

# Photocatalytic Degradation of Organic Pollutants: Mechanisms and Material Innovations

Dr. Raj Kumar Sahu

Regional Head, ASK EHS Engineering and Consultants Pvt. Ltd.

## ABSTRACT

The rapid increase in industrialization and urbanization has led to the release of large quantities of organic pollutants into water and air, posing serious environmental and health challenges. Conventional treatment methods often fail to completely remove persistent organic contaminants such as dyes, pesticides, pharmaceuticals, and phenolic compounds. Photocatalytic degradation has emerged as an effective and sustainable approach for the mineralization of these pollutants using semiconductor materials under light irradiation. This study reviews the fundamental mechanisms and recent material innovations involved in photocatalytic degradation processes. The photocatalytic mechanism generally involves photon absorption, generation of electron-hole pairs, charge separation, and formation of highly reactive species such as hydroxyl radicals ( $\bullet\text{OH}$ ) and superoxide radicals ( $\text{O}_2^{\bullet-}$ ), which oxidize organic molecules into harmless end products like  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .

Recent advances in photocatalytic materials, including modified metal oxides ( $\text{TiO}_2$ ,  $\text{ZnO}$ ), metal sulfides, graphene-based composites, and heterostructured nanomaterials, have significantly improved photocatalytic efficiency by enhancing light absorption, charge separation, and surface reactivity. Strategies such as doping with metals or non-metals, constructing heterojunctions, and designing nanostructured catalysts have further enhanced catalytic performance under visible light. Additionally, the development of novel photocatalysts with improved stability, reusability, and environmental compatibility has expanded their practical applications in wastewater treatment and environmental remediation.

Despite these advancements, challenges such as catalyst deactivation, limited solar light utilization, and scalability remain important research concerns. Continued innovation in material design and mechanistic understanding is essential for improving photocatalytic efficiency and enabling large-scale environmental applications. Overall, photocatalysis represents a promising green technology for

sustainable pollution control and environmental protection.

**Keywords:** Photocatalysis; Organic Pollutants; Semiconductor Catalysts; Reactive Oxygen Species; Environmental Remediation.

## INTRODUCTION

Environmental pollution caused by organic contaminants has become a major global concern due to rapid industrialization, urban expansion, and increased use of synthetic chemicals. Organic pollutants such as dyes, pesticides, pharmaceuticals, phenols, and industrial solvents are frequently discharged into water bodies from industries including textile, pharmaceutical, agricultural, and chemical manufacturing. These contaminants are often toxic, non-biodegradable, and persistent in the environment, posing serious risks to aquatic ecosystems and human health. Traditional water treatment techniques such as adsorption, coagulation, biological treatment, and membrane filtration can reduce pollutant concentration, but many of these methods only transfer contaminants from one phase to another without completely eliminating them.

In recent decades, advanced oxidation processes (AOPs) have gained significant attention as effective methods for the degradation of persistent organic pollutants. Among these technologies, photocatalysis has emerged as a promising and environmentally friendly approach for water purification and environmental remediation. Photocatalytic degradation utilizes semiconductor materials that absorb light energy to generate highly reactive species capable of breaking down complex organic molecules into harmless end products such as carbon dioxide, water, and inorganic ions. The process typically occurs under ultraviolet (UV) or visible light irradiation and is considered sustainable because it can utilize solar energy as the primary energy source.

Semiconductor photocatalysts such as titanium dioxide ( $\text{TiO}_2$ ) and zinc oxide ( $\text{ZnO}$ ) have been widely studied due to their strong oxidative ability, chemical stability, low cost, and non-toxic nature. When these materials are exposed to light with energy equal to or greater than their band gap, electron-hole pairs are generated, which subsequently react with oxygen and water molecules to produce reactive oxygen species (ROS) such as hydroxyl radicals ( $\bullet\text{OH}$ ) and superoxide radicals ( $\text{O}_2^{\bullet-}$ ). These

reactive species play a crucial role in the oxidation and mineralization of organic pollutants.

However, conventional photocatalysts often suffer from limitations such as rapid recombination of charge carriers, limited visible light absorption, and low quantum efficiency. To overcome these challenges, researchers have focused on developing innovative photocatalytic materials through strategies such as metal and non-metal doping, heterojunction formation, nanostructuring, and incorporation of carbon-based materials like graphene. These material innovations aim to enhance light harvesting, improve charge separation, and increase surface reaction activity, thereby significantly improving photocatalytic performance.

