Photocatalytic Degradation of Deltamethrin in Drinking Water Under Visible Light by Using Zno and Tio_2

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The use of deltamethrin is increasing due to its high demand in agriculture. However, it is toxic to both surface and groundwater. Agriculture plays a crucial role in the economy of any major nation. This study aims to enhance pesticide degradation by using specially designed catalysts optimized for visible light exposure. The key innovation lies in the customized catalyst design, which improves photocatalytic efficiency while offering a cost-effective and environmentally friendly approach. Various factors affecting degradation, including adsorbent quantity, pH, contact time, and initial concentration, were analyzed. The reactor consists of a 6-watt (380 nm) visible light lamp and a stirrer to ensure uniform mixing of the sample. Photocatalysts ZnO and TiO_2, in concentrations ranging from 0.1 to 3.0 g/L, were used to generate oxidizing agents. Under visible light, the impact of these factors on the degradation of different pesticide solutions was examined. The optimal doses were found to be 1.5 g/L for ZnO and 0.1 g/L for TiO_2. ZnO achieved a degradation rate of 96.3%, while TiO_2 slightly outperformed it with a rate of 96.34%. The study also investigated the effect of pH variations on deltamethrin degradation, revealing stronger degradation in alkaline conditions. Additionally, TiO_2 effectively reduced the COD value, demonstrating its superior efficiency in pesticide breakdown.

Keyword: Deltamethrin, Photo catalytic degradation, ZnO, TiO2, Oxidizing agents.

Introduction:

A significant portion of the economy depends on agricultural production. Due to the increasing demand for agricultural products, the use of pesticides has risen significantly. Agricultural zones are designated areas where occupation, enterprise, and lifestyles are interconnected. The agricultural sector is a crucial component of any country's economy, contributing approximately 23.4% to the global economy. The primary focus of agricultural zones is to ensure food security for the population and enhance crop yield. Pakistan's agricultural sector contributes 21% to the country's GDP, with an annual growth rate of 2.7%. According to the World Bank (World Development Indicator), the agricultural sector has added approximately 22.64% to Pakistan's Gross Domestic Product. Sustainable agriculture is a rapidly growing field aimed at producing food and energy in an environmentally friendly manner to support both current and future generations. It addresses pressing issues such as climate change, rising fuel prices, hunger, poverty, increasing food demand, pest control, soil degradation, erosion, biodiversity loss, and water contamination.

Modern agriculture heavily relies on chemical treatments, including pesticides and fertilizers [1]. There is no denying that agricultural production in the 20th century improved and stabilized primarily due to the control of harmful weeds, pests, and insects, alongside an adequate supply of essential plant nutrients through chemical means. Pesticides are the second leading contributor to aquatic pollution, with a significant increase in contamination of drinking water sources [2]. Various pesticides, differing in chemical composition and effectiveness, are widely used worldwide, raising concerns about their adverse effects on human health and the environment. Pesticides consist of both organic and inorganic compounds and are applied to crops to eliminate harmful weeds and pests such as moths and insects that feed on crops. These chemicals are complex, with some parent compounds being less toxic than their breakdown products [3]. However, they pose a threat to both surface and groundwater. Pesticides are identified as the second leading cause of water pollution (WHO Class II), particularly contaminating drinking water [4].

Deltamethrin, a widely used pesticide, has been found to adversely affect fish by disrupting their nervous system, blocking sodium channels, and inhibiting key enzymes such as acetylcholinesterase and gamma-aminobutyric acid. It also weakens their immune system and induces oxidative stress. Individuals with skin wounds should avoid using Deltamethrin in traditional forms such as sprays, soaps, spot-on applications, pour-on treatments, and shampoos, as excessive absorption through the skin can occur. According to EU standards, Deltamethrin concentrations should not exceed 0.1 ng/ml [2]. Pyrethroids, including Deltamethrin, are preferred over organophosphates and organochlorines due to their high potency, effectiveness in small doses, resistance to light-induced degradation, and minimal harm to birds and mammals [5]. Several chemical techniques have been developed for environmental remediation, including hybrid procedures, nanocrystalline materials, metal oxides, carbon nanotubes, ion exchange, graphene, ultrasound waves, photocatalysis, adsorption, bioremediation, and bio-purification [6]. Advances in water and wastewater treatment have incorporated various strategies to remove persistent organic contaminants from aqueous solutions. Effective methods include adsorption, coagulation/flocculation, membrane separation, electrochemical treatments, and reverse osmosis [7][8][9]. Adsorption processes utilize diverse materials, including waste substances, to remove pollutants such as dyes [10][11], lead (II) [12], chlorophenols [13], pesticides [14], zinc, and absorbed nickel [15]. However, most of these methods only transfer pollutants between phases, generating secondary waste without actual pollutant degradation.

