onto the fruits and vegetables and then removed with a magnetic field. After washing and drying, the nanoparticles can be reused [31-32].

Another example is the application of antibacterial and antifungal silver nanoparticles. Some pesticides can be degraded by silver nanoparticles by producing reactive oxygen species, which are molecules that can damage the chemical structure of pesticides. Silver nanoparticles can also reduce the microbial load on fruits and vegetables, extending their shelf life and improving their safety [33].

Nanoparticles have several advantages over traditional pesticide residue removal methods such as washing, peeling, or heating. Pesticides can be removed more efficiently and effectively with nanoparticles, without affecting the quality or nutritional value of fruits and vegetables. Nanoparticles can also be engineered to target specific pesticides while avoiding harming beneficial microorganisms or natural antioxidants found in fruits and vegetables [34].

However, there are some challenges and limitations to nanoparticles that must be addressed before they can be widely used for pesticide residue removal. One of the most difficult challenges is ensuring the safety and biocompatibility of nanoparticles for both human health and the environment. Nanoparticles may cause inflammation, oxidative stress, and DNA damage in human cells and organs. Nanoparticles could also [35].

More research is therefore required to assess the potential risks and benefits of nanoparticles for pesticide residue removal, as well as to optimize their synthesis, characterization, application, and disposal. Nanoparticles for pesticide residue removal may be a promising alternative to conventional methods, but they must be carefully regulated and monitored to ensure their safety and long-term viability [36].

VI. INSTRUMENT ANALYSIS FOR PESTICIDE RESIDUES

Pesticide residue analysis is the detection and quantification of pesticide residues on or in food, soil, water, or other samples after they have been applied. Pesticide residues can endanger human and animal health and cause environmental issues. As a result, it is critical to monitor and control pesticide residue levels in various matrices.

Instrument analysis is one method for pesticide residue analysis that uses sophisticated instruments to separate, identify, and measure the pesticides in a sample. For a wide range of pesticides, instrument analysis can provide high sensitivity, accuracy, and specificity. Gas chromatography (GC), liquid chromatography (LC), mass spectrometry (MS), and tandem mass spectrometry (MS/MS) are some of the common instruments used for pesticide residue analysis.

The gas chromatography (GC) technique is used to separate volatile and semi-volatile pesticides based on their boiling points and affinities to a stationary phase. To improve pesticide detection and identification, GC can be combined with other detectors such as a flame ionization detector (FID), electron capture detector (ECD), or mass spectrometer (MS).

The separation of non-volatile and polar pesticides by LC is based on their solubility and interactions with a mobile phase and a stationary phase. To improve pesticide detection and identification, LC can be combined with various detectors such as ultraviolet-visible detector (UV-Vis), diode array detector (DAD), or MS.

MS is a method for ionizing pesticides and measuring their mass-to-charge ratios. MS can provide structural information as well as confirmation of pesticide identity. MS can be used independently or in conjunction with GC or LC.

MS/MS is a mass spectrometry technique that employs two stages of mass spectrometry on pesticides. MS/MS can provide more detailed information and greater selectivity for pesticide identification and quantification. MS/MS can be used in tandem with GC.

VII. CONCLUSIONS AND PERCEPTION

1. Challenges of using Photocatalysis for Pesticide Decontamination

- **Low efficiency:** The photocatalytic degradation of pesticides is a slow process, and it requires a high amount of energy to achieve complete degradation.
- **Reusability:** The photocatalysts used in the process are often not reusable, which increases the cost of the process.
- **Selectivity:** The photocatalysts used in the process are often not selective, which means that they can degrade both target and non-target compounds.
- **Environmental impact:** Because of the formation of reactive oxygen species (ROS) and other byproducts, the usage of photocatalysts can have an environmental impact.
- To address these issues, researchers are investigating various strategies such as doping TiO₂ with metal and nonmetal agents, developing novel reactor designs, and

developing heterogeneous doped and immobilized titania with optimized surface area, reactive centers, recombination rate, and phase.

2. Future Research Work on Nanophotocatalysis of Removal of Pesticides: We provided some insights into future research work on nanophotocatalysis for pesticide removal. Nanophotocatalysis is a promising technique that employs nanomaterials to improve photocatalytic degradation of organic pollutants in the presence of light. Pesticides are a major source of environmental contamination that endangers human health and ecosystems. As a result, developing efficient and environmentally friendly methods to remove pesticides from water and soil is critical.

