

Photocatalytic degradation properties

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Abstract: Photocatalysis, an innovative technology, holds promise for addressing industrial pollution issues across aqueous solutions, surfaces, and gaseous effluents. The efficiency of photodegradation is notably influenced by light intensity and duration, underscoring the importance of optimizing these parameters. Furthermore, temperature and pH have a significant impact on pollutant speciation, surface chemistry, and reaction kinetics; therefore, process optimization must consider these factors. Photocatalytic degradation is an effective method for treating water in environmental remediation, providing a flexible and eco-friendly way to eliminate organic contaminants from wastewater. Selectivity in photocatalytic degradation is achieved by a multidisciplinary approach that includes reaction optimization, catalyst design, and profound awareness of chemical processes. To create efficient and environmentally responsible methods for pollution removal and environmental remediation, researchers are working to improve these components.

Keywords: catalyst dosage; pollutant degradation; environmental remediation; catalytic activity; reaction kinetics; water treatment; catalyst optimization; sustainable chemistry; environmental impact assessment

Introduction

Photocatalytic degradation refers to a process in which a substance is broken down into smaller, less harmful compounds under the influence of light and a photocatalyst. This phenomenon is often employed in environmental and industrial applications for the removal or transformation of pollutants, contaminants, or other undesirable substances. Here are some key aspects of photocatalytic degradation properties:

1. Photocatalyst

The photocatalyst is a material that facilitates the degradation process when exposed to light. The novel oxidation process known as photocatalysis works by using sunlight to cause electron-hole pairs to form on a photocatalyst's surface. An enhancement in this field is represented by composite photocatalysts, which improve doping, coupling, and sensitization of individual photocatalysts like ZnO, AgO₂, and TiO₂. These developments could lead to more innovative uses of environmental therapy [1]. Titanium dioxide (TiO₂) and zinc oxide (ZnO) are commonly used photocatalysts due to their stability, efficiency, and non-toxic nature. They are suitable for photocatalytic applications due to their broad bandgap, especially when subjected to ultraviolet (UV) light [2].

2. Light source

Typically, photocatalytic reactions require ultraviolet light to activate the catalyst.

However, advancements in photocatalytic materials and technologies have expanded the range of light sources to include visible light, making the process more practical and applicable in various settings. Photocatalysts produce electron-hole pairs when exposed to UV light, which excites electrons from the valence band to the conduction band. The breakdown of organic contaminants or the creation of beneficial compounds can result from these charge carriers engaging in redox reactions with adsorbed species on the oxide's surface [3]. Electrons in the valence band may be induced to move to the conduction band, forming a hole in the valence band, when a material absorbs photons with energy equal to or greater than the bandgap energy. The generation of superoxide radicals ($O_2^{\bullet-}$) is triggered by interactions between electrons in the conduction band and oxygen molecules on the crystal surface [4]. Concurrently, water molecules on the crystal surface may interact with positively charged holes in the valence band, resulting in oxidation processes that generate hydroxyl radicals ($\cdot OH$) [5]. **Figure 1** shows the process of photocatalytic water splitting [6]. These reactive oxygen species (ROS), which break down dye molecules and other organic pollutants, are essential to the photooxidation process. Some instances of ROS include superoxide and hydroxyl radicals [7].

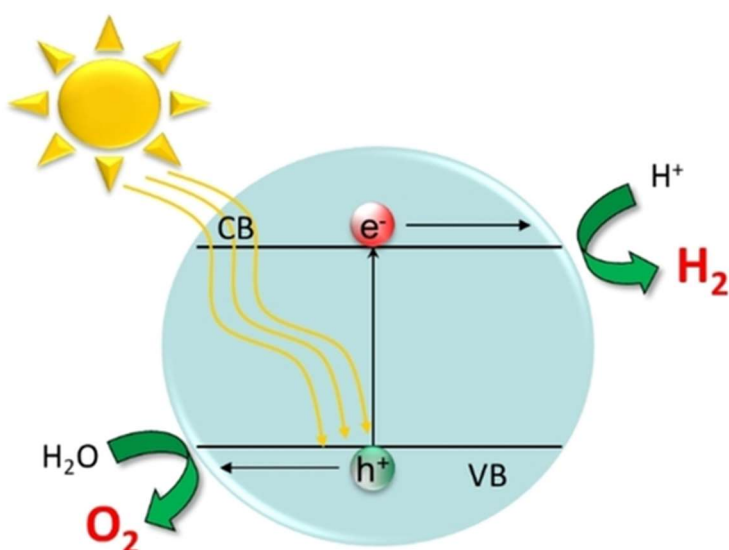


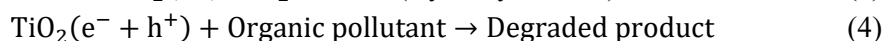
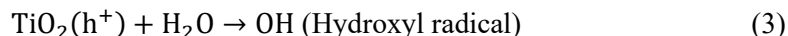
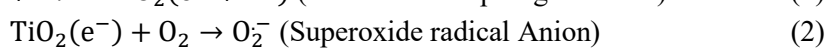
Figure 2. Process of Photocatalytic water splitting.

