ZnO/Au nanocomposites as efficient photocatalysts for pollutant degradation - A mini review

Nanocompuestos de ZnO/Au como fotocatalizadores eficientes para la degradación de contaminantes - Una mini revisión

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ABSTRACT

Nanotechnology has garnered significant attention across various fields due to the distinctive properties imparted by nanoscale dimensions. These properties diverge considerably from those observed in bulk materials, making nanomaterials highly attractive for research and application. This review highlights the synthesis and photocatalytic applications of zinc oxide-gold (ZnO/Au) nanocomposites for pollutant degradation. The formation of ZnO/Au heterojunctions enhances photocatalytic activity by facilitating effective charge separation between the components. Various synthesis methods for these nanocomposites are discussed, ranging from conventional chemical precipitation to eco-friendly green synthesis techniques. The photocatalytic efficacy of ZnO/Au nanocomposites is evaluated through the degradation of various pollutants, including dyes, pharmaceutical residues, and volatile organic compounds (VOCs), demonstrating their potential as efficient catalysts for environmental remediation.

Keywords: Zinc oxide, gold, nanocomposites, photocatalysis.

RESUMEN

Gracias a las propiedades distintivas que confieren las dimensiones a nanoescala, la nanotecnología ha acaparado una gran atención en diversos campos. Dichas propiedades difieren considerablemente de las observadas en los materiales a granel, por lo que los nanomateriales resultan muy atractivos para la investigación y la aplicación. En esta revisión se destacan la síntesis y las aplicaciones fotocatalíticas de nanocompuestos de óxido de zinc y oro (ZnO/Au) para la degradación de contaminantes. Mediante la formación de heterouniones ZnO/Au se mejora la actividad fotocatalítica al facilitar la separación efectiva de cargas entre los componentes. Varios métodos de síntesis de estos nanocompuestos se discuten, que van desde la precipitación química convencional a las técnicas de síntesis ecológicas. La eficiencia fotocatalítica de los nanocompuestos de ZnO/Au se evalúa mediante la degradación de diversos contaminantes, incluyendo tintes, residuos farmacéuticos y compuestos orgánicos volátiles (COVs), demostrando su potencial como catalizadores eficientes para la remediación medioambiental.

Palabras clave*: Óxido de zinc, oro, nanocomposites, fotocatálisis.*

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INTRODUCTION

Water pollution is a significant global issue affecting populations worldwide. Clean water is essential for human survival, yet the advent of the industrial revolution has made it nearly impossible to obtain uncontaminated water directly from natural sources. Industrial wastewater, often inadequately treated, is discharged into water bodies, leading to contamination and pollution. The textile industry is a major contributor to water pollution, with dyes being a primary pollutant. Statistics show that over 700,000 tons of organic dyes are produced yearly, with over 11% being lost in effluents during production and use [1]. Even minimal quantities of dyes in wastewater are highly noticeable and undesirable, leading to negative impacts on marine life and human health, as many dyes possess adverse properties such as high toxicity, potentially mutagenic, and carcinogenic [2]. When dyes are introduced into the water, their complex aromatic structures and synthetic origins make them stable and difficult to degrade [3]. Other emerging pollutants, such as pharmaceuticals products and by-products, are also hard to degrade due to their structure complexity.

In a standard wastewater treatment sequence, chemical coagulation typically follows biological treatment. While these methods effectively remove dyes, they are costly due to the need for specialized equipment and high energy consumption. Additionally, the process generates large amounts of by-products, leading to challenges in safe disposal [2]. Consequently, attention has shifted towards advanced oxidation processes (AOPs) for wastewater treatment. AOPs involve the generation and use of hydroxyl radicals, which are strong oxidants that degrade pollutants until they are mineralized into carbon dioxide and water [4]. Hydroxyl radicals can be produced via non-photochemical and photochemical methods, with photochemical processes attracting more attention for their cost-effectiveness. The primary techniques for generating hydroxyl radicals in photochemical processes include ultraviolet (UV) irradiation with hydrogen peroxide, using Fenton reagents with light, and photocatalysis in the presence of heterogeneous semiconductor. Of these, the latter method is the most favoured, attributed to its environmental safety and detoxification capabilities [5]. Photocatalysts commonly used in dye wastewater treatment include metal oxides such as titanium dioxide (TiO_2), iron oxide (Fe_3O_4), zinc oxide (ZnO), copper oxide (CuO), and metal sulphides such as cadmium sulphide (CdS).