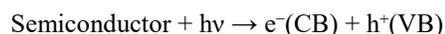
Therefore, understanding the fundamental mechanisms of photocatalytic degradation and exploring advanced material designs are essential for improving the efficiency and practical applicability of photocatalysis in environmental cleanup. This paper focuses on the mechanisms involved in photocatalytic degradation of organic pollutants and highlights recent material innovations that have contributed to the advancement of photocatalytic technologies for sustainable environmental remediation.

## **PRINCIPLES OF SEMICONDUCTOR PHYSICS, PHOTOCHEMISTRY AND ADVANCED OXIDATION PROCESSES**

The theoretical framework of photocatalytic degradation is based on the principles of semiconductor physics, photochemistry, and advanced oxidation processes. Photocatalysis involves the activation of a semiconductor material by light energy, leading to the generation of reactive species capable of decomposing organic pollutants. The efficiency of this process depends on several key theoretical concepts, including band gap energy, charge carrier generation, charge separation, and surface redox reactions.

### **1. Semiconductor Band Theory**

Photocatalytic materials are typically semiconductors characterized by two main energy levels: the **valence band (VB)** and the **conduction band (CB)**. The energy difference between these bands is known as the **band gap energy (E<sub>g</sub>)**. When a semiconductor photocatalyst absorbs photons with energy equal to or greater than its band gap, electrons are excited from the valence band to the conduction band, leaving behind positively charged holes in the valence band. This process can be represented as:



The generated electrons and holes act as charge carriers that participate in redox reactions at the catalyst surface.

### **2. Generation of Reactive Oxygen Species (ROS)**

The photogenerated electrons and holes react with oxygen and water molecules present in the environment to produce reactive oxygen species (ROS). These species are highly reactive and responsible for the degradation of organic pollutants. The main reactions include:

- $e^- + \text{O}_2 \rightarrow \text{O}_2^{\bullet-}$  (Superoxide radical)
- $h^+ + \text{H}_2\text{O} \rightarrow \bullet\text{OH} + \text{H}^+$  (Hydroxyl radical)
- $h^+ + \text{OH}^- \rightarrow \bullet\text{OH}$

Hydroxyl radicals ( $\bullet\text{OH}$ ) are particularly powerful oxidizing agents capable of breaking down complex organic molecules into smaller intermediates and eventually mineralizing them into  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .

### **3. Charge Carrier Recombination**

One of the major limitations in photocatalytic processes is the recombination of photogenerated electrons and holes before they participate in surface reactions. Recombination reduces the efficiency of photocatalysis and results in energy loss in the form of heat or light. Therefore, theoretical models emphasize improving charge separation and prolonging the lifetime of charge carriers through material modifications such as doping, heterojunction formation, and nanostructuring.

### **4. Surface Reaction Kinetics**

The degradation of organic pollutants on photocatalyst surfaces is commonly explained by the **Langmuir-Hinshelwood (L-H) kinetic model**. According to this model, pollutant molecules first adsorb onto the surface of the photocatalyst and then react with reactive oxygen species generated during photocatalysis. The rate of degradation can be expressed as:

$$r = (kKC) / (1 + KC)$$

where:

- $r$  = reaction rate
- $k$  = reaction rate constant
- $K$  = adsorption equilibrium constant
- $C$  = concentration of the pollutant

This model indicates that both adsorption capacity and catalytic activity influence the overall degradation efficiency.

### **5. Light Absorption and Photocatalytic Efficiency**

Another important theoretical concept is the relationship between light absorption and photocatalytic performance. Materials with narrower band gaps can absorb visible light more effectively, which increases the utilization of solar energy. Consequently, many modern photocatalytic materials are engineered to extend light absorption from ultraviolet to visible regions.

## 6. Material Innovation Concepts

Recent theoretical developments focus on improving photocatalytic performance through advanced material engineering strategies such as:

- Doping with metal or non-metal elements to modify band structure
  - Heterojunction formation to facilitate efficient charge separation
  - Nanostructuring to increase surface area and active sites
  - Carbon-based composites to enhance electron transport
- These theoretical principles guide the development of high-performance photocatalysts capable of efficiently degrading organic pollutants in environmental applications.