Advanced oxidation processes (AOPs) operate by generating hydroxyl radicals (•OH) and have proven effective in breaking down various contaminants, including dyes [12], aromatic amines [16], and agrochemicals [17]. Pesticide degradation has been successfully achieved using

the Fenton reagent and both natural and artificial photo-irradiation methods, such as photo-Fenton systems [18][19], photocatalytic degradation [20][21], and photo-peroxidation.

Membrane separation, photocatalysis, and adsorption techniques are being tested using various materials. Researchers are striving to develop efficient, cost-effective, and environmentally friendly methods that offer rapid and high pollutant removal rates. These procedures utilize visible light directed at a semiconductor material, which acts as a catalyst to break down pesticides. Photocatalysis is an environmentally friendly alternative for degrading organic pollutants. It has been widely studied for the degradation of various materials, with zinc oxide (ZnO) and titanium dioxide (TiO2) being the most commonly used photocatalysts. Keiichi et al. demonstrated the photocatalytic degradation of azo dyes using TiO2 suspensions, revealing that diazo dyes degrade more slowly than mono azo dyes (Photocatalytic Degradation of Commercial Azo Dyes). Another study compared the photocatalytic efficiency of ZnO and Degussa P25 TiO2 for degrading azo dyes under solar irradiation (Solar Photocatalytic Degradation of Azo Dye). Similarly, studies have examined the effects of UV and solar light irradiation on diclofenac degradation using ZnO as a photocatalyst, showing higher degradation rates under UV light, particularly in acidic conditions (Degradation of Diclofenac Under Irradiation of UV Lamp and Solar Light Using ZnO Photocatalyst). Additional research has investigated the photocatalytic degradation of phenol (Photocatalytic Degradation of Phenol), nitrophenols (Heterogeneous Photocatalytic Degradation of Nitro Phenols), 17-β-estradiol (Photocatalytic Degradation of 17-β-Estradiol on Immobilized TiO2), methyl orange (Photocatalytic Degradation of Methyl Orange as a Model Compound), and methylene blue (Photocatalytic Degradation Pathway of Methylene Blue in Water).

Despite these advancements, challenges remain in photocatalytic degradation research, emphasizing the need for further studies. Current photocatalytic applications are limited by low visible light absorption, rapid charge recombination, and the low migration ability of photo-generated electrons and holes (An Overview of Photocatalytic Degradation: Photocatalysts, Mechanisms, and Development of Photocatalytic Membrane). To improve wastewater treatment efficiency, more research is needed to optimize conditions for degrading a broader range of organic pollutants.

The objective of this study is to evaluate the effectiveness of different photocatalysts in degrading Deltamethrin pesticides while also analyzing parameters such as contact time, initial pH concentration, adsorbent dosage, and COD value.

Material and Methods:

Objectives of the Study:

This study aims to optimize process parameters for efficient and eco-friendly pesticide removal, contributing to sustainable water purification methods. The specific objectives are:

- To evaluate the efficiency of ZnO and TiO_2 in degrading Deltamethrin under visible light conditions.
- To determine the optimal photocatalyst dosage, pH, and reaction time for maximum pesticide degradation.
- To compare the degradation efficiency of ZnO and TiO_2 at different pH levels and catalyst concentrations.
- To analyze the kinetics of photocatalytic degradation and validate the reaction mechanism using the Langmuir-Hinshelwood model.
- To assess the impact of photocatalysis on Chemical Oxygen Demand (COD) reduction as an indicator of water quality improvement.
- To investigate the reusability and stability of ZnO and TiO_2 catalysts over multiple degradation cycles.