In photocatalysis, ZnO has become a prominent material attributed to its advantageous properties, including a direct and wide band gap (3.37 eV), strong oxidation potential, and excellent performance in terms of photocatalysis. It also boasts superior electrical, mechanical, and optical properties comparable to TiO_2. Moreover, ZnO is more cost-effective to produce than TiO_2. Unfortunately, ZnO has several drawbacks, namely limited light absorption in the visible spectrum associated with its wide band gap and rapid recombination of photogenerated charges, resulting in low photocatalytic efficiency. Various strategies can address these problems, such as nanoscale ZnO production to increase surface area, doping with metals or non-metals, coupling with other semiconductors, and surface modification [6].

The properties of ZnO nanoparticles (ZnO NPs) can be tailored by adjusting and controlling the synthesis parameters such as calcination conditions, reaction temperature, pH and others. Two key phenomena influencing ZnO NP properties, primarily particle size, are Ostwald ripening and the quantum confinement effect. Ostwald ripening involves particle growth through the diffusion of smaller particles, a process accelerated by higher reaction temperatures [7]. The quantum confinement effect occurs due to the small particle size, leading to the confinement of electrons within the nanoparticles and resulting in properties distinct from those of the bulk material [8]. By controlling synthesis parameters, ZnO NPs with optimal characteristics for photocatalysis can be produced.

Coupling ZnO nanoparticles with other materials can further enhance their photocatalytic properties. This combination enhances catalyst characteristics such as light absorption, photoinduced electron-hole pair recombination reduction, and enhanced charge separation. Noble metals like silver and gold are particularly effective for coupling with ZnO. Incorporating these metals can extend light absorption into the visible range and improve charge carrier mobility, thereby boosting photocatalytic activity [9]. Hence, this review focuses on producing zinc oxide-gold nanocomposites and their utilization as photocatalysts for pollutant degradation.

PHOTOCATALYSIS MECHANISM

Photocatalysis has emerged as a promising alternative for dye removal from wastewater. It is a subset of advanced oxidation processes (AOPs), which have become popular due to their reported success in achieving nearly complete dye degradation [10]. AOPs degrade dyes by producing hydroxyl (·OH) and superoxide ($\cdot O_2^-$) radicals, which are a type of reactive oxygen species. These radicals can be generated through several methods, the four most common being photolysis, ozonation, the Fenton process, and photocatalysis. Photolysis and ozonation use hydrogen peroxide with ultraviolet light and ozone, respectively, to produce radical species. The Fenton process, widely used in wastewater treatment, involves hydrogen peroxide and ferrous ions as catalysts. Photocatalysis generates radical species using light-absorbing semiconductor materials [11]. Among these methods, photocatalysis is favoured due to its reliance on renewable solar energy and the avoidance of additional chemicals, making it a green and sustainable process.

Pollutant degradation via photocatalysis can occur through two primary pathways: indirect and direct mechanisms, with the former being the most prevalent. The indirect mechanism is generally employed for individual components like zinc oxide, beginning with photoexcitation. When the semiconductor is exposed to light, it becomes activated, and photon energy excites electrons, creating holes (h^+) and electrons (e^-) at the valance band (VB) and conduction band (CB), respectively. These are generated due to the movement of electrons from VB to CB. The electrons in the CB react with dissolved oxygen to form superoxide radicals ($\cdot O_2^-$). These radicals can directly degrade pollutants or react with water to produce hydroxyl radicals (·OH). In the VB, the holes (h^+) react with water or hydroxide ions to form additional ·OH radicals. These hydroxyl radicals are essential as they are the primary agents involved in dye degradation [11].

