

A Review on Photocatalysts for Water Pollutant Removal

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ABSTRACT

Photocatalytic water filtration technology has been developed as an effective and sustainable method for removing a variety of water contaminants, including organic pollutants, heavy metals, and emerging compounds. Recent research has focused on improving the effectiveness of photocatalysts, particularly through the development of doped forms of titanium dioxide (TiO₂), zinc oxide (ZnO), and nanocomposites, with the aim of enhancing light absorption, particularly in the visible spectrum. Furthermore, advances in photocatalytic reactor designs and hybrid systems that combine photocatalysis with conventional methods, such as adsorption and biological treatment, have significantly improved the efficiency of pollutant degradation. Despite these advances, the transition from laboratory-scale to industrial applications still faces several challenges, due to factors such as catalyst stability, light penetration efficiency, and economic feasibility. This study highlights current advances in photocatalyst development, reactor design, and hybrid treatment systems, while discussing key challenges and future research paths toward expanded water treatment applications.

Keywords: Photocatalysis, Advanced Oxidation Processes, Water Treatment, TiO₂, ZnO, Semiconductor Catalysts, Environmental Remediation.

1. Introduction

Water pollution remains one of the most significant environmental challenges globally, posing serious threats to ecosystems, human health, and water security [1].

It is a major environmental issue, with negative impacts that jeopardize public health, harm aquatic biodiversity, and threaten the sustainability of water resources. Conventional water treatment methods, such as coagulation, sedimentation, filtration, and activated carbon adsorption, often fail to effectively remove persistent organic pollutants, heavy metals, and emerging contaminants like pharmaceuticals and endocrine-disrupting compounds [2].

In light of these limitations, advanced oxidation processes (AOPs), particularly photocatalysis, have

garnered increasing interest as highly effective and sustainable alternatives. "Photocatalysis is a light-activated process that employs semiconductor materials to generate reactive oxygen species (ROS), such as hydroxyl radicals ($\bullet\text{OH}$) and superoxide ions ($\text{O}_2\bullet^-$), which decompose pollutants into harmless byproducts" [3]. Titanium dioxide (TiO_2) and zinc oxide (ZnO) are widely studied photocatalysts due to their chemical stability, non-toxicity, and excellent oxidizing capabilities. However, their thermal applications are often hindered by microelectronic technologies that combine bright light with ultraviolet (UV) radiation. To overcome these limitations, current research focuses on improving photocatalysts through techniques such as doping and surface functionalization, as well as the development of heterojunctions to enhance visible light activity and charge separation [4].

Simultaneously, innovations in photocatalytic reactor designs and the integration of photocatalysis with alternative treatment methods have significantly improved the efficiency of pollutant removal. Despite these advancements, ongoing challenges remain, particularly with regards to catalyst deactivation, recovery, and the scalability of reactor systems for industrial applications. "This study aims to provide a comprehensive analysis of the latest developments in photocatalytic water treatment, focusing on material innovations, advanced reactor designs, and hybrid system approaches, while identifying key challenges and future research directions"[5].

2. Photocatalytic Processes

Photocatalysis is a process in which light energy is used to drive redox reactions on the surfaces of semiconductor materials. The energy from light activates chemical reactions on the photocatalyst's surface. When photons with energies equal to or greater than the bandgap are absorbed by the semiconductor, electron-hole pairs are generated. These charge carriers participate in redox reactions with adsorbed molecules, leading to the breakdown of pollutants, the generation of hydrogen from water, and the conversion of carbon dioxide (CO_2) into valuable chemicals.

The advantages of photocatalysis—"such as its high efficiency, operation under mild conditions, and environmental compatibility"—make it a promising technology for sustainable chemistry, renewable energy production, and environmental purification".

2.1. Homogeneous Photocatalytic Process

In homogeneous photocatalysis, both the catalyst and the reactants exist in the same phase, which is typically either gas or liquid. A well-known example of this process is the photo-Fenton system, which commonly involves $\text{Fe}^{2+}/\text{H}_2\text{O}_2$. This system has gained considerable attention due to its ability to utilize sunlight as an energy source, avoiding the need for expensive artificial (UV light sources). The process is influenced by several factors, such as pH, UV intensity, and the concentration of hydrogen peroxide. One of the main challenges is the necessity of maintaining a low pH (typically between 2.8 and 3.5), as iron tends to precipitate at higher pH levels, requiring additional steps to remove iron compounds [6,7].