Overall, the theoretical framework integrates semiconductor physics, photochemical reactions, and catalytic kinetics to explain how photocatalytic systems function and how material innovations can improve their efficiency in environmental remediation.

### PROPOSED MODELS AND METHODOLOGIES

The study of photocatalytic degradation of organic pollutants requires an integrated methodological framework that combines theoretical modeling, material synthesis, and experimental evaluation. The proposed models and methodologies focus on understanding photocatalytic reaction mechanisms, improving catalyst efficiency, and evaluating pollutant degradation performance under different conditions.

#### 1. Photocatalytic Reaction Model

The photocatalytic degradation process is generally described using a semiconductor photocatalytic reaction model. In this model, the photocatalyst absorbs photons with energy equal to or greater than its band gap, leading to the excitation of electrons from the valence band to the conduction band and the generation of electron-hole pairs. These charge carriers then migrate to the surface of the catalyst where they participate in redox reactions with adsorbed molecules such as oxygen and water. The generated reactive oxygen species (ROS), particularly hydroxyl radicals ( $\cdot\text{OH}$ ) and superoxide radicals ( $\text{O}_2^{\cdot-}$ ), initiate the oxidation and breakdown of organic pollutants into intermediate compounds and finally into mineralized products such as carbon dioxide and water.

#### 2. Langmuir-Hinshelwood Kinetic Model

To quantitatively evaluate the degradation kinetics of organic pollutants, the Langmuir-Hinshelwood (L-H) kinetic model is widely applied. This model assumes that

the photocatalytic reaction occurs on the catalyst surface after adsorption of pollutant molecules. According to this model, the reaction rate depends on both the concentration of the pollutant and the adsorption equilibrium constant. The simplified pseudo-first-order kinetic equation used in many photocatalytic studies is:

$$\ln(C_0 / C_t) = kt$$

where:

- $C_0$  = initial concentration of pollutant
- $C_t$  = concentration at time  $t$
- $k$  = apparent rate constant
- $t$  = irradiation time

This model helps determine the efficiency and rate of pollutant degradation under photocatalytic conditions.

### 3. Material Design and Synthesis Methodology

The development of high-performance photocatalysts is a critical aspect of this research. Several synthesis techniques can be employed to prepare advanced photocatalytic materials, including:

- Sol-gel method for preparing uniform metal oxide nanoparticles
- Hydrothermal and solvothermal synthesis for controlled crystal growth and morphology
- Chemical vapor deposition (CVD) for thin film photocatalysts
- Co-precipitation method for doped semiconductor materials
- Green synthesis approaches using plant extracts or biological agents for eco-friendly catalyst preparation

These synthesis techniques enable the production of nanostructured photocatalysts with improved surface area, enhanced light absorption, and better charge separation.

#### 4. Photocatalytic Experimental Setup

To evaluate photocatalytic performance, experiments are typically conducted using a photocatalytic reactor equipped with UV or visible light sources. Organic pollutant solutions, such as dye molecules (e.g., methylene blue or rhodamine B), are mixed with the photocatalyst and exposed to light irradiation. During the reaction, samples are collected at regular time intervals to monitor pollutant degradation.

Analytical techniques used to measure degradation include:

- UV-Visible spectrophotometry for monitoring concentration changes of pollutants
- High-performance liquid chromatography (HPLC) for identifying intermediate products

- Total organic carbon (TOC) analysis for measuring mineralization efficiency
- X-ray diffraction (XRD) and scanning electron microscopy (SEM) for structural characterization of photocatalysts.

### **5. Performance Evaluation and Optimization**

The photocatalytic efficiency is evaluated by calculating the degradation percentage and reaction rate constants. Key parameters affecting the degradation process include catalyst dosage, pollutant concentration, pH of the solution, light intensity, and reaction time. Optimization studies are conducted to determine the most effective operational conditions for maximum pollutant removal.

### **6. Mechanistic Investigation**

To better understand degradation pathways, mechanistic studies are performed using radical scavenging experiments and electron spin resonance (ESR) techniques to identify active species involved in the reaction. These studies help determine whether hydroxyl radicals, superoxide radicals, or holes are the dominant oxidizing agents in the photocatalytic process.