Moreover, the electrons and holes in the CB and VB can directly interact with pollutants to degrade them. Thus, the four species responsible for pollutant degradation are superoxide radicals ($\cdot O_2^-$), hydroxyl radicals (·OH), electrons (e^-), and holes (h^+). Figure 1 provides a schematic representation of the photocatalytic pollutant degradation process, and the reaction mechanism can be summarized as follows:

$$Photocatalyst + hv \longrightarrow h_{VB}^{+} + e_{CB}^{-}$$
$$h_{VB}^{+} + H_2O \longrightarrow H^+ + \cdot OH$$
$$e_{CB}^{-} + O_2 \longrightarrow \cdot O_2^-$$
$$\cdot O_2^- + H_2O \longrightarrow 2 \cdot OH$$
$$Pollutants + \cdot OH \longrightarrow CO_2 + H_2O + intermediate\ product$$
$$h_{VB}^{+} + dye \longrightarrow oxidation\ products$$
$$e_{CB}^{-} + dye \longrightarrow reduction\ products$$

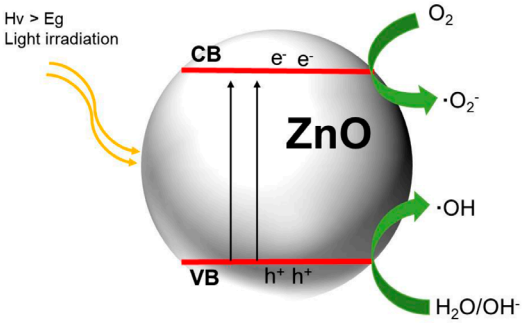

Figure 1. Schematic representation of photocatalytic degradation process of with ZnO [12].

As a singular component, ZnO exhibits excellent photocatalytic activity, but several drawbacks hinder its utilization. These include a high recombination rate of electron-hole pairs, which reduces its activity, and low efficiency in harnessing solar light due to its large band gap. A promising solution to these issues is the formation of nanocomposites with gold nanoparticles (Au NPs). Gold can act as a surface sensitizer due to its surface plasmon resonance and as an electron trap that reduces the recombination rate. These properties help improve the catalyst's ability to utilize a more comprehensive light spectrum range and enhance photocatalytic activity. The photocatalytic degradation of pollutants with ZnO-Au nanocomposites (NCs) can proceed through two pathways depending on the light source. Figure 2a illustrates the degradation process under UV irradiation. The process is similar to the previously explained mechanism, with some variations. After generating electron-hole pairs, electrons in the CB of ZnO can transfer to Au NPs due to the lower Fermi level (E_F) of Au NPs. This transfer prolongs charge carrier separation, leading to higher photocatalytic activity [15]. Under visible light irradiation, the small size of Au NPs allows them to behave similarly to semiconductor materials, where a gap is generated between the VB and CB. As a result, electron-hole pairs are generated on Au NPs. The electrons in the CB of Au NPs react with dissolved oxygen to produce superoxide anion radicals, and some of these electrons transfer to

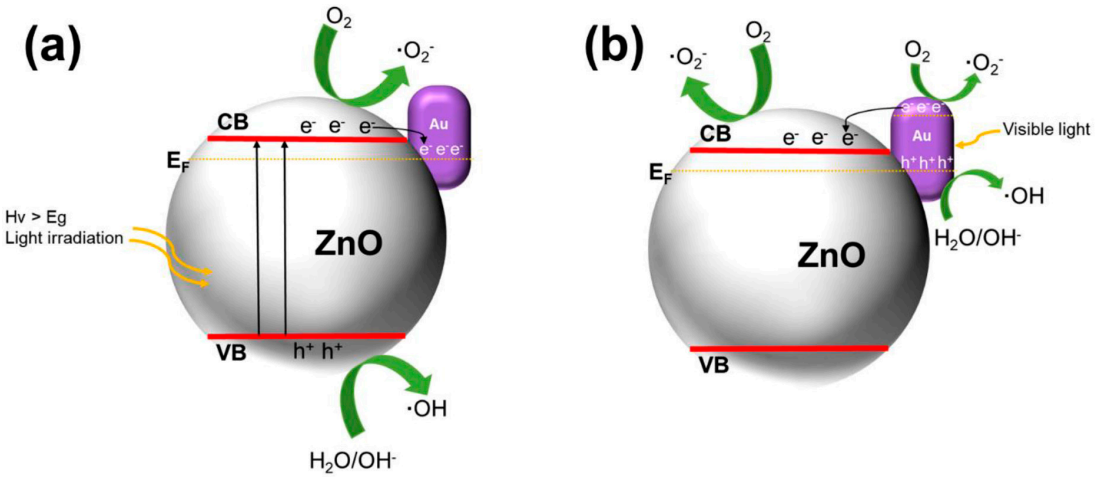

Figure 2. Schematic representation of photocatalytic degradation process with ZnO-Au NCs. a) Under UV irradiation and b) under visible light irradiation.

the CB of ZnO, prolonging charge separation and generating superoxide anion radicals in the CB of ZnO. The holes in the VB of Au NPs react with water and hydroxide ions to produce hydroxyl radicals.