2.2. Heterogeneous Photocatalytic Process

In heterogeneous photocatalytic systems, the photocatalyst—typically a solid—is in a distinct phase from the reactants, which are usually in liquid form. Titanium dioxide (TiO_2) is one of the most extensively researched photocatalysts in heterogeneous systems, especially under UV light irradiation [8].

These systems are utilized in various applications, including water purification, hydrogen production, partial or complete oxidation of organic compounds, and removal of gaseous pollutants. Heterogeneous photocatalysis involves semiconductor materials that generate electron-hole pairs when exposed to light. The photocatalytic activity is governed by the bandgap, which represents the energy difference between the valence and conduction bands [9][55].

"When the energy of incident photons is equal to or greater than the bandgap, electrons are excited from the valence band to the conduction band within femtoseconds, resulting in the formation of holes". If these charge carriers do not recombine before reaching the catalyst surface, they can trigger redox reactions with adsorbed species[10].

Since the discovery of the photocatalytic properties of TiO_2 , considerable research has focused on enhancing heterogeneous photocatalytic processes. These reactions typically generate hydroxyl radicals ($\bullet\text{OH}$) and superoxide ions ($\text{O}_2\bullet^-$), which lead to the degradation of organic pollutants into CO_2 and H_2O [12]. Figure 1 illustrates the proposed mechanism for the photocatalytic degradation of organic dyes using semiconductor mesoporous silica nanoparticles (MSNs) under various light sources.

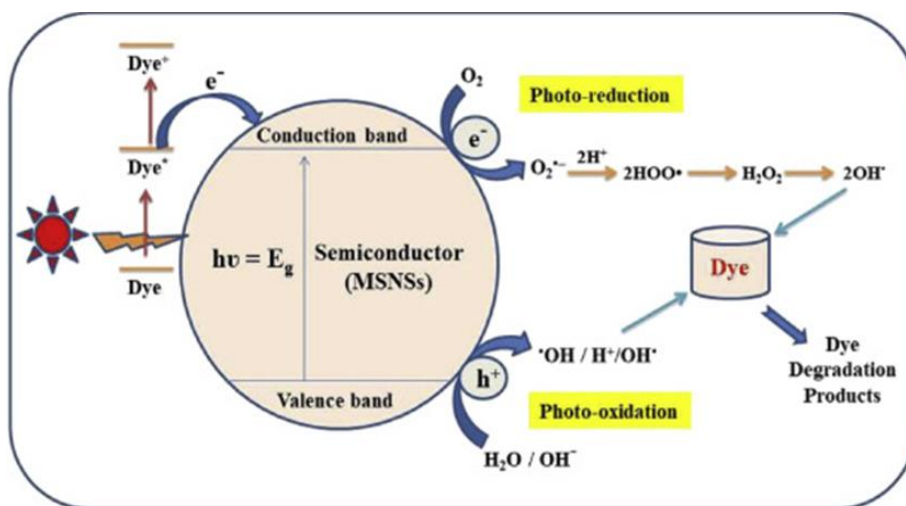


Figure 1. Schematic representation of the photocatalytic degradation process [6][12].

3. Photocatalyst Materials

Semiconductor-based photocatalysts are the core of photocatalysis research. The most studied materials include:

3.1. Titanium dioxide (TiO_2)

Titanium dioxide (TiO_2) has garnered significant attention as a photocatalyst owing to its remarkable chemical stability, low environmental toxicity, and cost-effectiveness. It crystallizes in three primary phases: anatase, rutile, and brookite, with the anatase phase exhibiting the most pronounced photocatalytic efficiency [11][13]. Possessing a bandgap of approximately 3.2 eV, TiO_2 can absorb ultraviolet (UV) radiation, generating electron-hole pairs that drive redox reactions on its surface. Nevertheless, this wide bandgap restricts its activity under visible light, prompting the need for structural modifications—such as elemental doping or hybridization with other materials—to enhance its photocatalytic performance in the visible spectrum[14].

3.2. Zinc oxide (ZnO)

Zinc oxide (ZnO) is a widely utilized semiconductor photocatalyst, characterized by a relatively wide bandgap of around 3.37 eV. Like titanium dioxide (TiO_2), ZnO is capable of generating electron-hole pairs under ultraviolet (UV) irradiation, thereby initiating various photocatalytic reactions[15]. Its notable photocatalytic efficiency, along with excellent biocompatibility and optical transparency, renders ZnO a promising candidate for diverse applications, including wastewater remediation, antimicrobial coatings, and biomedical technologies[16].