3. Substrate

The substance targeted for degradation is referred to as the substrate. Photocatalytic degradation is effective for various pollutants, including organic compounds, dyes, pesticides, and even some inorganic contaminants. TiO_2 [8], Ag, and ZnO [9] nanoparticles are the most commonly used substrates in the photocatalytic degradation of dyes in water and are effective due to their antimicrobial properties, UV radiation blocking capabilities, and photocatalytic characteristics [9]. These nanoparticles are commonly employed in the textile industry for various purposes such as self-cleaning, UV protection, and antibacterial properties. By harnessing their photocatalytic abilities, these nanoparticles facilitate the degradation of dyes present in water, thus aiding in water purification processes [1,2]. This multifunctional approach not only removes dyes but also provides additional benefits such as

microbial control and UV protection, making it a versatile solution for water treatment and environmental remediation [10]. Heterogeneous photocatalysis has undergone a significant change in the last ten years, especially in the application of titania in its anatase form [1,2]. The majority of the applications for this photocatalyst were moderate oxidation processes in gaseous or liquid organic phases. But in more recent times, there has been a shift towards using it for the complete oxidation and breakdown of different organic chemicals and contaminants, especially in situations with humid air or water [1,2,11].

Reaction Mechanism: The photocatalytic degradation process involves the generation of ROS on the surface of the photocatalyst when exposed to light. These ROS, such as hydroxyl radicals ($\bullet\text{OH}$), superoxide radicals ($\text{O}_2^{\bullet-}$), and others, then react with the substrate molecules, leading to their degradation into simpler and less harmful byproducts. The production of OH° radicals resulting from the presence of water has been ascribed to this alteration in photocatalytic behavior. This process's mechanism is based on the interaction of titania with water, which produces OH^\bullet radicals. These radicals are essential for promoting the complete oxidation and destruction of organic molecules and environmental contaminants. For instance, water molecules react with e^- -hole pairs on the TiO_2 surface and generate radicals. These highly reactive species are the cause of photocatalytic degradation of organic molecules [12] through Equations (1)–(4):



4. Factors influencing efficiency

4.1. Catalyst surface area

A larger surface area provides more active sites for the photocatalytic reaction. Surface area can be increased by different strategies like coating, treating plasma, heating or cooling, and changing the shapes (thin films, cylindrical, etc.). Using ionic liquids for surface modification offers dual advantages as both a supply and an agent for enhancing the photocatalytic properties of materials. Through the introduction of external elements or functional groups onto the surface of photocatalysts, such as nitrogen or sulfur in bismuth oxyhalides, additional active sites can be created, impacting the material's electrical properties positively.

When a semiconductor material is illuminated, positive charges (h^+) are produced that combine with OH^- anions to produce hydroxyl radicals. When water and oxygen are available, these radicals are crucial for the oxidation of organic materials [13]. Therefore, increasing the coating surface area helps to increase the photocatalytic activity of the coating. The increased specific surface area boosts the film's hydroxyl group concentration. When a semiconductor is exposed to light in the context of heterogeneous photocatalysis, electron-hole pairs (e^- and h^+) are produced. Hydroxyl radicals are produced when the negatively charged OH^- ions and positively charged holes (h^+) interact. The hydroxyl radicals generated at the photocatalyst's surface

function as oxidizing agents, which ultimately increase the efficiency of the photocatalytic activity [14]. Additionally, the incorporation of organic groups facilitates improved charge carrier separation and enhanced adsorption of contaminants, thereby increasing surface area and photocatalytic efficiency. This surface modification process aims to capture photogenerated electrons, thus inhibiting the recombination of electron-hole pairs generated during photoinduction. Ultimately, the utilization of ionic liquids as a means of surface modification presents a versatile approach to optimize photocatalytic performance, leveraging their unique properties to enhance material functionality and effectiveness in environmental remediation and other applications [15].