While ZnO exhibits excellent photocatalytic activity as a standalone material, its use is limited by several factors. These include a high electron-hole pair recombination rate that diminishes its effectiveness and a low efficiency in capturing solar light due to its large band gap. A promising approach to overcome these limitations is forming nanocomposites with gold nanoparticles (Au NPs). Gold functions as a surface sensitizer via its surface plasmon resonance and as an electron trap to reduce the recombination rate [13]. These attributes enhance the catalyst's ability to exploit a broader light spectrum, thereby improving photocatalytic performance. The photocatalytic degradation of pollutants using ZnO-Au nanocomposites (NCs) can proceed via two mechanisms based on the light source. Under UV light, the degradation process is akin to the established mechanism but with modifications. Post electron-hole pair generation, electrons from the CB of ZnO can migrate to Au NPs due to the lower Fermi level of Au NPs. This migration extends charge carrier separation, enhancing photocatalytic activity [14]. In visible light (Figure 2b), the small size of Au NPs enables them to act like semiconductors, creating a gap between the VB and CB, leading to electron-hole pair generation on Au NPs. The reaction between electrons in the CB of Au NPs and the dissolved oxygen will generate superoxide anion radicals, while at the same time, some electrons transfer to the CB of ZnO, furthering charge separation and generating superoxide anion radicals in the CB of ZnO. Meanwhile, holes in the VB of Au NPs can generate hydroxyl radicals through their reaction with water and hydroxide ions.

There are many factors that can affect photocatalytic degradation. Some of the most common factors are catalyst dosage, pH, and initial dye concentration.

Catalyst dosage

Determining the optimum catalyst dosage is crucial for efficient photocatalytic degradation. The ideal amount of catalyst varies depending on factors such as the targeted pollutants, reactor type, particle morphology, light intensity, and reactor configuration. Consequently, the optimal catalyst dosage needs to be more consistent across different studies [15]. Vidya and colleagues reported that the degradation of Rose Bengal dye increased with the catalyst amount up to 60 mg. However, the degradation rate was reduced when the catalyst amount increased to 80 mg. This reduction in degradation efficiency is attributed to increased inter-particle collisions, which impede light from reaching the catalyst surface, thereby reducing its activity in producing radical species [16]. In another study, the percentage of dye decolorization for ethyl violet and Astrazon Brilliant Red 4G dyes increased by approximately 10% with an increase in the concentration of the

catalyst xylan/TiO2/Polyvinylalcohol from 60 to 100 mg/L. This observation is attributed to the higher number of active sites, resulting in a generation of a more significant number of radicals. However, further increases in catalyst concentration resulted in a lower decolorization percentage. This decline occurred because excessive amounts of catalyst blocked and scattered light [17].

pH

The pH is one of the most significant factors affecting photocatalytic degradation, as it influences the adsorption of pollutants on the catalyst surface. Ghanbari, Ahmadi, and Gohari, describe how pH affects the surface charge of the catalyst, which can be explained based on the point of zero charge (PZC). They discovered that the decolorization rate decreases at alkaline pH. The PZC of the catalyst CeO_2-Fe_3O_4 (CeFe) is 8.84, resulting in a positively charged surface below pH 8.8 and a negatively charged surface above pH 8.8. At alkaline pH, repulsion occurs between peroxymonosulfate, the compound responsible for generating radical species, leading to a lower amount of radical species and, consequently, a lower decolorization rate [18]. In a study conducted by Yang et al, it was found that moxifloxacin degrades rapidly at pH 3, and indicating that the type of pollutants will have different optimum pH for degradation [19].

Initial pollutants concentration

The interaction between the catalyst and dye molecule depends on the functional groups present and their concentration in the reactor. Generally, an increment in the dye concentration resulted in a reduction of photocatalytic activity. This trend is evident in the research reported by Chen, Wu, Liu, and Gao [20], who found that higher initial dye concentrations significantly reduce the degradation percentage. One possible reason for this outcome is that the occupation of active sites by dye molecules decreases the adsorption of O_2 and OH, producing fewer radicals. Additionally, an increment in dye concentration raises the turbidity of the solution, reducing the amount of light reaching the catalyst and thus leading to lower radical production [20].