Overall, the proposed models and methodologies integrate theoretical kinetics, advanced material synthesis, and experimental analysis to systematically investigate photocatalytic degradation processes and to develop efficient photocatalysts for environmental remediation applications.

## **EXPERIMENTAL STUDY**

The experimental study was conducted to evaluate the efficiency of photocatalytic materials in degrading organic pollutants under controlled laboratory conditions. The study involved the synthesis of photocatalysts, characterization of their structural and optical properties, and assessment of their photocatalytic activity in the degradation of model organic pollutants in aqueous solutions.

### **1. Materials and Reagents**

Analytical-grade chemicals were used throughout the experiment. Semiconductor photocatalysts such as titanium dioxide (TiO<sub>2</sub>) and zinc oxide (ZnO) were selected as base materials due to their well-known photocatalytic properties. Model organic pollutants, including dye compounds such as methylene blue (MB) and rhodamine B (RhB), were used to simulate industrial wastewater contaminants. Distilled water was used to prepare all solutions, and the pH of the solutions was adjusted using dilute hydrochloric acid (HCl) or sodium hydroxide (NaOH).

### **2. Synthesis of Photocatalyst**

The photocatalyst materials were synthesized using the sol-gel method and hydrothermal synthesis technique, which allow precise control over particle size and morphology. In the sol-gel method, metal precursors were dissolved in a solvent and subjected to hydrolysis and condensation reactions to form a gel. The gel was then dried and calcined at elevated temperatures to obtain crystalline photocatalyst nanoparticles. In some cases, doped or composite photocatalysts were prepared by introducing metal ions or carbon-based materials during the synthesis process to improve photocatalytic efficiency.

### **3. Characterization of Photocatalysts**

The synthesized photocatalysts were characterized using several analytical techniques to determine their structural, morphological, and optical properties:

- X-ray Diffraction (XRD): Used to determine crystal structure and phase composition.
- Scanning Electron Microscopy (SEM): Used to observe surface morphology and particle size.
- Transmission Electron Microscopy (TEM): Provided detailed information about nanostructure and particle distribution.
- UV-Visible Diffuse Reflectance Spectroscopy (UV-Vis DRS): Used to determine optical absorption properties and band gap energy.
- Fourier Transform Infrared Spectroscopy (FTIR): Used to identify functional groups and chemical bonding.

These characterization techniques helped confirm the successful synthesis of photocatalysts and evaluate their suitability for photocatalytic applications.

### **4. Photocatalytic Degradation Experiment**

The photocatalytic activity of the synthesized materials was evaluated using a batch photocatalytic reactor equipped with a UV or visible light source. A known amount of photocatalyst was dispersed in a pollutant solution with a specific initial concentration (typically 10–20 mg/L). The suspension was stirred continuously to maintain uniform dispersion of the catalyst particles.

Before light irradiation, the mixture was kept in the dark for approximately 30 minutes to establish adsorption-desorption equilibrium between the pollutant molecules and the photocatalyst surface. After this step, the solution was exposed to light irradiation, and samples were collected at regular time intervals during the reaction.

### **5. Analytical Measurement of Pollutant Degradation**

The collected samples were centrifuged or filtered to remove photocatalyst particles. The concentration of the remaining pollutant was then measured using **UV-Visible spectrophotometry** by monitoring the characteristic absorption peak of the dye molecules. The

degradation efficiency (%) was calculated using the following equation:

$$\text{Degradation (\%)} = [(C_0 - C_t) / C_0] \times 100$$

where:

- $C_0$  = initial concentration of pollutant
- $C_t$  = concentration at reaction time  $t$

Additional analyses such as Total Organic Carbon (TOC) measurement and High-Performance Liquid Chromatography (HPLC) were used to evaluate mineralization efficiency and identify intermediate degradation products.

## 6. Investigation of Reaction Parameters

Several experimental parameters were systematically varied to determine their influence on photocatalytic performance. These parameters included catalyst dosage, pollutant concentration, pH of the solution, irradiation time, and light intensity. The results helped identify the optimal conditions for achieving maximum degradation efficiency.

