

Synergistic photocatalysis: Metal oxide composites for enhanced wastewater treatment

Fotocatálisis sinérgica: Compuestos de óxidos metálicos para la mejora en el tratamiento de aguas residuales

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ABSTRACT

The growing concern over water pollution has sparked a demand for practical and durable wastewater treatment systems. This study investigates composite materials, specifically metal oxides, and fabrics, for the photocatalytic degradation of pollutants in wastewater. Metal oxides, including zinc oxide (ZnO) and titanium dioxide (TiO₂), naturally show remarkable photocatalytic properties. The incorporation of these metal oxides within fabric matrices produces a synergistic effect that enhances the photocatalyst's energy level, boosting pollution removal. This composite improves the catalyst's properties, leading to increased photocatalytic performance and easy separation after treatment. This article focuses on the characteristics and photocatalytic performance of these composites. Metal oxide-fabric composites show promising catalysts with a high potential for solving water pollution issues. Therefore, further research is needed before their various environmental uses can be fully used.

Keywords: Water pollution, photocatalytic degradation, metal oxides.

RESUMEN

La creciente preocupación por la contaminación del agua ha generado una demanda por sistemas de tratamientos de aguas residuales efectivos y duraderos. Para obtener una comprensión más profunda del tema, este estudio investiga el uso de materiales compuestos, específicamente óxidos metálicos y telas, para la degradación fotocatalítica de contaminantes en aguas residuales. Los óxidos metálicos, incluyendo óxido de zinc (ZnO) y óxido de titanio (TiO₂), exhiben propiedades fotocatalíticas notables por naturaleza. La incorporación de estos óxidos metálicos en matrices de telas produce un efecto sinérgico que mejora el nivel de energía del catalizador, lo que aumenta la eliminación de contaminantes. Este compuesto mejora las propiedades del catalizador, lo que conduce a un rendimiento fotocatalítico aumentado y una separación fácil después del proceso de tratamiento. Este artículo se centra en las características y el rendimiento

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fotocatalítico de estos compuestos. Los compuestos óxido-fabrica muestran un catalizador prometedor que tiene un alto potencial para resolver problemas de contaminación del agua. Por lo tanto, se requiere más investigación antes de que puedan ser utilizados plenamente en diversas aplicaciones ambientales.

Palabras clave: Contaminación del agua, degradación fotocatalítica, óxidos metálicos.

INTRODUCTION

Water is the most crucial and essential natural resource in life. Fast industrialization and urbanization worldwide have created water supply problems that cause about 80% of the world's population to experience water scarcity. Roughly from 2% of fresh water on Earth, only 0.036% is drinkable, and the remaining 1.96% is contained in aquifers, underground wells, and polar ice caps [1]. Hence, given its limited and crucial nature, the utmost attention must be focused on preserving natural resources, particularly water.

Water pollution is a significant challenge to the effectively utilizing water resources [2]. Water pollution results from inadequate precautions to protect water quality and ensure proper hygiene. Many streams, such as rivers, bays, and other waterways, were transformed into locations for trash disposal. Significant factors contributing to water pollution include industrialization, discharge of domestic trash, radioactive waste, population growth, excessive use of pesticides and fertilizers, and chemical leaking from tanks. According to the Department of Environment (DOE), 195 rivers in Malaysia experience slight pollution, while 34 rivers face severe pollution. Selangor has three rivers categorized as polluted, while 30 other rivers are listed as slightly polluted. River pollution is primarily caused by Biological Oxygen Demand (BOD), Ammoniacal Nitrogen (AN), and Suspended Solids (SS). The accumulation of abandoned materials and industrial waste in lakes and rivers exposes humans and animals to high concentrations of these materials and adversely disrupts aquatic ecosystems. Consequently, water pollution has led to outbreaks of severe illnesses including typhoid fever, kidney issues, gastroenteritis, eczema, diarrhea, and cholera [3].

As stated by the Global Water Partnership, Domestic and industrial sewage are Malaysia's primary sources of water pollution. These sources primarily consist of organic pollutants and harm the ecosystem and

aquatic life. Industrial sites often generate a significant amount of hazardous chemicals. Unfortunately, in some instances, irresponsible personnel have improperly disposed of chemical waste near water systems, contaminating the nearby water streams. Rivers within the Klang Valley have been discovered to have an estimated 80 metric tons of solid waste daily. These waste materials have the potential to produce more toxins and persistent organic pollutants through uncontrolled reactions.

Before consumption or reuse, it is necessary to filter the water. The purification of water requires various quick procedures. The processes involved are coagulation, sedimentation, filtration, and disinfection. Water treatment combines physical, biological, and chemical methods [4]. However, standard procedures prove ineffectual in eliminating hazardous chemicals such as heavy metals, nitrogen, and phosphorus. Furthermore, no specific method exists to break down other complex molecules [5]. Therefore, advanced oxidation processes (AOPs) are implemented to break down these complex molecules enduring contaminants.

Among the AOPs, photocatalysis is a potentially innovative method for degrading organic contaminants in water by mineralizing compounds using complex mechanics and a catalyst. The addition of catalysts or the immobilization of catalysts with other materials can be employed in photocatalytic to improve the degradation efficiency [6]. Extensive research has been conducted on photocatalysis, demonstrating its cost-effectiveness and efficiency in breaking down diverse organic contaminants [7]. The synthesis of semiconductor metal oxides for photocatalytic applications has shown that surface area, bandgap energy, and form of the synthesized metal oxide nanoparticles significantly enhance their photocatalytic activity [8]. Moreover, much research has focused specifically on doping and increasing the energy band gap. These approaches have been found to further enhance these catalysts' photocatalytic activity.