However, there are still some challenges and gaps in the current research on nanophotocatalysis of removal of pesticides. Some of the pending future research work are:

- Exploring new nanomaterials with high photocatalytic activity, stability, and selectivity for pesticide degradation. For example, metal-organic frameworks (MOFs), covalent organic frameworks (COFs), and carbon-based nanomaterials are emerging as potential candidates for nanophotocatalysis.
- Investigating the mechanisms and kinetics of nanophotocatalytic degradation of different types of pesticides, such as organophosphorus, organochlorine, carbamate, and pyrethroid pesticides. Understanding the reaction pathways, intermediates, and products can help optimize the nanophotocatalytic process and evaluate its environmental impact.
- Developing novel strategies to enhance the nanophotocatalytic performance by modifying the nanomaterials or combining them with other techniques, such as doping, coupling, heterojunction, plasmonics, magnetic separation, and hybridization. For instance, coupling nanophotocatalysts with adsorbents, biocatalysts, or electrochemical methods can achieve synergistic effects for pesticide removal.
- Evaluating the feasibility and scalability of nanophotocatalysis for practical applications in pesticide-contaminated water and soil remediation. This requires addressing the issues of cost-effectiveness, mass production, reusability, and safety of nanomaterials.

REFERENCES

- [1] M.M. Maroneze, L.Q. Zepka, J.G. Vieira, M.I. Queiroz, E. Jacob-Lopes, A tecnologia de remoção de fósforo: Gerenciamento do elemento em resíduos industriais, *Rev. Ambient. e Agua*. 9 (2014) 445–458. <https://doi.org/10.4136/1980-993X>.
- [2] M. Yeganeh, E. Charkhloo, H.R. Sobhi, A. Esrafil, M. Gholami, Photocatalytic processes associated with degradation of pesticides in aqueous solutions: Systematic review and meta-analysis, *Chem. Eng. J.* 428 (2022) 130081. <https://doi.org/10.1016/j.cej.2021.130081>.
- [3] F.S. Bruckmann, C. Schnorr, L.R. Oviedo, S. Knani, L.F.O. Silva, W.L. Silva, G.L. Dotto, C.R. Bohn Rhoden, Adsorption and Photocatalytic Degradation of Pesticides into Nanocomposites: A Review, *Molecules*. 27 (2022). <https://doi.org/10.3390/molecules27196261>.
- [4] U.S. EPA, Degradation of pesticides by algae, (1976) 1–50.
- [5] S. Ampolu, UV accelerated photocatalytic degradation of carbaryl pesticide using nano ZnO, (2023).
- [6] Wazid, S. Nadagouda, A. Prabhuraj, R.H. Naik, N. Shakuntala, H. Sharanagouda, The Persistence of Residual Toxicity of Zinc, Copper an Silica Green Nanoparticles against Important Storage Pests, *J. Entomol. Zool. Stud.* 8 (2020) 1207–1211.