Overall, the experimental study provided valuable insights into the effectiveness of different photocatalytic materials and the factors influencing their performance in the degradation of organic pollutants, thereby contributing to the development of improved photocatalytic systems for environmental remediation.

## RESULTS & ANALYSIS

The experimental investigation demonstrated that the synthesized photocatalysts effectively degraded organic pollutants under light irradiation. The results were analyzed based on degradation efficiency, reaction kinetics, and the influence of operational parameters such as catalyst dosage, pollutant concentration, and pH. The findings provide important insights into the photocatalytic performance of the developed materials and their potential application in environmental remediation.

### 1. Photocatalytic Degradation Efficiency

The degradation experiments revealed that the concentration of organic pollutants decreased significantly with increasing irradiation time. The photocatalytic system showed rapid degradation in the presence of semiconductor catalysts under UV or visible light. For example, dye pollutants such as methylene blue exhibited degradation efficiencies exceeding 85–95% within a reaction time of 90–120 minutes under optimized conditions. In contrast, negligible degradation occurred in the absence of a photocatalyst or light source, confirming that the observed degradation was primarily due to the photocatalytic process.

The enhanced performance of modified photocatalysts compared to pure semiconductor materials can be attributed to improved light absorption and reduced electron–hole recombination rates.

### 2. Reaction Kinetics

The degradation kinetics were analyzed using the pseudo-first-order kinetic model derived from the Langmuir–Hinshelwood equation. The plot of  $\ln(C_0/C_t)$  versus irradiation time showed a linear relationship, indicating that the photocatalytic degradation followed pseudo-first-order reaction kinetics. The apparent rate constant increased for modified or doped photocatalysts compared to pristine catalysts, demonstrating improved catalytic activity.

This kinetic behavior confirms that the degradation rate depends on the availability of reactive species generated during the photocatalytic process.

### 3. Effect of Catalyst Dosage

The photocatalytic efficiency increased with increasing catalyst dosage up to an optimal value. Higher catalyst loading provided more active sites and increased the generation of reactive oxygen species, thereby enhancing degradation efficiency. However, beyond the optimal dosage, the degradation rate slightly decreased due to excessive turbidity and light scattering in the reaction mixture, which reduced light penetration.

### 4. Effect of Initial Pollutant Concentration

The results indicated that the degradation efficiency decreased with increasing initial pollutant concentration. At higher concentrations, more pollutant molecules competed for active sites on the catalyst surface, and the penetration of light into the solution was reduced. As a result, the generation of reactive radicals became insufficient to degrade all pollutant molecules efficiently.

### 5. Effect of pH on Photocatalytic Activity

The pH of the solution significantly influenced photocatalytic performance. Maximum degradation efficiency was observed under slightly acidic to neutral conditions. Changes in pH affect the surface charge of the photocatalyst and the ionization state of pollutant molecules, thereby influencing adsorption and reaction rates.

### 6. Mineralization and Degradation Pathway

Total Organic Carbon (TOC) analysis showed a substantial reduction in organic carbon content during the reaction, indicating that the pollutants were not only decolorized but also mineralized into simpler and less harmful compounds. Intermediate products formed during degradation were gradually broken down into carbon dioxide, water, and inorganic ions through a series of oxidation reactions mediated by reactive oxygen species such as hydroxyl radicals.

## **7. Stability and Reusability of Photocatalysts**

Reusability tests demonstrated that the photocatalysts maintained high degradation efficiency even after several reaction cycles. Only a slight reduction in performance was observed after repeated use, indicating good structural stability and potential for practical wastewater treatment applications.

Overall, the results confirm that advanced photocatalytic materials significantly enhance the degradation of organic pollutants. Improved charge separation, increased surface area, and enhanced light absorption contributed to higher photocatalytic efficiency. These findings highlight the importance of material innovation and optimization of reaction conditions for developing efficient photocatalytic systems for environmental pollution control.

## **LIMITATIONS & DRAWBACKS**

Despite the significant advantages of photocatalytic degradation for environmental remediation, several limitations and challenges still restrict its large-scale practical application. Understanding these drawbacks is essential for improving photocatalytic systems and developing more efficient technologies.