Methodology:

Chemical Analysis and Materials:

High-purity laboratory-grade materials were selected for the experiment. Deltamethrin (97.8% pure) was procured from Jaffar Group of Companies, Lahore. ZnO nanoparticles, with a purity of over 93.5% and particle sizes ranging from 10 to 30 nm, were obtained from Global Chemical Co. Ltd. TiO_2 nanoparticles, with a purity exceeding 98.4% and particle sizes between 10 and 25 nm, were purchased from KRONOS (ISO 9001 certified).

A pH meter (model BASIC-20, UK) was used to measure pH levels. The photocatalytic reactor, designed for small-scale experiments, has a single inlet and outlet with an upper-side valve to prevent flooding. It is equipped with a 6V DC motor for efficient mixing and a 6W, 9-inch fluorescent tube emitting violet light (380 nm wavelength) for illumination. The reactor has a solution capacity of approximately one liter.

Acetonitrile (CHROMASOLV, 99.9% pure) was sourced from Honeywell Riedelde Haen for HPLC analysis. Gas chromatography vials (2 mL, black caps with hole spots) were obtained from Hadi Traders, Antalkali, Lahore. Nylon syringe filters (pore size 0.45 µm, diameter 13 mm, item code SFNY01304 5NA) were used. An ultrasonic cleaner (DSA-100-SK1-2.8 L) was employed for 10-minute sonication to mix water and acetonitrile solutions properly.

The HPLC system (Model SHIMADZU) was equipped with a UV detector and a C-18 column (4.6 × 250 mm). The mobile phase consisted of acetonitrile and purified water (25:75 v/v) with a flow rate of 1 mL/min. Deltamethrin samples were analyzed at a wavelength of 230 nm.

Experimental Procedure:

The photocatalytic activity of the catalysts was evaluated by degrading Deltamethrin in a small-scale reactor. A stock solution of Deltamethrin (1000 mg/L) was prepared by dissolving Lambda-cyhalothrin in pure water. From this stock, samples with varying concentrations (5, 15, 30, 40, and 50 mg/L) were placed in the reactor. Absorbent (0.1-3.0 g/L) was added to each solution at different pH levels (3 to 9).

To maintain temperature stability, water circulation was used to counteract the heat generated by the lamp. A 500 mL Deltamethrin solution mixed with the appropriate absorbent was left in the dark for different time intervals (5 minutes to 1 hour) to establish adsorption-desorption equilibrium. A tungsten lamp (Philips Lighting Co.) served as the visible light source, and each experiment was conducted with a 2-hour irradiation period. To minimize environmental effects, the experiment was carried out in a glass-covered, closed-box reactor. A hygrometer was used to monitor ambient humidity, and power readings were taken regularly to ensure consistent illumination.

Samples were collected from the reactor at 5, 15, 30, 45, and 60-minute intervals and centrifuged at 5000 rpm for 5 minutes. The ultrasonic cleaner (DSA-100-SK1-2.8 L) was used for 10-minute sonication to properly mix the water and acetonitrile solution. The HPLC injector tube was immersed in the mobile phase, and the system was connected and powered on. GC-HPLC was used to analyze Deltamethrin degradation. The system's LC software was pre-installed on a PC, where parameters such as retention time, temperature, wavelength, and injection volume were set. A 5 µL sample extract was injected into the column and eluted with the mobile phase (water: acetonitrile, 25:75 v/v) at a flow rate of 1.0 mL/min. An absorption wavelength of 230 nm was used to generate degradation curves. The obtained data was then used to calculate pesticide degradation percentages.

$$Percentage\ Degradtion\ = \left(\frac{C_0 - C}{C_0}\right) x\ 100$$

Denote "C0" = initial absorbance sample before degradation and "C" = absorbance sample of the Lambda-cyhalothrin after degradation solution at time "t."