3.3. Tungsten trioxide (WO₃).

Tungsten oxide (WO₃), a transition metal oxide, possesses a relatively narrow bandgap of approximately (2.5) eV, which allows it to absorb light within the visible spectrum[17]. This property makes WO₃ a promising material for solar-driven photocatalytic applications. It has been successfully employed in various processes, including photocatalytic water splitting, degradation of organic contaminants, and solar energy harvesting[18][19].

3.4 Bismuth vanadate (BiVO₄).

Bismuth vanadate (BiVO₄) is a visible-light-responsive photocatalyst with a bandgap of approximately (2.4) eV. It demonstrates strong photochemical stability and notable quantum efficiency under visible irradiation, positioning it as a suitable material for solar-driven applications[20]. BiVO₄ has proven effective in facilitating water oxidation, the degradation of organic pollutants, and the photocatalytic reduction of carbon dioxide[21,22].

3.5. Metal–Organic Frameworks (MOFs)

Metal-organic frameworks (MOFs) are "a unique class of porous crystalline materials constructed through the coordination of metal ions or clusters with organic linkers". Their high surface area, tunable porosity, and structural versatility render them highly promising for photocatalytic applications[23]. Recent advancements have focused on integrating photoresponsive components into MOFs to enhance their photocatalytic performance in processes such as CO₂ reduction, hydrogen generation, and the breakdown of environmental pollutants [24].

To better illustrate the fundamental characteristics and comparative advantages of different photocatalytic materials, Table 1 summarizes their key properties, including bandgap energy, light absorption range, and notable applications in water treatment.

Table 1. A Comparative Analysis of Photocatalytic Properties: TiO₂, ZnO, WO₃, BiVO₄, and Metal-Organic Frameworks (MOFs).

Property	Titanium Dioxide (TiO ₂)	Zinc Oxide (ZnO)	Tungsten Trioxide (WO ₃)	Bismuth Vanadate (BiVO ₄)	Metal-Organic Frameworks (MOFs)
Band Gap (eV)	3.2 – 3.4	3.3	2.6	2.4 – 2.5	Varies (1.5 – 3.5)
Photocatalytic Efficiency	High (UV active)	High (UV active)	Moderate (Visible active)	High (Visible active)	Varies (depends on structure)
Stability	High	Moderate	High	Moderate	Varies
Environmental Impact	Low	Low	Low	Low	Can be more sustainable
Surface	Moderate	High	High	High	Very high

Area					
Cost	Low	Low	Moderate	High	High

4. Advanced Oxidation Processes (AOPs)

Advanced oxidation processes (AOPs) are a group of treatment techniques designed to generate hydroxyl radicals ($\bullet\text{OH}$), highly reactive species capable of non-selectively oxidizing a broad range of organic pollutants. These processes aim to break down contaminants in polluted water, ultimately producing water suitable for domestic use and human consumption[25]. AOPs have attracted considerable attention for their ability to effectively degrade persistent and complex pollutants, including antibiotics, pesticides, and pharmaceutical compounds[26].

The core mechanism of AOPs involves the production of reactive oxygen species—particularly hydroxyl radicals—known for their strong oxidative potential. These radicals can mineralize organic substances into less harmful forms or fully degrade them into carbon dioxide and water.

AOPs encompass a variety of techniques, such as homogeneous and heterogeneous photocatalysis, Fenton and Fenton-like reactions, ozonation, ultrasonic and microwave-assisted oxidation, gamma irradiation, electrochemical oxidation, and wet oxidation methods [27][54]. These methodologies are used in multiple applications, including:

- 4.1. Drinking water treatment plants: for removing micro-contaminants.
- 4.2. Wastewater treatment facilities: targeting biorecalcitrant and emerging pollutants.
- 4.3. Disinfection technologies: including photo-assisted disinfection techniques.

The success of AOPs lies in their ability to degrade complex organic molecules into simpler, less harmful compounds or even mineralize them to CO_2 and H_2O [28], as shown in Figure 2.