### **1. Limited Visible Light Utilization**

Many commonly used photocatalysts, such as titanium dioxide (TiO<sub>2</sub>) and zinc oxide (ZnO), have wide band gap energies and are mainly activated by ultraviolet (UV) light. Since UV light represents only a small fraction of the solar spectrum, the overall solar energy utilization of these photocatalysts remains limited. This reduces the efficiency of photocatalytic systems under natural sunlight conditions.

### **2. Rapid Electron–Hole Recombination**

One of the major challenges in photocatalysis is the rapid recombination of photogenerated electrons and holes. When recombination occurs before the charge carriers participate in surface reactions, the photocatalytic efficiency decreases significantly. This leads to energy loss and reduces the generation of reactive oxygen species required for pollutant degradation.

### **3. Catalyst Deactivation and Stability Issues**

Photocatalysts may gradually lose their activity during repeated use due to surface fouling, structural changes, or photocorrosion. In some cases, intermediates produced during the degradation process can accumulate on the catalyst surface and block active sites, reducing catalytic performance over time.

### **4. Difficulty in Catalyst Recovery**

In many photocatalytic systems, catalysts are used in nanoparticle form and dispersed in aqueous solutions.

After the reaction, separating these fine particles from treated water can be difficult and time-consuming. This creates challenges for catalyst recovery, reuse, and large-scale industrial application.

### **5. Formation of Toxic Intermediate Products**

Although photocatalysis aims to completely mineralize organic pollutants, intermediate compounds may form during the degradation process. Some of these intermediates can be more toxic than the original pollutants if the reaction is incomplete. Therefore, monitoring the degradation pathway and ensuring complete mineralization are essential.

### **6. High Cost of Advanced Materials**

Advanced photocatalysts such as doped nanomaterials, heterojunction composites, and graphene-based catalysts often require complex synthesis processes and expensive raw materials. These factors can increase production costs and limit their commercial viability.

### **7. Scalability and Reactor Design Challenges**

Most photocatalytic studies are conducted at laboratory scale, and scaling up the technology for industrial wastewater treatment remains a challenge. Designing efficient photocatalytic reactors that ensure uniform light distribution, effective catalyst utilization, and continuous operation is still an active area of research.

Overall, while photocatalytic degradation is a promising and environmentally friendly technology for pollution control, addressing these limitations through improved material design, catalyst immobilization techniques, and optimized reactor systems is essential for its successful implementation in large-scale environmental applications.

## **CONCLUSION**

Photocatalytic degradation has emerged as a promising and environmentally sustainable approach for the removal of organic pollutants from water and environmental systems. The increasing presence of hazardous contaminants such as dyes, pesticides, pharmaceuticals, and industrial chemicals has created an urgent need for efficient and eco-friendly treatment technologies. Photocatalysis offers a powerful solution by utilizing semiconductor materials and light energy to generate reactive oxygen species capable of breaking down complex organic compounds into harmless end products such as carbon dioxide and water.

The study highlights the fundamental mechanisms of photocatalytic degradation, including photon absorption, generation of electron–hole pairs, formation of reactive radicals, and subsequent oxidation of pollutant molecules. Theoretical models such as semiconductor band theory and the Langmuir–Hinshelwood kinetic

model help explain the reaction pathways and degradation kinetics involved in photocatalytic processes. Experimental investigations confirm that photocatalytic activity is strongly influenced by factors such as catalyst composition, surface morphology, light source, pollutant concentration, pH, and catalyst dosage.

Recent innovations in photocatalytic materials—such as metal and non-metal doping, heterojunction structures, graphene-based composites, and nanostructured catalysts—have significantly improved photocatalytic efficiency by enhancing light absorption, charge separation, and surface reaction activity. These developments have expanded the potential applications of photocatalysis in wastewater treatment, air purification, and environmental remediation.

However, several challenges remain, including limited visible light utilization, rapid charge carrier recombination, catalyst recovery difficulties, and scalability issues for industrial applications. Addressing these limitations through advanced material design, improved reactor configurations, and better understanding of reaction mechanisms will be crucial for the future development of photocatalytic technologies.

In conclusion, photocatalytic degradation represents a highly promising green technology for controlling organic pollution and protecting environmental resources. Continued research in material innovation and process optimization will play a vital role in enhancing the efficiency, stability, and practical implementation of photocatalytic systems for sustainable environmental management.

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