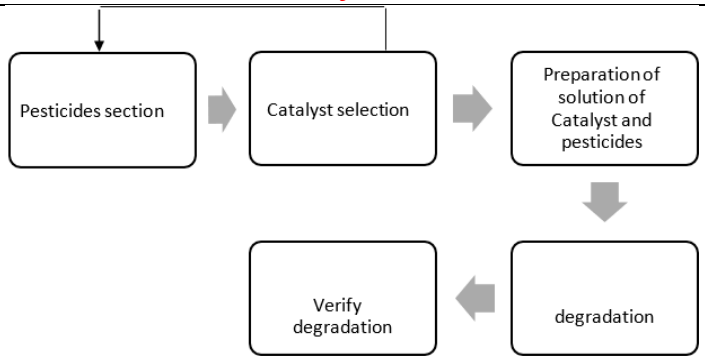

Figure 1. Flow Diagram of Methodology

Kinetic Study:

The study on the photodegradation of Deltamethrin included a kinetic analysis. The results showed that its degradation followed a pseudo-first-order kinetic pattern under photocatalytic conditions, aligning with theLangmuir–Hinshelwood model [22]. The developed model for Deltamethrin degradation was documented as follows.

$$\ln\frac{C_t}{C_0} = -k\ x\ t$$

Here, **C** represents the concentration of Deltamethrin pesticide (measured in parts per million, ppm), while **k** denotes the pseudo-first-order rate constant.

The coefficient of determination (**R^2**) is used to determine the reaction order and is calculated as follows:

$$R^2 = 1 - \frac{\sum(y_i - \hat{y}_i)^2}{\sum(y_i - \bar{y}_i)^2}$$

The coefficient of determination (R^2) was found to be 0.9955, demonstrating a strong correlation between the kinetic model and the photodegradation of Deltamethrin using ZnO/TiO_2 as the catalyst [23].

Table 1. Rate constant and R^2

Pollutant	Catalyst	Light Source	k (min^{-1})	R^2
Deltamethrin	TiO_2	Visible light	0.031	0.9955
Deltamethrin	ZnO	Visible light	0.026	0.9873

After that, get the HPLC findings for several samples. A calibration curve is drawn. After that, we use the formula to calculate the deterioration efficiency in percentage (percent).

$$Percentage\ Degradtion = \left(\frac{C_0 - C}{C_0}\right)$$

C_0 = concentration before Degradation C= concentration after Degradation

Results:

TiO_2 Degradation Efficiency at Different PH:

Figure 2 illustrates the effect of pH variation on the degradation efficiency of Deltamethrin insecticides across different samples. The graph highlights that S-1 exhibits the highest degradation, particularly in a basic medium, reaching a peak efficiency of 96.1%. When synthesized catalysts were used, a steady increase in degradation rates was observed across all pH levels. However, TiO_2 demonstrated the best performance in the basic pH range.

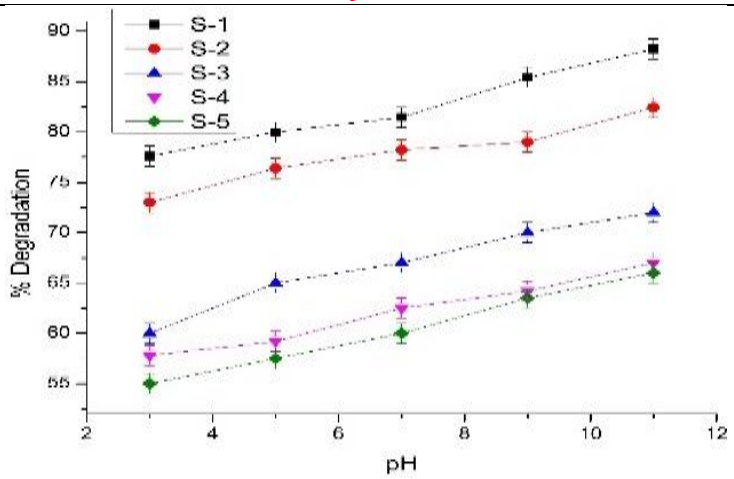

Figure 2. Efficiency of degradation at various pH of Deltamethrin Samples with TiO2

TiO_2 Catalyst: Different Dosing and Degradation Efficiency

Figure 3 shows that the highest degradation, around 96%, is achieved with catalyst dosage C-1 of S-1. This occurs because increasing the TiO_2 concentration eventually reduces the degradation rate as the catalyst dosage increases. Higher concentrations are more challenging to degrade, which is why the graph indicates minimal degradation for the S-5 sample.