However, despite the advancements in photocatalytic treatment, powder-form catalysts still face challenges in the post-treatment process. Specifically, difficulties in recovering, recycling, and separating particle catalysts can lead to potential health and environmental hazards, highlighting the need for further research and development to address these issues [9]. Therefore, introducing metal oxides into fabric materials is a proposed strategy to enhance photocatalytic water treatment processes cost-effectiveness and environmental sustainability. The composite materials use the benefits of metal oxides and fabric substrates, leading to improved performance, reusability, and reduced environmental impact.

CHARACTERISTICS OF WASTEWATER

Wastewater is a mixture of used water from various sources, including residential, industrial, land, and agricultural facilities. This wastewater stream often has a range of contaminants, including hazardous and non-hazardous substances. As a result, it can be categorized based on its physical, chemical, and biological characteristics [40]. These characteristics are crucial in understanding the composition and impact of wastewater on the environment and human health. They also play a vital role in identifying suitable methods for effective wastewater treatment.

Physical characteristics

The physical characteristics of wastewater are mainly focused on its color, odor, temperature, turbidity, and total solids. For color, especially for industrial dyes, the unreacted or excess dye from the reaction can contaminate nearby soil and turn the stream dark, which may lead to water pollution [41]. If the wastewater remains untreated and stagnant for a while, it can give off an unpleasant odor to the surroundings. It can also cause the generation of anaerobic microbes that release hydrogen sulfide gas and other sulfurs once the oxygen starts to deplete. As for turbidity, it shows the quantity of suspended solid particles that can be measured using a specific instrument, such as a turbidity rod. The higher the turbidity level, the higher the concentration of the wastewater itself. The total solids are dependent on the turbidity. There are total solids in wastewater, such as suspended particles, colloidal solids, and dissolved solids.

Biological characteristics

Wastewater also holds a diverse array of microorganisms, including bacteria, viruses, protozoa, and fungi, due to the nature of the material contaminating the wastewater. These microorganisms can pose significant risks to public health and the environment if not effectively managed.

Chemical characteristics

The vital parameters in the chemical characteristics of wastewater include pH value, chloride contents, nitrogen contents, surfactants, toxic compounds, oxygen demand, dissolved oxygen, and others. Ideally, wastewater pH should fall within the range of 7.3 to 7.5. However, polluted wastewater could sometimes reach levels that are considered acidic due to the prominent level of contamination. Accurate measurement of these chemical characteristics is crucial, as they significantly affect the cleanliness and quality of the wastewater.

METHOD OF WASTEWATER REMOVAL

Pollutants in wastewater can be eliminated using diverse techniques, including physical, biological, or chemical methods.

Physical method

The physical method is employed when physical forces are widely used. Physical procedures involve adsorption and membrane-filtration methods such as nanofiltration, reverse osmosis, and electrodialysis. The physical method is used to manage and treat wastewater without relying on substantial chemical or biological transformations. Physical wastewater treatment systems utilize natural phenomena such as gravity, electrostatic attraction, and van der Waal forces to eliminate contaminants [10].

Adsorption is an effective technique for removing organic contaminants from wastewater. Adsorption is a crucial surface phenomenon where impurities are selectively eliminated from a liquid by binding them to a solid surface known as an adsorbent [11]. This method has several limitations, including its ability to remove organic pollutants altogether. The absorbent material generates secondary pollution after the treatment process. This absorbent may block the filtration process by blocking the filter, affecting pollution removal efficiency [12]. Therefore, physical treatments are not practical for large-scale use.

Biological method

The biological method is the procedure for mainly eliminating biodegradable organic pollutants. This treatment method is more economically efficient than physical and chemical methods. It employs fungal decolorization, microbial degradation, adsorption using live or dead microbial biomass, and bioremediation systems that rely on microorganisms like bacteria, yeast, algae, and fungi. These microorganisms break down and collect various contaminants to treat industrial effluent [10].

While this technology offers cost-effectiveness and environmental advantages, it does have limitations. These include the need for substantial amounts of land due to its vulnerability to daily changes, potential chemical toxicity, and limited flexibility in terms of design and operation. Although this method successfully breaks down various organic compounds, certain ones are resistant to degradation because of their complex chemical structure or because they are synthetic [13].

Chemical method

The chemical method encompasses treatment methods that employ chemicals or chemical reactions to neutralize or modify contaminants. Chemical treatment is often employed for industrial wastewater due to the ineffectiveness of physical or biological treatment methods in removing various pollutants in these waters. Usually, some agents are combined in this method to improve pollutant elimination [10].

Chemical treatment technologies, such as Fenton's reagent oxidation [14], ozone-based processes [15], photolysis and photocatalysis [16], and sonolysis [17], employ methods that enhance the generation of the hydroxyl free radical. This highly reactive radical acts as an effective oxidant to eliminate substances that cannot be oxidized by conventional agents like oxygen, ozone, and chlorine [18].

The interest in AOPs has increased due to their efficacy in pollutant degradation. The generation of efficient oxidizing agents, such as hydroxyl radicals, serves as the main element of this method. This approach is highly efficient in accelerating the oxidation process. The presence of either ozone, catalysts, or UV irradiation helps provide a potent wastewater treatment. Pharmaceuticals and personal care products (PPCPs), pesticides, dyes,

and hazardous metals can be eliminated from water bodies using the AOPs.