ZINC OXIDE-GOLD NANOCOMPOSITES AS PHOTOCATALYSTS

Various synthesis techniques have been reported to produce zinc oxide-gold (ZnO-Au) nanocomposites, which are used as photocatalysts for degrading different classes of pollutants, including dyes, pharmaceuticals, volatile organic compounds (VOCs), and others. One of the most common methods to synthesize these nanocomposites is through chemical pathways, such as precipitation. Bai and Mei reported producing Au nanoparticles (NPs) on ZnO nanorods using a chemical precipitation method. They employed urea as the precipitating agent and varied the concentration of gold salts to investigate the impact on Au NPs particle size. The study's results indicated that X-ray diffraction (XRD) analysis did not reveal any peaks corresponding to Au NPs at low concentrations of gold salts, but these peaks emerged at higher concentrations of gold salts. The size of the Au NPs produced on ZnO nanorods increased proportionally with the concentration of gold salts.

Additionally, the generated Au NPs exhibited a spherical morphology. These samples were subsequently utilized as photocatalysts for the degradation of 4-nitrophenol. The nanocomposites synthesized with the lowest concentration of gold salts exhibited the highest photocatalytic activity. This outcome could be attributed to the interaction between ZnO and the smaller size of Au NPs. It is important to note that the photocatalytic activity was evaluated under UV irradiation, leveraging the capability of both ZnO and Au NPs to generate electron-hole pairs, thereby enhancing the degradation of 4-nitrophenol [21]. However, it is noteworthy that this study did not assess the catalysts' activity under visible light, which is the primary objective of producing ZnO-Au nanocomposites. Furthermore, the impact of other parameters such as catalyst dosage, pH, and initial pollutant concentration were not evaluated, thereby failing to determine the optimal conditions for achieving the highest activity.

Another technique gaining popularity is green synthesis, particularly in light of current research focus on sustainability. In the production of ZnO-Au nanocomposites, green synthesis refers to using biomaterials like plant extracts to assist in their production and employing simple, cost-effective methods such as the photoreduction of gold salt to deposit Au nanoparticles (NPs) onto ZnO. Ahmad and colleagues reported producing ZnO-Au nanocomposites using Carya illinoinensis leaf extract as the reducing agent. X-ray diffraction (XRD)

analysis confirmed successful deposition of Au NPs on ZnO NPs, and transmission electron microscopy (TEM) showed well-distributed spherical Au NPs with an average size of 4.9 nm. The photocatalytic activities of these nanocomposites were evaluated by degrading rhodamine B dye and studying the effects of catalyst dosage, pH, and initial concentration. Comparing the activity of singular ZnO and ZnO-Au nanocomposites, it was found that the nanocomposites exhibited superior performance. Optimal conditions for the highest degradation of rhodamine B were identified as a catalyst dose of 0.4 g/L, pH 10, and 10 ppm initial dye concentration. The nanocomposites' reusability was also assessed; while the first cycle showed the highest degradation percentage, by the fifth cycle, degradation had reduced to 64%, attributed to catalyst loss during recovery [22]. Unfortunately, the nanocomposites' photocatalytic activity under visible light was not evaluated. Corrado and co-workers reported synthesizing ZnO-Au nanocomposites through the photoreduction of gold salt in the presence of ZnO particles. This study focused on the impact of ZnO NPs' morphology on overall photocatalytic activity. Various ZnO NP morphologies were explored, including nanorods, nanobullets, hexagonal-based nanocones, and nanoplates, with Au NPs deposited on each shape through UV irradiation. Overall results indicated that nanocomposites demonstrated enhanced photodegradation of toluidine blue dye, attributed to improved charge separation of electron-hole pairs [23].