4.2. Light intensity and duration

The duration and intensity of light are important factors in photodegradation, especially in photocatalysis, where light is utilized to start chemical reactions. Higher light intensity and longer exposure times generally enhance the degradation process. Through photocatalysis, a substance is activated by light, speeding up chemical reactions without permanently altering the catalyst's chemical composition. In contrast, conventional thermal catalysts require heat to activate them. The activation mode is the primary difference: photosensitive catalysts are activated by light, whereas thermal catalysts are activated by heat [16]. The rate of photodegradation is directly impacted by the light source intensity. Since more photons are available to activate the photocatalyst and produce reactive species, higher light intensities usually lead to faster degradation rates. Beyond a certain optimal intensity, nevertheless, additional increases might not appreciably speed up the rate of degradation. The optimal intensity varies based on the target pollutant and the particular photocatalyst. Another important consideration is the period spent in the light. Extended exposure periods typically result in higher deterioration rates because the photocatalyst absorbs more photons over time, producing a greater number of reactive species. Like light intensity, there might be an ideal time frame, though, after which the rate of degradation plateaus or increases just slightly.

Reaction kinetics principles lead to the link between light intensity, duration, and photodegradation rate. First-order kinetics, which states that the rate of reaction is proportional to the concentration of the pollutant and the concentration of the active species produced by the photocatalyst, is typically followed by the photodegradation process. The concentration of these active species is influenced by both the length and intensity of the light, which affects the overall response rate. Although photodegradation rates can be increased by longer exposure times and stronger light, there are realistic concerns about cost and energy efficiency. In large-scale applications, it might not be practical or cost-effective to use extremely high-intensity light sources or extended exposure times. To attain the intended degradation rate while consuming the least amount of energy, light intensity and duration must be optimized.

4.3. pH and temperature

The pH of the solution and the temperature can affect the rate of photocatalytic degradation. Advanced oxidation processes, or AOPs, are finding a broader

application in environmental applications such as wastewater cleaning. These reactions are based on oxidation by reactive species and are usually catalyzed by photocatalysts like ZnO, TiO₂, CdS, Co₃O₄, or WO₃. These semiconductor photocatalysts undergo photoexcitation when they come into contact with an intense light source and an oxidizing agent such as air or oxygen, which produces reactive species [17]. The organic contaminants in the wastewater are then efficiently oxidized by these reactive species, leading to their elimination. The semiconductor used, the pH of the solution, and the light source intensity are some of the variables that affect the process efficiency [18]. The adsorption and interaction between the target pollutants and the photocatalyst are influenced by pH, which also changes their surface charges. The ideal pH range for many photocatalytic processes is one in which the photocatalyst surface charge and chemical makeup are most advantageous to the degradation process. Reduced efficiency may result from pH deviation because of variations in surface charge, surface chemistry, or pollutant speciation. The stability and solubility of the photocatalyst, which in turn impacts its duration and efficacy in the degradation process, can also be influenced by pH.

Temperature modifies the reaction kinetics, which affects how quickly photodegradation processes occur. Since more energy is available to activate surface reactions at higher temperatures, reactions often proceed more quickly. Nevertheless, overly high temperatures may cause the photocatalyst and the intended pollutants to thermally degrade, which would reduce the process' overall effectiveness. The ideal temperature range is frequently found through experimentation and can change based on the particular photocatalyst and contaminants present. Reaction kinetics may also be affected by temperature changes in the physical characteristics of the reaction environment, such as the viscosity and diffusion rates of reactants and products.

4.4. Catalyst dosage and Pollutant degradation

Catalyst dosage plays a crucial role in pollutant degradation efficiency. Ongoing research and literature reviews indicate that an appropriate catalyst dosage can significantly enhance degradation rates, leading to more effective pollutant removal. the need to strike a balance between increased catalyst dosage and economic feasibility. Excessive dosages may not proportionally improve degradation rates and can lead to diminishing returns in terms of cost-effectiveness. Photocatalysis using nanoparticles (NPs) is a promising method for dye removal from water due to their exceptional and highly tunable surface properties compared to bulk materials. NPs offer a wider scope in catalytic processes thanks to their unique surface characteristics, and they have higher diffusion rates coupled with lower reinforcing capabilities, all of which collectively enhance their catalytic performance [8,9,19,20]. Like the potential of rGO-250 as a robust photocatalyst for dye degradation, highlighting its adaptability and efficiency in well-defined circumstances that require pH, dye concentration, catalyst dosage, and recyclability into consideration. These results facilitate the creation of effective and long-lasting methods for environmental remediation that make use of cutting-edge substances like catalysts based on graphene [21].

5. Challenges

5.1. Selectivity

Ensuring that the photocatalytic process selectively targets the desired pollutants without causing unintended side reactions. The method of utilizing photocatalysts and light energy to decompose organic pollutants in wastewater or other environmental contaminants is known as photocatalytic degradation. Selectivity, or the photocatalyst's capacity to preferentially target and break down particular contaminants while mostly unaffected by other chemicals, is a crucial component of this process. Because it maximizes the effectiveness of pollution removal while minimizing the formation of hazardous byproducts, selective photocatalytic degradation is desired. Selectivity is attained via several factors: catalyst choice, reaction conditions, targeted modification, light source, and controlled reaction pathways.