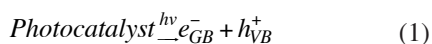
Photocatalysis is one of the AOPs that focuses on using photocatalysts to promote chemical processes through light absorption by one or more reactive substances. During a photochemical reaction, two concurrent processes occur. The initial process involves oxidation due to photogenerated positive charge carriers, whereas the subsequent process involves reduction caused by photogenerated negative charge carriers [19]. A photocatalyst, usually a semiconductor, is the most crucial part of the reaction. A semiconducting material produces an electron-hole pair when exposed to light, aiding photocatalysis [20].

PHOTOCATALYSIS

Photocatalysis is one of the branches of AOPs that attract researchers' attention. Photocatalysis is a photoinduced reaction with a photocatalyst to accelerate the reaction in the presence of light irradiation, e.g., UV, visible light, or solar radiation [21].

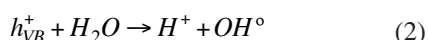
Photon excitation

In the reaction process, the photocatalyst will be activated by the absorption of a photon from the light source to excite the electron from the valence band (VB) to the conduction band (CB), thus leading to the generation of the hole (h^+) in the VB and photo-induced electrons (e_{CB}^-) in the CB, as in equation (1). This phenomenon is known as "electron-hole pair production" (e^-/h^+).



Reaction with moisture

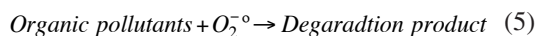
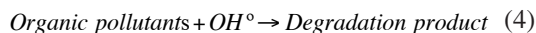
A series of reactions will occur, which will result in the formation of active radicals following equations (2) and equation (3), respectively [8]. The hole will react with moisture, generating H^+ ions and the hydroxyl radical H° [22]. Meanwhile, the electron interacts with oxygen to generate superoxide anion radicals. These radicals play a significant role in photocatalysis process since they attack most of the organic structure, thus changing them into non-hazardous products.





Degradation Process

Subsequently, hydroxyl radicals and superoxide anion radicals will break down the organic contaminants into less hazardous and environmentally favorable substances, such as carbon dioxide (CO₂) or a variety of minerals (equation (4) and equation (5)).



Several variables have been identified to impact the photocatalytic breakdown of organic contaminants. These include the type and composition of the catalyst, light intensity, the contaminant type and concentration, catalyst amount, and solution pH. The diagram in Figure 1 depicts the process of photocatalytic degradation of pollutant compounds using metal oxides as a photocatalyst.

TYPES OF PHOTOCATALYST

Various photocatalysts have demonstrated favorable results in photocatalytic reactions [23]. These include TiO₂, ZnO, tungsten trioxide (WO₃), vanadium (V) oxide (V₂O₅), iron (III) oxide (Fe₂O₃), niobium pentoxide (Nb₂O₅), and zirconia (ZrO₂). Several factors must be considered when selecting the proper photocatalyst, as they will significantly impact

the photocatalysis process outcome. Two crucial factors to consider are the electronic band structure and the energy of the band gap. An essential factor for a photocatalyst to be efficient is its band-gap energy, which should fall between 2.0 and 3.0 eV. This range is crucial as it enables effective light absorption in the visible region [24].

Metal oxides composite catalyst

TiO₂ and ZnO are widely recognized semiconductors used as photocatalysts for breaking down persistent organic contaminants. These materials are chosen for their chemical stability, lack of toxicity, and cost-effectiveness [25]. The energy differences between the VB and the CB for TiO₂ and ZnO are 3.2 eV and 3.3 eV, respectively. Furthermore, researchers have explored the doping method to produce composite catalysts that further improve the efficiency of photocatalytic degradation. These composite catalysts effectively reduced the recombination of electron-hole pairs and improved visible light absorption by creating imperfections in the energy band gap [26].

Therefore, numerous researchers have investigated the process of employing metal oxides doped with other substances to enhance the efficiency of photocatalytic degradation in breaking down organic pollutants. In a study by Ahmadi *et al.*, modified TiO₂ was employed as a catalyst to break down tetracycline, a pharmaceutical medication often found in hospital effluents and used as an

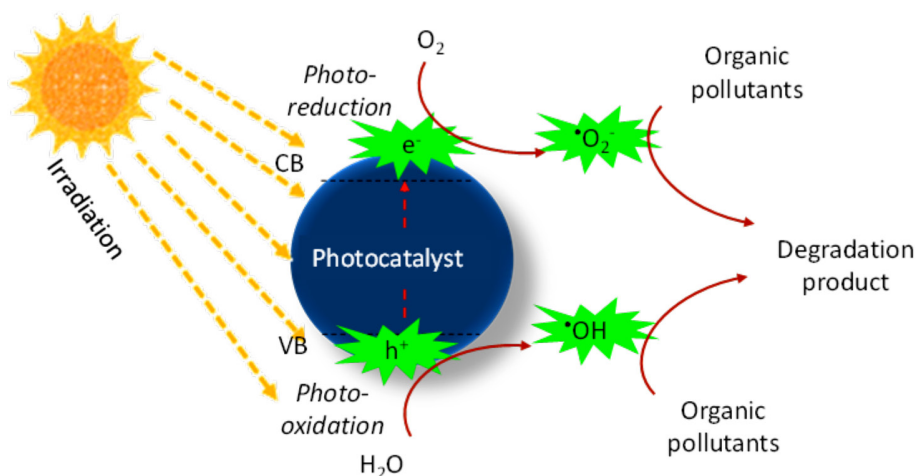


Figure 1. The illustration of photocatalytic degradation mechanism.

animal antibiotic [27]. The TiO_2 was modified by incorporating multi-walled carbon nanotubes (MWCNTs) to increase the photocatalytic degradation activity). Various adjustments were performed to the weight of MWCNTs, catalyst dosage, pH, initial concentration of pollutants, and irradiation periods to find the most effective conditions for breaking down the pollutants. The findings show that complete degradation of tetracycline can be achieved by adding 1.5 (w/w%) of MWCNT to TiO_2 , using a catalyst concentration of 0.2 g/L and a tetracycline concentration of 910 mg/L, at a pH of 5, within a time frame of 100 minutes. This study proves that employing modified TiO_2 as a catalyst can significantly speed up the degradation of pharmaceutical drugs, resulting in a shorter duration and a more significant percentage of removal.