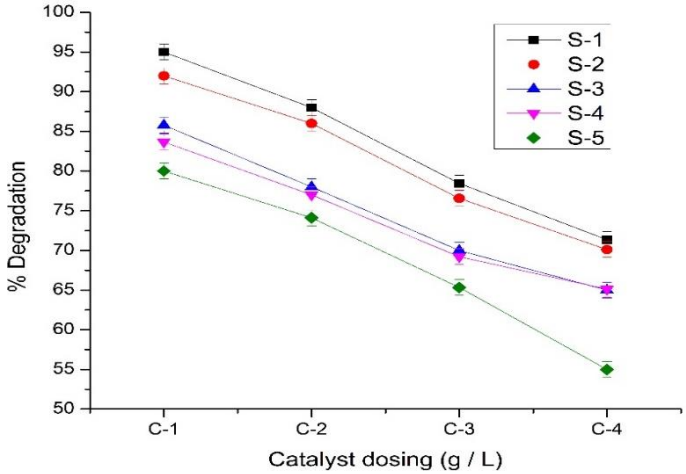

Figure 3. The efficiency of degradation of TiO2 of various samples

Efficiency of ZnO Degradation at Different pH Levels for Deltamethrin Samples:

The effect of pH variation on the degradation efficiency of different samples was analyzed. Figure 4 shows that the highest degradation for S-1 occurred at pH 9, compared to other pH levels. This pH test was conducted using C-2 ZnO.

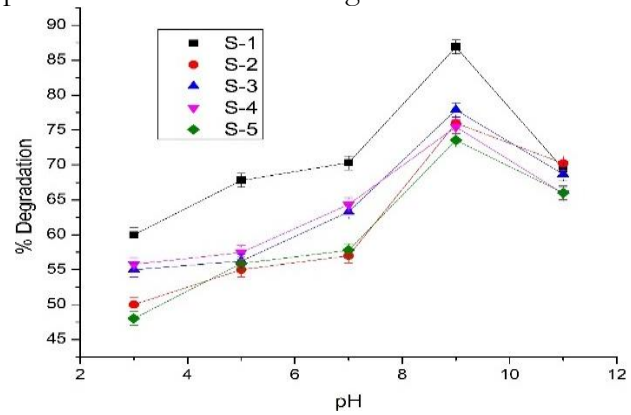

Figure 4. The efficiency degradation at various pH of the Deltamethrin Sample with ZnO

ZnO Catalyst Different Dosing Efficiency of Degradation:

The catalyst dosage C-3 of S-1 achieves the highest degradation rate, approximately 82%. As shown in Figure 5, increasing the concentration of ZnO positively impacts degradation efficiency. With ZnO C-1, the degradation rate is the slowest, around 62% for S-1. As the ZnO dosage increases, both the degradation rate and efficiency improve. However, the highest degradation value is observed at C-3 ZnO.

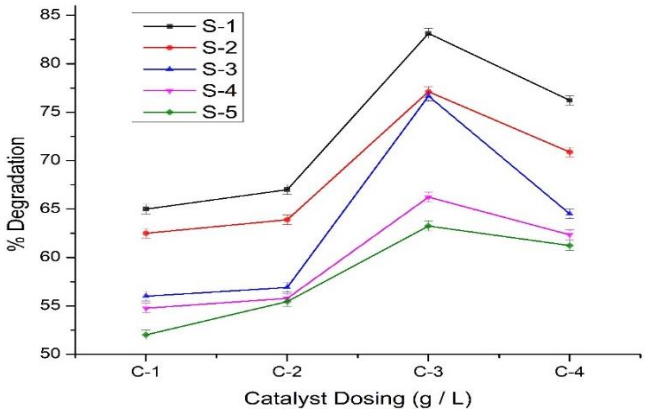

Figure 5. The efficiency of degradation of ZnO with various samples

Comparability of Efficiency of ZnO and TiO_2 in Degradation

Figure 6 illustrates the degradation efficiency of Deltamethrin insecticides using two different catalysts at various pH levels. When TiO_2 is used, the degradation rate is lower in acidic conditions but increases in basic conditions, reaching its highest efficiency at pH 11. In contrast, ZnO achieves its fastest degradation rate at pH 9.