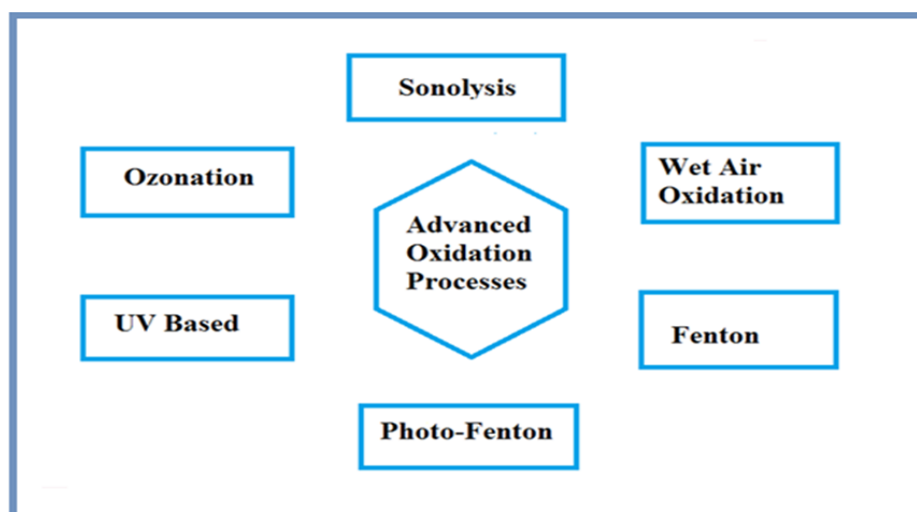


Figure 2. Classification of Advanced Oxidation Processes.

5. Applications in Pollutant Degradation

Photocatalysis has demonstrated considerable effectiveness in the degradation of various environmental contaminants. In the context of water treatment, it has been successfully employed to break down a wide range of pollutants, including organic dyes (e.g., methylene blue and rhodamine B), pharmaceutical residues, pesticides, herbicides, and persistent organic pollutants (POPs)[29].

Advanced photocatalysts—such as doped titanium dioxide (TiO₂) and novel semiconductor materials—exhibit promising capabilities in mineralizing complex organic molecules into benign byproducts. Beyond the degradation of organic compounds, photocatalysis also plays a significant role in the removal of heavy metals from water systems. Through photocatalytic reduction mechanisms, toxic metal ions can be transformed into less hazardous or more easily removable forms[30].

Since its emergence in the late 20th century, photocatalysis has transitioned from a research-focused methodology to a commercially applicable technology. Present-day implementations span across wastewater purification, air cleaning systems, self-cleaning coatings, solar energy harvesting, and photovoltaic devices. Continued advancements in the design and optimization of photocatalytic materials are critical for enhancing the efficiency, selectivity, and scalability of these emerging applications[31][32].

6. Advancements in Photocatalytic Materials

Recent developments in photocatalytic materials and modification techniques have focused on addressing the limitations of conventional photocatalysts. The performance of photocatalytic water treatment is largely determined by the physical and chemical properties of the photocatalysts employed [33]. Titanium dioxide (TiO₂) remains the most widely used material; however, its limited absorption in the visible light spectrum has prompted the creation of modified photocatalysts. Current approaches to enhancing TiO₂ performance include:

6.1. Elemental Modification

Introducing transition metals or nonmetals into the TiO₂ lattice to narrow the bandgap and enhance its absorption of visible light[34].

6.2. Nanostructuring

The fabrication of nanomaterials with improved surface properties and charge transport capabilities, which increases photocatalytic activity.

6.3. Composite Materials

The incorporation of TiO₂ into composite structures with other active materials, such as carbon-based or graphene-based composites, has been shown to improve photocatalytic efficiency and long-term stability. The modification of TiO₂ with transition metals has proven effective in boosting its performance under visible light irradiation[4]. Additionally, hybrid materials like β -Bi₂O₃/graphene composites have demonstrated enhanced efficacy in degrading organic pollutants when exposed to visible light[35][36].

7. Innovative Reactor Designs

New reactor designs aim to enhance light distribution and catalyst recovery, which are crucial for improving the degradation of pollutants in photocatalytic systems³⁶. Recent innovations have primarily focused on optimizing light scattering and material transport within reactors to increase the overall efficiency of photocatalytic processes [37]. A promising approach is the integration of photocatalysis with membrane technology.

Hybrid photocatalytic membrane systems combine the filtration efficiency of membranes with the oxidative power of photocatalysts, offering superior decontamination performance and increased

sustainability[6]. Another notable advancement involves the immobilization of photocatalysts on porous or structured substrates. This technique improves catalyst stability and facilitates its recovery and reuse, addressing key challenges associated with continuous-phase systems. These developments significantly enhance the processing capabilities of photocatalytic systems, pushing them closer to practical and scalable applications [38][39].