Verma and Haritash investigated the photocatalytic of amoxicillin, a by-product of antibiotic manufacture in the pharmaceutical industry, using TiO_2 -doped H_2O_2 [28]. The study used photocatalysis and sono-photocatalysis techniques to find the most effective approach for degrading amoxicillin. The degradation process was studied using the response surface methodology (RSM). The results showed that 80% of amoxicillin can be degraded using an optimal amount of 30 mg/L of amoxicillin, 0.45 g/L of catalyst under a pH of 7, and UV irradiation at a rate of 672 W/m^2 . Hence, a different material doped with TiO_2 can help degrade several types of pharmaceutical drugs.

An attempt by Thang *et al.* successfully synthesized an environmentally friendly catalyst, Ag/g-C₃N₄/ZnO nanorods, utilizing a straightforward self-assembly technique followed by a photoreduction pathway [29]. This catalyst was used to degrade three commonly produced drugs: amoxicillin, paracetamol, and cefalexin. Thus, analyzing the results, it was found that using a catalyst concentration of 0.08 g/L, 85.3% of paracetamol, 71.74% of cefalexin, and 41.36% of amoxicillin can be removed. Furthermore, the catalyst's stability was evaluated over five cycles, resulting in 78% of paracetamol removal. The catalyst's effectiveness in decomposing pharmaceutical residues, even after multiple cycles, is thus demonstrated.

In addition to its application in the degradation of pharmaceutical drugs, ZnO can also be used to

eliminate dye pollution. For instance, Kumar *et al.* performed an investigation employing doped ZnO as a catalyst for the elimination of hazardous organic dyes, such as direct red-23 (DR-23) dyes [30]. The combustion approach was employed to use Ce-doped ZnO nanoparticles as a catalyst, followed by the application of photocatalytic degradation with various concentrations of doped-Ce. The findings show that DR-23 can be effectively eliminated by 99.5% when the concentration of Ce is 3.28% within 70 minutes.

In another case, Anju Chanu *et al.* carried out a study was to degrade methylene blue (MB) dyes from the textile dye industry using doped ZnO [31]. In this instance, manganese Mn was employed as a supplementary material to enhance the band gap of ZnO. The Mn-doped ZnO catalyst was synthesized using the wet chemical co-precipitation method. Its ability to degrade MB was assessed by adjusting the initial dye concentration, dye pH, and catalyst dose. Under UV irradiation, combining a catalyst concentration of 0.3 g/L, a dye concentration of 10 ppm, and a pH of 10 can effectively eliminate 99% of MB within 120 minutes. The study concludes that ZnO can be doped with diverse types of doping materials to boost photocatalytic degradation activity by enhancing the catalyst's energy level. Table 1 summarizes the results obtained from the photocatalytic degradation process using various metal oxide composite catalysts.

Metal oxides/fabric composite catalyst

A comprehensive review of the outcomes achieved using various metal oxide composite catalysts in the photocatalytic degradation process reveals that these catalysts are highly effective in breaking down diverse organic pollutants, including pharmaceutical drugs and organic dyes. Nevertheless, several disadvantages are associated with the benefits of its components. One concern is that the powdered catalyst may hinder the catalyst's recovery after treatment. Extensive filtration is required to remove the photocatalytic powder from the cleaned solution, increasing time and space requirements [32]. In addition, the catalyst tends to leach during the reaction, mainly when a continuous reactor is used. The leached catalyst may then react with other substances in water streams, raising the likelihood of generating other toxins and compounds. Therefore, researchers have explored

Table 1. Summary of the photocatalytic degradation employing metal oxides composite catalyst.

Ref. no.	Catalyst	Pollutants	Outputs				
			Time (mins)	Catalyst Conc. (g/L)	Initial Conc. (mg/L)	pH	Efficiency (%)
[27]	MWCNT/TiO ₂	Tetracycline	100	0.2	910	5	100
[28]	TiO ₂ -doped H ₂ O ₂	Amoxicillin	–	0.45	30	7	80
[29]	Ag/g-C ₃ N ₄ /ZnO nanorods	Amoxicillin	–	0.08	–	–	41.4
		Paracetamol					85.3
		Cefalexin					71.7
[30]	Ce-doped ZnO nanoparticles	DR-23	70	3.28%	–	–	99.5
[31]	Mn-doped ZnO	MB	120	0.3	10	10	99

the alternative method by embedding the metal oxide catalyst into specific fabrics to break down pollutant chemicals and improve the effectiveness and feasibility of the photocatalyst.

Kim *et al.* employed metal oxides coated onto specific fabrics to enhance the effectiveness of photocatalytic degradation of organic pollutants. The authors examined the efficacy of a plastic optical fiber fabric layered with TiO₂ (POF/TiO₂) for breaking down MB [33]. The POF/TiO₂ synthesis involves the dip-coating technique, which is dried at a consistent temperature of 50 °C to inhibit fabric degradation. The findings show a positive correlation between catalyst loading and pH and a negative correlation between the initial amount of MB and MB breakdown. The POF/TiO₂ photocatalyst exhibits sustained photocatalytic activity even after multiple cycles.