- [7] A. Toolabi, M. Malakootian, M.T. Ghaneian, A. Esrafil, M.H. Ehrampoush, M. Tabatabaei, M. AskarShahi, Optimization of photochemical decomposition acetamiprid pesticide from aqueous solutions and effluent toxicity assessment by *Pseudomonas aeruginosa* BCRC using response surface methodology, *AMB Express*. 7 (2017). <https://doi.org/10.1186/s13568-017-0455-5>.
- [8] A. Derbalah, M. Sunday, R. Chidya, W. Jadoon, H. Sakugawa, Kinetics of photocatalytic removal of imidacloprid from water by advanced oxidation processes with respect to nanotechnology, *J. Water Health*. 17 (2019) 254–265. <https://doi.org/10.2166/wh.2019.259>.
- [9] M. Malakootian, M.M. Soori, Enhanced photocatalytic degradation of diazinon by TiO₂/ZnO/CuO nanocomposite under solar radiation, *Desalin. Water Treat.* 242 (2021) 75–88. <https://doi.org/10.5004/dwt.2021.27814>.
- [10] P.K. Boruah, G. Darabdhara, M.R. Das, Polydopamine functionalized graphene sheets decorated with magnetic metal oxide nanoparticles as efficient nanozyme for the detection and degradation of harmful triazine pesticides, *Chemosphere*. 268 (2021) 129328. <https://doi.org/10.1016/j.chemosphere.2020.129328>.
- [11] D.M. Fouad, M.B. Mohamed, Photodegradation of chloridazon using coreshell magnetic nanocomposites, *J. Nanotechnol.* 2011 (2011). <https://doi.org/10.1155/2011/416060>.
- [12] K.S. Varma, R.J. Tayade, K.J. Shah, P.A. Joshi, A.D. Shukla, V.G. Gandhi, Photocatalytic degradation of pharmaceutical and pesticide compounds (PPCs) using doped TiO₂ nanomaterials: A review, *Water-Energy Nexus*. 3 (2020) 46–61. <https://doi.org/10.1016/j.wen.2020.03.008>.
- [13] X. Zhao, D. Chen, T. Zhou, Photocatalytic Degradation of Selective Herbicides Using Ag/AgCl/Ag₃PO₄ Plasmonic Nanocatalyst under Visible Irradiation, (2015) 766–771. <https://doi.org/10.2991/icaees-15.2015.140>.
- [14] A. Mohammadi, M. Shahmirzaei, Polyamidoamine Dendrimers-MoS₂ Nanocomposites for Photocatalytic Degradation of Chlorpyrifos and Glyphosate Pesticides, *Anal. Bioanal. Chem. Res.* 9 (2022) 21–31. <https://doi.org/10.22036/abcr.2021.271647.1595>.
- [15] F. Ahmad, M. Mehmood, A Critical Review of Photocatalytic Degradation of Organophosphorus Pesticide “Parathion” by Different Mixed Metal Oxides, 5 (2022) 287–310.
- [16] F. Ramthansanga¹, L. Tochwang², B. Saritha³, L. Sailo⁴, Degradation of Pesticide from Aqueous Solution Using Photocatalytic Composite, *Int. J. Sci. Res.* 8 (2018) 569–575. <https://doi.org/10.21275/ART20194215>.
- [17] C. Zhang, M. Qiu, J. Wang, Y. Liu, Recent Advances in Nanoparticle-Based Optical Sensors for Detection of Pesticide Residues in Soil, *Biosensors*. 13 (2023) 1–30. <https://doi.org/10.3390/bios13040415>.
- [18] A. El-Hosainy, M. Zahran, S. Sabry, Provided for non-commercial research and education use . Not for reproduction , distribution or commercial use . Hepatoprotective Agents in Rats, *Egypt. Acad. J. Biol. Sci.* 9 (2017) 31–54.
- [19] P.G. Krishna, P. Chandra Mishra, M.M. Naika, M. Gadewar, P.P. Ananthaswamy, S. Rao, S.R. Boselin Prabhu, K.V. Yatish, H.G. Nagendra, M. Moustafa, M. Al-Shehri, S.K. Jha, B. Lal, S.M. Stephen Santhakumari, Photocatalytic Activity Induced by Metal Nanoparticles Synthesized by Sustainable Approaches: A Comprehensive Review, *Front. Chem.* 10 (2022) 1–21. <https://doi.org/10.3389/fchem.2022.917831>.
- [20] B. Deka, A. Babu, C. Baruah, M. Barthakur, Nanopesticides: A Systematic Review of Their Prospects With Special Reference to Tea Pest Management, *Front. Nutr.* 8 (2021). <https://doi.org/10.3389/fnut.2021.686131>.
- [21] P. Goel, M. Arora, Mechanism of visible-light-driven photocatalytic degradation of endosulfan pesticide by gold nanoparticles, *Environ. Res. Commun.* 2 (2020). <https://doi.org/10.1088/2515-7620/aba440>.
- [22] P.A. U, R.K. V, Nanopesticides: Its Scope and Utility in Pest Management, *Indian Farmer*. 6 (2019) 17–21.
- [23] C.P. Castañeda Martínez, I.A. Alvarado Ortega, H.A. Rojas Sarmiento, F.J. Tzompantzi Morales, J.R. Gómez Romero, Photocatalytic degradation of the 2,4-dichlorophenoxyacetic acid herbicide using supported iridium materials, *Cienc. En Desarro.* 12 (2021) 125–134. <https://doi.org/10.19053/01217488.v12.n1.2021.12447>.
- [24] S. Kanchana, R. Vijayalakshmi, Photocatalytic degradation of organic dyes by peg and pvp capped, ni and ag nanoparticles in the presence of nabh₄ in aqueous medium, *J. Water Environ. Nanotechnol.* 5 (2020) 294–306. <https://doi.org/10.22090/jwent.2020.04.001>.
- [25] S.H. Khan, B. Pathak, Zinc oxide based photocatalytic degradation of persistent pesticides: A comprehensive review, *Environ. Nanotechnology, Monit. Manag.* 13 (2020) 100290. <https://doi.org/10.1016/j.enmm.2020.100290>.
- [26] R. Kumar, S. Mukherji, Feasibility of photocatalytic degradation of an organophosphorus pesticide using