Previous studies have predominantly focused on the degradation of dyes. In recent years, nanocomposites have also been used to photodegrade atmospheric pollutants such as nitrogen oxides and volatile organic compounds (VOCs). For the degradation of air pollutants, nanocomposites were deposited on a solid substrate-in this case, mortar. Samples were placed in a cylindrical reactor where nitrogen oxide-polluted air was circulated at specific flow rates and concentrations. UV irradiation initiated the photodegradation process. Relative humidity was identified as a necessary parameter for air pollutants. The study conducted photodegradation experiments under UV and visible light irradiation, achieving 47% and 24% degradation percentages, respectively. Higher degradation under UV irradiation was expected due to the ability of both ZnO and Au NPs to generate radical species and prolong charge carrier separation, enhancing photocatalytic activity [24]. In another study, ZnO-Au NPs were synthesized and used as photocatalysts for degrading VOCs such as toluene, ethanol, and formaldehyde. The degradation process occurred under solar irradiation, which is more sustainable as it utilizes sunlight as an energy source to activate the catalyst. Since VOCs are air pollutants, powdered ZnO-Au NPs were packed and placed in a continuous flow reactor where VOC-polluted air was circulated. Results indicated successful conversion of VOCs to carbon dioxide through photocatalytic reactions [25]. While the product of photocatalytic reactions is carbon dioxide-a greenhouse gas-it can be addressed through carbon capture technology. Table 1 summarizes other literature on producing ZnO-Au nanocomposites as photocatalysts, highlighting various types of pollutants studied for degradation. However, most studies only assessed the photocatalyst activity under undefined experimental parameters, which resulted in the absence of data in Table 1.

CONCLUSIONS

Numerous studies have explored the production of ZnO-Au nanocomposites using various synthesis techniques ranging from chemical precipitation to environmentally friendly green synthesis methods. These nanocomposites exhibit promising potential as photocatalysts capable of degrading diverse pollutants, including dyes, pharmaceuticals, and VOCs. While most studies have utilized UV irradiation to activate these nanocomposites, their properties suggest they can also operate effectively under visible light. However, experiments under visible light generally show lower activity compared to than UV irradiation, which is attributable to UV light's enhanced activation of radical species. In summary, ZnO-Au nanocomposites demonstrate significant promise as versatile catalysts for pollutant degradation in wastewater. Their effectiveness, however, is influenced by the light source used for activation. UV light proves more efficient due to its ability to activate both components of the nanocomposites. Limitations identified in current research include a need for more comprehensive exploration under visible light conditions, which is crucial for optimizing their performance in practical applications. Future research should address this gap and investigate strategies to enhance the stability and recyclability of ZnO-Au nanocomposites.

Table 1. ZnO-Au nanocomposites synthesized via various techniques and their photocatalytic activities.

Synthesis process	Photocatalytic conditions					Degradation percentage (%)	Ref.
	Pollutants	Dosage	pH	Pollutants concentration	Light		
Chemical	Rhodamine B	N/A	N/A	N/A	N/A	78	[26]
Chemical	Rhodamine B	N/A	N/A	N/A	UV	~60	[27]
Chemical	p-nitrophenol	0.4 g/L	N/A	5	Visible	80	[21]
Chemical	Acid Black 1	5 g/L	3	100	Visible	100	[28]
Chemical	Toluene Formaldehyde	0.1 g	N/A	N/A	Visible	95 85	[25]
Chemical	Rhodamine B Oxytetracycline	0.6 g/L	N/A	1 x 10^{-5} M 50 ppm	Visible	85 63	[29]
UV-irradiation	Nitrogen oxides	10 g/L		400 ppb	UV-Visible	34	[24]
UV-irradiation	Rhodamine 6G Erythrosine B	N/A	N/A	10	UV		[30]
UV-irradiation	Toluidine Blue dye	8.44 mM	N/A	0.132 mM	UV	51	[23]
Microwave	4-chlorophenol	N/A	N/A	10 ppm	Sunlight	97	[15]
Laser ablation	Rhodamine 6G	N/A	N/A	N/A	UV		[31]
Green synthesis (pecan nut leaves extract)	Rhodamine B	0.4 g/L	10	10 ppm	UV	99	[22]
Green synthesis (Starch)	Methylene blue	1 g/L	7	10	UV	98	[32]
Green synthesis (burdock extract)	Rhodamine B	0.05 g/L	N/A	2 x 10^{-5} M	Visible	38.1	[33]

Further studies are needed to determine optimal operational parameters such as catalyst dosage, pH conditions, and initial pollutant concentrations to maximize their efficiency and applicability in diverse environmental settings.

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