Additionally, Kumar *et al.* utilized nanosized TiO₂ particles attached to cotton cloth to eliminate the amaranth dye [34]. This research aimed to tackle the problems encountered in prior investigations about powdered TiO₂ suspensions. Nanosized TiO₂ was synthesized on cotton fabric using the sol-gel method. The half-life ($t^{1/2}$) of amaranth's photocatalytic degradation was determined to be 1.54 hours when employing a sol-gel-coated cotton fabric, showing that the dye may be effectively eliminated from the water. These pollutants break down following the Langmuir-Hinshelwood (L-H) law. 0.45 hr⁻¹ was the rate constant determined by the pseudo-first-order reaction.

Another study investigated the capacity to degrade rhodamine 6G (Rh6G) and MB by utilizing woven

cotton fabrics coated with TiO₂ as a photocatalyst [35]. The sol-gel method was used to synthesize TiO₂. Then, the fabrics were treated with TiO₂ under ultrasonic conditions at 120 °C and had their properties evaluated. This photocatalyst was characterized using STDR, X-ray Photoelectron Spectroscopy (XPS), Scanning Electron Microscopy (SEM), laser-generated luminescence, and ground-state diffuse reflectance. The impact on the breakdown of Rh6G was investigated, revealing that 90% of MB underwent deterioration during a 30-minute time. With the positive results of the previously mentioned studies, it is recommended that the use of TiO₂ loaded onto fabrics to treat and purify industrial wastewater be expanded [33]-[35].

In contrast with the previous studies, Du *et al.* utilized other types of metal oxides for the photocatalytic degradation of rhodamine B [36]. The author used bismuth tungstate/graphene oxide materials attached to polyethylene terephthalate fabric to produce Bi₂WO₆/GO/PET composites. Characterization through XPS, SEM, Transmission Electron Microscopy (TEM), X-Ray Diffraction (XRD), UV-Visible Spectroscopy (UV-vis), Brunauer-Emmett-Teller (BET) analysis, and Photoluminescence Spectroscopy (PL) enabled investigation into their chemical composition, crystallographic structure, morphology, optical behaviors, surface characteristics, and photochemical properties. The composite catalyst degraded 97.3% of rhodamine B dye with this characteristic.

Similarly, Cheng *et al.* successfully loaded CuFe₂O₄ nanoparticles onto polydopamine-treated alumina ceramics/polyester blended fabrics (CuFe₂O₄/CPF), which was confirmed using SEM and XPS analysis

[37]. Additionally, adding CuFe_2O_4 nanoparticles to a CPF substrate has enhanced its thermal stability. The best loading amount was quantified and determined to be 6%. The CuFe_2O_4 /CPF photocatalyst achieved a degradation rate of 98.2% for MB under visible light irradiation over 80 minutes. The degradation of MB by composite materials remained consistent after three recycling cycles, showing that the inclusion of polydopamine facilitated a strong connection between CuFe_2O_4 and CPF. Therefore, using various metal oxides on diverse fabric materials can improve the photocatalytic degradation efficiency and simultaneously overcome the limitations of utilizing catalysts in powdered form. Table 2 summarizes the results of the photocatalytic degradation process employing metal oxide composite/fabric catalysts. In addition, a few researchers have conducted studies on using ZnO placed onto certain fabrics as a photocatalyst. All the findings also indicate a positive outcome in photodegradation of organic contaminants.

For example, Zhu *et al.* investigated the photo-degradation characteristics of ZnO and utilized a straightforward immersion-coating-drying process to create cotton fabrics with self-cleaning abilities [38]. MB was used to evaluate the fabric's self-cleaning properties. ZnONP-coated cotton fabric was characterized using Fourier Transform Infrared Spectroscopy (FTIR), XRD, Field Emission Scanning Electron Microscopy (FESEM), and thermogravimetric studies. The removal efficacy of fabrics containing ZnO was assessed by altering the duration of UV irradiation. The findings show that coated fabrics containing a more significant weight percentage of ZnONPs exhibited enhanced

degradation of contaminants during extended irradiation periods. Following three cycles of photocatalytic degradation, the fabric's performance with a higher weight percentage of ZnONP was reduced. Therefore, fabrics coated with ZnONP have excellent UV-blocking characteristics.

Nozari *et al.* studied a catalyst composed of ZnO nanoparticles supported on silica (ZnO@SiO_2 NPs) loaded onto PET fabric [39]. The catalyst was synthesized using a straightforward chemical in-situ synthesis method in an alkaline solution. Zinc acetate and sodium silicate reacted in an aqueous ammonia solution to produce ZnO@SiO_2 nanoparticles on PET fabric at a temperature of 90 °C. The sample was characterized using XRD, FESEM, Energy-Dispersive X-ray spectroscopy (EDS), and FTIR. MB was employed to evaluate the photocatalytic degradation process. The results show that the presence of silica on ZnO leads to rapid discoloration of MB, particularly in ambient and acidic conditions; this, in turn, enhances the fabric's photocatalytic activity. Because of Si's high-temperature resistance, ZnO@SiO_2 NPs also functioned as heat-driven catalysts on the fabric, enhancing the fire-resistant properties of PET by preventing dripping. The ZnO@SiO_2 nanoparticles catalyst enhanced the thermal and photocatalytic properties of PET fabric.