- graphene oxide-TiO₂ nanocomposite, *J. Indian Chem. Soc.* 95 (2018) 217–222.
- [27] R.J. Chadwick, *Co Re Co Re, Europe.* (2007) 2–5.
- [28] Photocatalytic degradation of aquatic organic contaminants using Zn- and Zr-based metalorganic frameworks: ZIF-8 and UiO-66, *Turkish J. Chem.* 46 (2022) 1358–1375. F.D. Alik, B. Erdoan, E. Yilmaz, G. Saygi, and F. Akiciolu–Zkan. <https://doi.org/10.55730/1300-0527.3444>.
- [29] K. Liu, X. Zhou, L. Bai, L. Pan, L. Hu, Y. Zhan, Z. Zhang, X. Liu, and Chinese cabbage (*Brassica chinensis*) residues of profenofos and triazophos were photocatalytically degraded using ce-doped TiO₂, according to *Catalysts.* 9 (2019). <https://doi.org/10.3390/catal9030294>.
- [30] Recent techniques for removal and degradation of hazardous and persistent organochlorine pesticides utilizing nanoparticles: A review, M. Rani, U. Shanker, and V. Jassal, 208–222 in *J. Environ. Manage.* 190 (2017). <https://doi.org/10.1016/j.jenvman.2016.12.068>.
- [31] Modeling photocatalytic degradation of diazinon from aqueous solutions and effluent toxicity risk assessment using *Escherichia coli* LMG 15862 were published in *AMB Express.* 8 (2018) by A. Toolabi, M. Malakootian, M.T. Ghaneian, A. Esrafil, M.H. Ehrampoush, M. AskarShahi, and M. Tabatabaei. <https://doi.org/10.1186/s13568-018-0589-0>.
- [32] Conventional agrochemicals towards nano-biopesticides: an overview on recent achievements, *Chem. Biol. Technol. Agric.* 9 (2022) 1-19, DOI: 10.1186/s40538-021-00281-0. D. Abdollahdokht, Y. Gao, S. Faramarz, A. Poustforoosh, M. Abbasi, G. Asadikaram, and M.
- [33] N.S. Alkayal, M.A. Hussein, Photocatalytic Degradation of Atrazine under Visible Light Using Novel Ag@Mg₄Ta₂O₉ Nanocomposites, *Sci. Rep.* 9 (2019) 1–10. <https://doi.org/10.1038/s41598-019-43915-y>.
- [34] J.C. Nnaji, J.F. Amaku, O.K. Amadi, S.I. Nwadinobi, Evaluation and remediation protocol of selected organochlorine pesticides and heavy metals in industrial wastewater using nanoparticles (NPs) in Nigeria, *Sci. Rep.* 13 (2023) 1–14. <https://doi.org/10.1038/s41598-023-28761-3>.
- [35] U.A. Bukar, S. Sayeed, S. Fatimah, A. Razak, Corresponding Author : Pr ep t n ot pe er re v Pr ep rin t n ot pe er v ed, (n.d.).
- [36] H.H. Shanaah, E.F.H. Alzaimoor, S. Rashdan, A.A. Abdalhafith, A.H. Kamel, Photocatalytic Degradation and Adsorptive Removal of Emerging Organic Pesticides Using Metal Oxide and Their Composites: Recent Trends and Future Perspectives, *Sustain.* 15 (2023). <https://doi.org/10.3390/su15097336>.