Different photocatalysts exhibit varying affinities for different types of pollutants. By selecting a suitable photocatalyst based on the nature of the contaminants, researchers can enhance selectivity. Parameters such as pH, temperature, and the presence of co-catalysts or electron donors can influence the selectivity of the photocatalytic process. Optimizing these conditions can help tailor the degradation process toward specific pollutants. Surface modification of photocatalysts with specific functional groups or nanoparticles can enhance their affinity towards certain pollutants, thus improving selectivity. The wavelength and intensity of the light source used for photoexcitation can also influence selectivity. Tuning the light source to match the absorption spectrum of the target pollutant or photocatalyst can enhance the efficiency of degradation. Understanding the reaction pathways involved in photocatalytic degradation allows researchers to design strategies that promote the selective degradation of target pollutants while minimizing the formation of unwanted byproducts.

5.2. Catalyst recyclability

Strategies for reusing and recycling the photocatalyst to improve the economic and environmental sustainability of the process. The potential of catalyst recyclability is one of the major benefits of photocatalytic degradation. When subjected to light and an oxidizing agent, photocatalytic degradation is the process of breaking down organic contaminants in wastewater using catalysts, usually semiconductors such as TiO₂ [22], ZnO [23], CdS, Co₃O₄, or WO₃. By absorbing photons, these catalysts create electron-hole pairs, which when combined with oxygen and water, produce extremely reactive species like hydroxyl radicals. These free radicals can oxidize and break down organic contaminants into innocuous byproducts like water and CO₂. The catalyst may frequently be recovered and utilized again after the degrading process, which lowers operating costs and minimizes waste. To extract the catalyst from the wastewater that has been treated, a variety of techniques, including centrifugation and filtration, can be used. Furthermore, methods such as catalyst immobilization onto support materials can improve recyclability by limiting catalyst loss in the process. Overall, the combination of photocatalytic degradation and catalyst recyclability offers a

promising approach for efficient and sustainable wastewater treatment, contributing to environmental protection and resource conservation.

5.3. Scale-up

Transitioning from laboratory-scale experiments to large-scale applications poses challenges in maintaining efficiency and cost-effectiveness. Many semiconductor materials have been investigated for photocatalytic water splitting since 1972. Their limited ability to absorb visible light has presented a significant obstacle, impeding their practicality for widespread use [24]. Significant progress has been achieved in the last few years in the identification and synthesis of semiconductor materials specifically designed for solar water splitting, especially in the visible light spectrum [25]. Scale-up in photocatalytic degradation involves transitioning laboratory-scale processes to larger industrial or municipal scales. This scaling-up process requires careful consideration of various factors to ensure efficient and effective operation:

Reactor Design: Designing reactors suitable for larger volumes while maintaining optimal contact between the photocatalyst and wastewater is crucial. Different reactor configurations, such as slurry reactors, fixed-bed reactors, or immobilized photocatalyst reactors, may be employed depending on the specific requirements.

Light Source: Ensuring adequate and uniform illumination across the entire reactor volume is essential. This may involve using powerful and efficient light sources, such as UV lamps or natural sunlight, along with appropriate light distribution mechanisms.

Catalyst Preparation: Developing scalable methods for preparing and immobilizing photocatalysts onto suitable supports or substrates is necessary. These methods should ensure consistent catalyst properties and performance at larger scales.

Mass Transfer: Optimizing the mass transfer of pollutants to the catalyst surface and products away from it is critical for efficient degradation. This may involve adjusting flow rates, agitation methods, or reactor geometries to minimize mass transfer limitations.

Operational Parameters: Identifying and optimizing operational parameters such as pH, temperature, catalyst loading, and residence time for larger-scale systems is essential to maximize degradation efficiency while minimizing operational costs.

Safety and Environmental Considerations: Ensuring safety protocols are in place for handling potentially hazardous materials and byproducts and assessing any potential environmental impacts of the scaled-up process.

Overall, successful scale-up of photocatalytic degradation processes requires interdisciplinary collaboration between scientists, engineers, and stakeholders to address technical, economic, and regulatory challenges while realizing the full potential of this environmentally friendly wastewater treatment technology.

Conflict of interest: The author declares no conflict of interest.

Abbreviations

TiO ₂	Titanium dioxide
ZnO	Zinc oxide
UV	Ultraviolet
O ₂ ^{•-}	Superoxide radicals
•OH	Hydroxyl radicals
ROS	Reactive oxygen species
CO ₂	Carbon dioxide
e ⁻	Electron
h ⁺	Hole
Ag	Silver
AOPs	Advanced oxidation processes
CdS	Cadmium sulfide
WO ₃	Tungsten oxide
Co ₃ O ₄	Cobalt oxide
H ₂ O	Water
rGO	Graphene oxide

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