CONCLUSIONS

Photocatalysis is a crucial process in wastewater purification, even if various other technologies are available for addressing water pollution. Prior research has shown that metal oxide composite is

Table 2. Summary of the photocatalytic degradation employing metal oxides composite/fabrics catalyst

Ref. No	Catalyst	Pollutants	Outputs				
			Time (mins)	Catalyst Conc. (g/L)	Initial Conc. (mg/L)	pH	Efficiency (%)
[33]	POF/ TiO_2	MB	1440	0.025 to 0.1	10 μM	9	80
[34]	TiO_2 /cotton fabric	Amaranth Dyes	150	–	4	–	67.8
[35]	TiO_2 / cotton fabrics	Rhodamine 6G	120	0.005	–	–	–
		MB	30		4	–	90
[36]	Bi_2WO_6 /GO/PET	Rhodamine B	120	2 (GO content)	250	–	97.3
[37]	CuFe_2O_4 /CPF	MB	80	–	–	–	98.2
[38]	ZnONPs/cotton	MB	24 hours	–	10 μL –	–	~90
[39]	ZnO@SiO_2 NPs/PET	MB	–	–	–	Acid	–

a photocatalyst that can treat water contamination with various stubborn pollutants. Nevertheless, a few disadvantages have arisen because of photocatalytic degradation. Therefore, an enhanced formulation of the photocatalyst has been developed by incorporating metal oxide composites onto a specific fabric to improve the catalyst's effectiveness and tackle the concerns raised. A comprehensive analysis of the incorporation of metal oxide composites into fabrics through doping has been conducted. Photocatalytic metal oxide composites can be used in multiple cycles. Finally, the problem of limited access to sufficient and fresh drinking water can be effectively resolved using photocatalytic treatment techniques that positively impact society. The findings of this study can serve as a foundation for future research into the development of advanced photocatalysts for photocatalytic degradation. Therefore, to further improve the efficacy of photocatalysts, future studies should focus on evaluating their life cycle during preparation and application and their regeneration capacity. Additionally, comparisons of various characterizations of advanced or doped photocatalysts based on their material properties should be conducted to find which ones act as better photocatalysts. As a result, this will help to improve the overall performance and sustainability of photocatalytic processes.

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REFERENCES

- [1] K. Jayaswal, V. Sahu, and B.R. Gurjar, "Water pollution, human health and remediation," in *Water Remediation. Energy, Environment, and Sustainability*, S. Bhattacharya, A. Gupta, A. Gupta, and A. Pandey, Eds., 2018, pp. 11-27, doi: 10.1007/978-981-10-7551-3_2.
- [2] J. Halder and N. Islam, "Water pollution and its impact on the human health," *Journal of Environment and Human*, vol. 2, no. 1, pp. 36-46, 2015, doi: 10.15764/eh.2015.01005.
- [3] M. Haseena, M.F. Malik, A. Javed, N.A. S. Arshad, S. Zulfiqar, and J. Hanif, "Water pollution and human health," *Environmental Risk Assessment and Remediation*, vol. 1, no. 3, 2017, doi: 10.4066/2529-8046.100020
- [4] M. Grzegorzec, K. Wartalska, and B. Kaźmierczak, "Review of water treatment methods with a focus on energy consumption," *International Communications in Heat and Mass Transfer*, vol. 143, Art. no. 106674, 2023, doi: 10.1016/j.icheatmasstransfer.2023.106674.
- [5] P. Rajasulochana and V. Preethy, "Comparison on efficiency of various techniques in treatment of waste and sewage water – A comprehensive review," *Resource-Efficient Technologies*, vol. 2, no. 4, pp. 175-184, 2016, doi: 10.1016/j.reffit.2016.09.004.
- [6] M. Pelaez *et al.*, "A review on the visible light active titanium dioxide photocatalysts for environmental applications," *Applied Catalysis B: Environmental*, vol. 125, pp. 331-349, 2012, doi: 10.1016/j.apcatb.2012.05.036.
- [7] R. Ameta, S. Benjamin, A. Ameta, and S.C. Ameta, "Photocatalytic degradation of organic pollutants: A review," *Materials Science Forum*, vol. 734, pp. 247-272, 2012, doi: 10.4028/www.scientific.net/MSF.734.247.
- [8] C. Karthikeyan, P. Arunachalam, K. Ramachandran, A.M. Al-Mayouf, and S. Karuppuchamy, "Recent advances in semiconductor metal oxides with enhanced methods for solar photocatalytic applications," *Journal of Alloys and Compounds*, vol. 828, Art. no. 15242, 2020, doi: 10.1016/j.jallcom.2020.154281.
- [9] A.M. Ali, E.A.C. Emanuelsson, and D.A. Patterson, "Photocatalysis with nanostructured zinc oxide thin films: The relationship between morphology and photocatalytic activity under oxygen limited and oxygen rich conditions and evidence for a Mars Van Krevelen mechanism," *Applied Catalysis B: Environmental*, vol. 97, no. 1-2, pp. 168-181, 2010, doi: 10.1016/j.apcatb.2010.03.037.
- [10] M.F.S. Hanafi and N. Sapawe, "A review on the current techniques and technologies of organic pollutants removal from water/wastewater," *Materials Today: Proceedings*, vol. 31, pp. A158-A165, Jan. 2020, doi: 10.1016/j.matpr.2021.01.265.