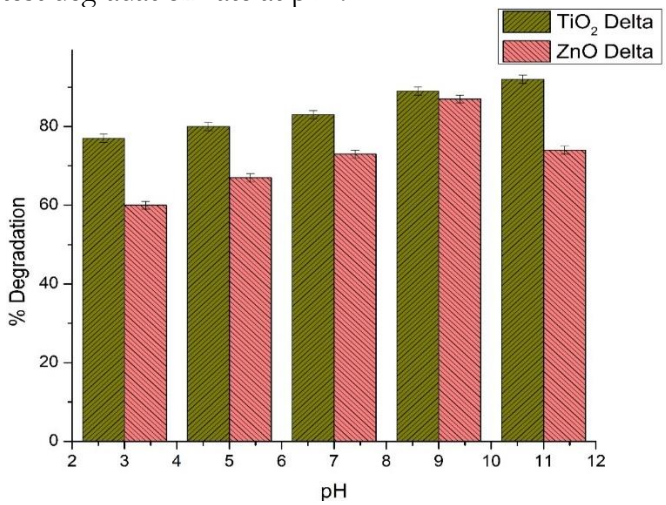

Figure 6. The efficiency of degradation at different pH of Deltamethrin Sample with ZnO and TiO2

Comparison of COD Values of ZnO and TiO2 W.R.T Time:

Figure 7 shows that the COD value decreases over time gradually. Maximum value of degradation of COD of Deltamethrin with TiO2.

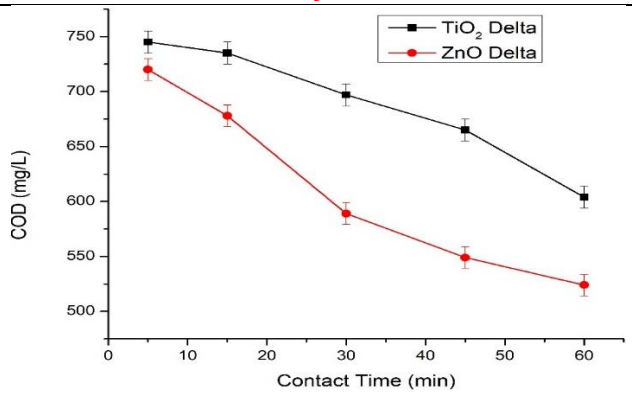

Figure 7. COD degradation concerning time

Discussion:

Reusability of ZnO/TiO2 Nano Catalyst:

The modification of ZnO and TiO_2 photocatalysts has been extensively studied to enhance their efficiency, stability, and practical use in wastewater treatment. Pure ZnO and TiO_2 have limitations, such as rapid charge recombination, limited absorption of visible light, and reduced effectiveness under real environmental conditions. To address these challenges, various modification techniques have been employed, including metal doping, non-metal doping, heterojunction formation, and surface functionalization. These modifications improve charge separation, enhance light absorption, and increase the degradation efficiency of persistent organic pollutants like pesticides.

Given the importance of cost-effectiveness in nanocatalyst usability, an in-depth analysis was conducted through multiple iterations. After each cycle, the used ZnO/TiO_2 photocatalyst was collected magnetically [24]. Metal doping is one of the most effective strategies to improve photocatalytic performance. Transition metals such as silver (Ag), copper (Cu), and iron oxide (Fe_3O_4) are incorporated into the ZnO or TiO_2 lattice. Ag-doped TiO_2 and ZnO enhance visible light absorption through surface plasmon resonance (SPR), enabling more efficient charge carrier generation. Similarly, Cu-doped TiO_2 increases electron transfer rates, reducing recombination losses and improving effectiveness under visible light. The addition of Fe_3O_4 to ZnO creates a magnetic photocatalyst, allowing easy recovery and reuse, thereby enhancing long-term sustainability. These modifications result in higher degradation rates, improved catalyst stability, and better selectivity for organic pollutants in water treatment applications.