8. Challenges in Industrial Application

Several barriers hinder the large-scale implementation of photocatalysis, primarily related to achieving efficient light penetration and uniform distribution within large-scale reactors, as photocatalysis heavily depends on the interaction between photons and the catalyst. Moreover, variations in water flow dynamics and environmental conditions (e.g., temperature, turbidity) can significantly impact the system's performance in real-world applications [40][51][52].

Another critical challenge is the long-term stability of photocatalysts. Over time, many photocatalysts experience a decline in activity due to factors such as surface contamination, photocorrosion, or structural degradation. Developing durable materials that retain high catalytic activity under diverse operating conditions is essential for ensuring industrial viability [41][42].

Additionally, enhancing catalyst recovery and regeneration processes is vital to ensure both sustainability and economic feasibility in continuous-flow systems. This study focuses on addressing the engineering and material challenges required to transition photocatalysis from laboratory-scale experiments to large-scale industrial applications [50][43].

9. Comparative Analysis with Conventional Methods

In comparison to conventional water treatment technologies, photocatalysis offers a sustainable and environmentally friendly alternative by utilizing solar energy to degrade contaminants without generating harmful by-products [44,45]. Unlike traditional chemical treatments, which often result in the production of chemical sludge and secondary pollution, photocatalysis significantly reduces sludge formation, addressing one of the major environmental concerns associated with conventional methods [46][53].

Additionally, photocatalysis has the potential to lower long-term operational costs, particularly when sunlight is harnessed as an energy source. Unlike conventional treatments such as coagulation and leaching with activated carbon, which require continuous chemical inputs and high energy consumption, photocatalytic systems operate with minimal external energy requirements [45][47][58].

While conventional methods may offer quick initial removal of contaminants, they often fall short in dealing with persistent organic pollutants, pharmaceuticals, and personal care products. Photocatalysis, on the other hand, facilitates the thorough degradation and conversion of these complex molecules into harmless by-products without generating secondary waste [46-49]. Recent studies have further validated that photocatalysis is a more energy-efficient and effective alternative to biological treatments, particularly for emerging pollutants [48-51].

The continued advancement of photocatalyst materials and scalable reactor designs signals a shift toward the commercial viability of photocatalysis [52-55]. Furthermore, photocatalytic devices show significant potential for decentralized, off-grid water purification in remote areas, particularly when powered by solar energy [56-60]. In light of the comparison discussed above, Table 2 presents a summarized comparison between photocatalysis and conventional water treatment methods, highlighting key differences in energy source, by-products, pollutant removal efficiency, and environmental impact. This comparison emphasizes the potential superiority of photocatalysis as a

sustainable water treatment option[61].

Table 2. A Comparison Between Photocatalytic Water Treatment and Traditional Techniques Based on Operational and Environmental Factors.

Criteria	Photocatalysis	Conventional Methods
Energy Source	Light (UV/Visible)	Electricity or chemical reagents
By-products	Mostly harmless (CO ₂ , H ₂ O)	Potentially toxic (e.g., chlorinated by-products)
Target Pollutants	Organic dyes, pharmaceuticals, pesticides	General contaminants, not always specific
Operating Conditions	Mild (ambient temperature and pressure)	May require high pressure/temp or pH adjustment
Cost	Moderate to High (depends on catalyst)	Varies (can be low for basic filtration)
Environmental Impact	Eco-friendly if solar light is used	Can have negative impact (e.g., chemical use)
Efficiency for Recalcitrant Pollutants	High	Low to Moderate
Need for Chemicals	No or minimal	Often required
Sludge Production	Minimal	Can be significant
Scalability	Still under development for large scale	Well-established for large scale

10. Conclusion

Photocatalysis represents an environmentally friendly solution to the growing issue of water pollution. It has proven to be an effective and sustainable technology for water purification, demonstrating significant potential in laboratory-scale applications. However, several challenges remain before photocatalysis can be fully implemented on an industrial scale. Key obstacles include enhancing catalyst durability in real-world conditions, optimizing light distribution in large reactors, and improving catalyst recovery and reuse processes. Future research should prioritize the development of stable and cost-effective photocatalytic materials, the design of advanced reactor systems, and the integration of photocatalysis with other treatment technologies in hybrid systems.

Addressing these challenges will be crucial for advancing photocatalysis to a commercial and industrial level. With ongoing advancements in this field, photocatalysis is expected to play a vital role in future water treatment technologies, particularly as environmental concerns intensify and the demand for sustainable solutions increases.

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Ethical Consideration: The ethical committee approved the study at University of Babylon, Hilla Iraq.

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