- [11] M. Nageeb, "Adsorption technique for the removal of organic pollutants from water and wastewater," in *Organic Pollutants. Monitoring, Risk and Treatment*, Rijeka, M. Nageeb, Ed., Croatia: IntechOpen, 2013.
- [12] S. Moosavi, C.W. Lai, S. Gan, G. Zamiri, O. Akbarzadeh Pivehzhani, and M.R. Johan, "Application of efficient magnetic particles and activated carbon for dye removal from wastewater," *ACS Omega*, vol. 5, no. 33, pp. 20684-20697, 2020, doi: 10.1021/acsomega.0c01905.
- [13] W.N.A. Kadir, M.K. Lam, Y. Uemura, J.W. Lim, and K.T. Lee, "Harvesting and pre-treatment of microalgae cultivated in wastewater for biodiesel production: A review," *Energy Conversion and Management*, vol. 171, pp. 1416-1429, 2018, doi: 10.1016/j.enconman.2018.06.074.
- [14] S.M. Aramyan, "Advances in Fenton and Fenton Based oxidation processes for industrial effluent contaminants control -A review," *International Journal of Environmental Sciences & Natural Resources*, vol. 2, no. 4, 2017, doi: 10.19080/ijesnr.2017.02.555594.
- [15] K. Ikehata and Y. Li, "Ozone-Based processes," in *Advanced Oxidation Processes for Waste Water Treatment*, S. C. Ameta y R. Ameta, Eds., London, UK: Academic Press, 2018, pp. 115-134.
- [16] R. Ahmad, Z. Ahmad, A.U. Khan, N.R. Mastoi, M. Aslam , and J. Kim, "Photocatalytic systems as an advanced environmental remediation: Recent developments, limitations and new avenues for applications," *Journal of Environmental Chemical Engineering*, vol. 4, no. 4, pp. 4143-4164, 2016, doi: 10.1016/j.jece.2016.09.009.
- [17] N. Kerabchi, S. Merouani, and O. Hamdaoui, "Numerical insight into the sonolytic ozonation applied for water treatment," in *Water Engineering Modeling and Mathematic Tools*, P. Samui, H. Bonakdari, and R. Deo, Eds., Cambridge, MA, USA: Elsevier, 2021, pp. 1-23.
- [18] N. Nordin, L.N. Ho, S.A. Ong, A.H. Ibrahim, A.L.A. Rani , S.L. Lee, Y.P. Ong, "Hydroxyl radical formation in the hybrid system of photocatalytic fuel cell and peroxi-coagulation process affected by iron plate and UV light," *Chemosphere*, vol. 244, Art. no. 125459, 2020, doi: 10.1016/j.chemosphere.2019.125459.
- [19] A. Fujishima, X. Zhang, and D.A. Tryk, "TiO₂ photocatalysis and related surface phenomena," *Surface Science Reports*, vol. 63, no. 12, pp. 515-582, 2008, doi: 10.1016/j.surfrep.2008.10.001.
- [20] R. Ameta, M.S. Solanki, S. Benjamin, and S.C. Ameta, "Photocatalysis," in *Advanced Oxidation Processes for Waste Water Treatment*, S. C. Ameta, and R. Ameta, Eds., London, UK: Academic Press, 2018, pp. 135-175.
- [21] S.H. Khan and B. Pathak, "Zinc oxide based photocatalytic degradation of persistent pesticides: A comprehensive review," *Environmental Nanotechnology, Monitoring & Management*, vol. 13, Art. no. 100290, 2020, doi: 10.1016/j.enmm.2020.100290.
- [22] S. Baruah, M.A. Mahmood, M.T. Myint, T. Bora, and J. Dutta, "Enhanced visible light photocatalysis through fast crystallization of zinc oxide nanorods," *Beilstein Journal of Nanotechnology*, vol. 1, pp. 14-20, 2010, doi: 10.3762/bjnano.1.3.
- [23] K.M. Lee, C.W. Lai, K.S. Ngai, and J.C. Juan, "Recent developments of zinc oxide based photocatalyst in water treatment technology: A review," *Water Research*, vol. 88, pp. 428-448, 2016, doi: 10.1016/j.watres.2015.09.045.
- [24] J. Wang, M. Zhang, J. Meng, Q. Li, and J. Yang, "Single- and few-layer BiOI as promising photocatalysts for solar water splitting," *RSC Advances*, vol. 7, no. 39, pp. 24446-24452, 2017, doi: 10.1039/c7ra01723e.
- [25] K.S. Varma *et al.*, "Photocatalytic degradation of pharmaceutical and pesticide compounds (PPCs) using doped TiO₂ nanomaterials: A review," *Water-Energy Nexus*, vol. 3, pp. 46-61, 2020, doi: 10.1016/j.wen.2020.03.008.
- [26] M.R.D. Khaki, M. S. Shafeeyan, A.A.A. Raman, and W. Daud, "Application of doped photocatalysts for organic pollutant degradation - A review," *Journal of Environmental Management*, vol. 198, pp. 78-94, 2017, doi: 10.1016/j.jenvman.2017.04.099.