Non-metal doping, where oxygen atoms in the ZnO or TiO_2 lattice are replaced with elements such as nitrogen (N), sulfur (S), and carbon (C), is another effective method for enhancing photocatalytic efficiency. N-doped TiO_2 introduces mid-gap energy states, shifting light absorption from UV to the visible spectrum, making it suitable for outdoor applications. Similarly, S-doped ZnO creates oxygen vacancies that enhance reactive oxygen species (ROS) generation, leading to more effective oxidative degradation of pesticides. Carbon doping forms graphitic carbon-TiO_2 hybrids, significantly increasing electron conductivity and photocatalytic efficiency. These modifications broaden the light absorption range of photocatalysts, making them more energy-efficient and effective under natural sunlight.

The formation of heterojunction and composite photocatalysts, such as ZnO-TiO_2, $BiVO_4$-TiO_2, and g-C_3N_4/ZnO, further improves charge separation and reaction kinetics. ZnO-TiO_2 composites benefit from ZnO's high charge mobility and TiO_2's strong oxidation ability, creating an efficient heterojunction that minimizes electron-hole recombination. $BiVO_4$-TiO_2 hybrids establish a Z-scheme charge transfer system, enhancing the degradation of complex organic pollutants. Additionally, coupling graphitic carbon nitride (g-C_3N_4) with ZnO stabilizes the catalyst structure, improving photocatalytic activity under sunlight. These

heterojunctions offer synergistic benefits, resulting in faster reaction rates, increased catalyst longevity, and better efficiency under real-world conditions.

To cleanse the photocatalyst of any residual compounds adsorbed onto its surface, multiple washes with water were performed [25]. Notably, even after seven cycles of photocatalytic activity, the degradation efficiency remained at approximately 82%. This result highlights the reusability potential of the ZnO/TiO_2 catalyst and its ability to suppress electron-hole recombination. Ultimately, the ternary magnetic photocatalyst demonstrated strong effectiveness in pesticide degradation [26][27].

The study focuses on improving pesticide decomposition by adjusting concentration, using catalysts, and modifying pH levels [28]. The findings indicate that optimizing these factors significantly enhances pesticide degradation efficiency. Additionally, the decrease in Chemical Oxygen Demand (COD) confirms the efficient mineralization of pesticide residues, suggesting a reduced environmental impact [29]. These results provide a foundation for developing more effective and environmentally friendly pesticide remediation techniques, supporting sustainable wastewater treatment and agricultural practices [24]. Further research is recommended to refine these methods and explore their broader applications [3].

Limitations of the Study:

- **Environmental Variability**: Factors such as temperature, humidity, and soil composition can affect pesticide degradation, making it challenging to generalize the data.
- **Limited Pesticide Scope**: The study may focus on specific pesticides, limiting their applicability to others with different chemical properties.
- **Analytical Restrictions**: The accuracy of degradation rate measurements may be affected by the sensitivity limits of detection techniques.
- **Time and Resource Constraints**: Long-term degradation studies require extended monitoring and substantial resources, which may not always be feasible.

Conclusion:

Under optimal conditions, TiO_2 and ZnO photocatalysts effectively degrade these pollutants. Deltamethrin degradation reached 96.34% for C-1 and 83.2% for C-3 using TiO_2 and ZnO, respectively, at varying adsorption concentrations. In terms of contact time, TiO_2's efficiency decreased after 10 minutes, while ZnO remained effective for up to 30 minutes, making ZnO more impactful in pollutant removal. The optimal degradation rate for TiO_2 with Deltamethrin was observed at pH 11, whereas ZnO exhibited the highest breakdown rate at pH 9. This technique can be applied in various chemical industries to degrade harmful pollutants. Compared to ZnO, TiO_2 nanoparticles under visible light irradiation demonstrated superior efficiency in decomposing Deltamethrin.

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