- [27] M. Ahmadi *et al.*, "Enhanced photocatalytic degradation of tetracycline and real pharmaceutical wastewater using MWCNT/TiO(2) nano-composite," *Journal of Environmental Management*, vol. 186, pp. 55-63, 2017, doi: 10.1016/j.jenvman.2016.09.088.
- [28] M. Verma and A.K. Haritash, "Photocatalytic degradation of amoxicillin in pharmaceutical wastewater: A potential tool to manage residual antibiotics," *Environmental Technology & Innovation*, vol. 20, Art. no. 101072, 2020, doi: 10.1016/j.eti.2020.101072.
- [29] N.Q. Thang, A. Sabbah, L.C. Chen, K.H. Chen, C.M. Thi, and P. Van Viet, "High-efficient photocatalytic degradation of commercial drugs for pharmaceutical wastewater treatment prospects: A case study of Ag/g-C₃N₄/ZnO nanocomposite materials," *Chemosphere*, vol. 282, Art. no. 130971, 2021, doi: 10.1016/j.chemosphere.2021.130971.
- [30] R. Kumar, A. Umar, G. Kumar, M.S. Akhtar, Y. Wang, and S.H. Kim, "Ce-doped ZnO nanoparticles for efficient photocatalytic degradation of direct red-23 dye," *Ceramics International*, vol. 41, no. 6, pp. 7773-7782, 2015, doi: 10.1016/j.ceramint.2015.02.110.
- [31] L.A. Chanu, W.J. Singh, K.J. Singh, and K.N. Devi, "Effect of operational parameters on the photocatalytic degradation of methylene blue dye solution using manganese doped ZnO nanoparticles," *Results in Physics*, vol. 12, pp. 1230-1237, 2019, doi: 10.1016/j.rinp.2018.12.089.
- [32] C.L. Bianchi *et al.*, "Photocatalytic degradation of dyes in water with micro-sized TiO₂ as powder or coated on porcelain-grès tiles," *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 280, pp. 27-31, 2014, doi: 10.1016/j.jphotochem.2014.02.002.
- [33] S. Kim, M. Kim, S. K. Lim, and Y. Park, "Titania-coated plastic optical fiber fabrics for remote photocatalytic degradation of aqueous pollutants," *Journal of Environmental Chemical Engineering*, vol. 5, no. 2, 2017, doi: 10.1016/j.jece.2017.03.036.
- [34] J. Kumar and A. Bansal, "Photocatalytic degradation of amaranth dye in aqueous solution using sol-gel coated cotton fabric," in *Proceedings of the World Congress on Engineering and Computer Science 2010, WCECS 2010*, vol. 2, October 20-22, 2010, San Francisco, USA, 2010.
- [35] Z. Ait-Touchente *et al.*, "Ultrasonic effect on the photocatalytic degradation of Rhodamine 6G (Rh6G) dye by cotton fabrics loaded with TiO₂," *Cellulose*, vol. 27, no. 2, pp. 1085-1097, 2020, doi: 10.1007/s10570-019-02817-y.
- [36] Z. Du *et al.*, "Visible-light-driven photocatalytic degradation of rhodamine B using Bi₂WO₆/GO deposited on polyethylene terephthalate fabric," *Journal of Leather Science and Engineering*, vol. 2, no. 1, Art. no. 16, 2020, doi: 10.1186/s42825-020-00029-w.
- [37] D. Cheng *et al.*, "Loading CuFe₂O₄ onto ceramic fabric for photocatalytic degradation of methylene blue under visible light irradiation," *Ceramics International*, vol. 48, no. 1, pp. 1256-1263, 2022, doi: 10.1016/j.ceramint.2021.09.210.
- [38] C. Zhu, J. Shi, S. Xu, M. Ishimori, J. Sui, and H. Morikawa, "Design and characterization of self-cleaning cotton fabrics exploiting zinc oxide nanoparticle-triggered photocatalytic degradation," *Cellulose*, vol. 24, no. 6, pp. 2657-2667, 2017, doi: 10.1007/s10570-017-1289-7.
- [39] B. Nozari, M. Montazer, and M.M. Rad, "Stable ZnO/SiO₂ nano coating on polyester for anti-bacterial, self-cleaning and flame retardant applications," *Materials Chemistry and Physics*, vol. 267, Art. no. 124674, Jul. 2021, doi: 10.1016/j.matchemphys.2021.124674.
- [40] K. Sharma, "Characteristics of Wastewater: Physical Chemical, Biological," *scienceinfo.com*. Accessed: Jun. 19, 2024. [Online]. Available: <https://scienceinfo.com/characteristics-of-wastewater/>
- [41] D.A. Yaseen and M. Scholz, "Textile dye wastewater characteristics and constituents of synthetic effluents: a critical review," *International Journal of Environmental Science and Technology*, vol. 16, no. 2, pp. 1193-1226, 2019, doi: 10.1007/s13762-018-2130-z.

APPENDIX

List of abbreviations

AN	Ammoniacal Nitrogen
AOPs	Advanced Oxidation Processes
BET	Brunauer-Emmett-Teller
BOD	Biological Oxygen Demand
CB	Conduction Band
CO ₂	Carbon Dioxide
CuFe ₂ O ₄ /CPF	Polydopamine-Treated Alumina Ceramics/Polyester Blended Fabrics
DOE	Department Of Environment
DR-23	Direct Red-23
EDS	Energy-Dispersive X-Ray Spectroscopy
Fe ₂ O ₃	Iron (III) Oxide
FESEM	Field Emission Scanning Electron Microscopy
L-H	Langmuir-Hinshelwood
MB	Methylene Blue
MWCNTs	Multi-Walled Carbon Nanotubes
Nb ₂ O ₅	Niobium Pentoxide
PL	Photoluminescence Spectroscopy
POF/ TiO ₂	A Plastic Optical Fiber Fabric That Was Coated with TiO ₂
PPCPs	Pharmaceuticals And Personal Care Products
Rh6G	Rhodamine 6G
RSM	Response Surface Methodology
SEM	Scanning Electron Microscopy
SS	Suspended Solids
t ^{1/2}	Half-Life
TEM	Transmission Electron Microscopy
TiO ₂	<i>Titanium Dioxide</i>
UV	Ultraviolet
UV-vis	UV-Visible Spectroscopy
V ₂ O ₅	Vanadium (V) Oxide
VB	Valence Band
WO ₃	Tungsten Trioxide
XPS	X-Ray Photoelectron Spectroscopy
XRD	X-Ray Diffraction
ZnO	<i>Zinc Oxide</i>
ZnO@SiO ₂ NPs	ZnO Nanoparticles Supported on Silica
ZrO ₂	Zirconia