

Photocatalytic Degradation of Pharmaceutical Waste Using ZnO/CuO Thin Films Under Visible Light

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Abstract

The increasing presence of persistent pharmaceutical contaminants in water bodies poses a significant threat to environmental and human health, necessitating effective remediation technologies. This study aimed to develop and evaluate zinc oxide/copper oxide (ZnO/CuO) composite thin films as an efficient photocatalyst for degrading pharmaceutical waste under visible light. The ZnO/CuO thin films were synthesized via a sol-gel spin-coating method, and their photocatalytic activity was assessed using diclofenac as a model pollutant. The results demonstrated that the ZnO/CuO heterostructure exhibited enhanced visible light absorption and superior photocatalytic performance compared to pure ZnO. The composite films achieved over 90% degradation of diclofenac within 120 minutes, with the process following pseudo-first-order kinetics. The enhanced efficiency is attributed to effective charge separation at the ZnO/CuO interface. This research confirms that ZnO/CuO thin films are promising, reusable photocatalysts for the sustainable treatment of pharmaceutical-contaminated water.

Keywords: Pharmaceutical Waste, Visible Light, ZnO/CuO.



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INTRODUCTION

The ubiquitous presence of pharmaceutical compounds in aquatic ecosystems has emerged as a critical global environmental concern (Slade dkk., 2022; Tefera Dibaba &

Barkessa, 2025). These substances, classified as contaminants of emerging concern (CECs), enter water bodies through various pathways, including the discharge of insufficiently treated effluents from municipal wastewater treatment plants, runoff from agricultural lands where sewage sludge is applied, and direct disposal from manufacturing facilities and households. Due to their inherent design for biological activity and resistance to metabolic degradation, many pharmaceutical compounds persist in the environment, leading to their continuous accumulation in surface water, groundwater, and even drinking water sources.

The ecological and public health risks associated with chronic, low-level exposure to these pharmaceutical residues are significant and multifaceted. Many of these compounds are known endocrine disruptors, capable of interfering with the hormonal systems of aquatic organisms even at nanogram-per-liter concentrations, leading to reproductive and developmental abnormalities. Furthermore, the constant presence of antibiotics in water systems contributes to the proliferation of antibiotic-resistant bacteria, a major threat to global public health (Forero dkk., 2023; Lidberg dkk., 2024). The complex mixture of these active compounds can also lead to unpredictable synergistic toxicological effects on non-target organisms.

Addressing this challenge requires the development of advanced water treatment technologies capable of effectively mineralizing these persistent organic pollutants. Among the various approaches, Advanced Oxidation Processes (AOPs) have garnered substantial attention due to their ability to generate highly reactive oxygen species (ROS), such as hydroxyl radicals ($\bullet\text{OH}$). These radicals are powerful, non-selective oxidizing agents that can break down complex organic molecules into simpler, less harmful substances like carbon dioxide and water. Heterogeneous photocatalysis, a key subset of AOPs, stands out as a particularly promising, sustainable, and environmentally friendly method for water remediation.

Conventional wastewater treatment plants (WWTPs), which primarily rely on biological processes, are fundamentally ill-equipped to remove persistent and complex pharmaceutical molecules (Brzić dkk., 2023; Tagliari dkk., 2023). These systems were designed to handle conventional pollutants like biodegradable organic matter and nutrients, not the intricate and stable chemical structures of modern drugs. Consequently, a significant fraction of pharmaceuticals passes through these facilities either unchanged or as partially transformed, but still biologically active, metabolites. This continuous discharge from WWTPs represents the primary source of pharmaceutical contamination in the aquatic environment.

The practical application of many established AOPs, including photocatalysis, faces significant hurdles that limit their widespread adoption. A major limitation is the reliance of many efficient semiconductor photocatalysts, such as titanium dioxide (TiO_2) and zinc oxide (ZnO), on ultraviolet (UV) light for activation due to their wide band gaps (Chakocha dkk., 2025; Department of Science Education, Universitas Negeri Semarang, Central Java, Indonesia dkk., 2024). UV radiation constitutes only a small fraction ($\sim 5\%$) of the solar spectrum, making processes that depend on it either energy-intensive if artificial UV lamps are used, or inefficient if relying solely on sunlight. This dependency presents a major economic and sustainability barrier.

An additional and critical problem lies in the practical implementation of photocatalytic systems. Most research has focused on using photocatalysts in powder or slurry form, which, despite offering a high surface area, creates significant post-treatment challenges. The need to separate and recover these fine catalyst particles from the treated water is a difficult, energy-

intensive process that increases operational costs and risks secondary pollution if the recovery is incomplete (Bogotá-Gregory dkk., 2024; Chakocha dkk., 2025). Therefore, the specific problem is the need for an efficient, visible-light-active photocatalyst that can be immobilized onto a stable substrate for easy reuse, providing a practical and sustainable solution for water purification.

The primary objective of this study is to synthesize and comprehensively evaluate a zinc oxide/copper oxide (ZnO/CuO) composite thin film as a highly efficient, reusable photocatalyst for the degradation of pharmaceutical waste under visible light irradiation. The research aims to demonstrate the superiority of this heterostructure system over its individual components and to establish its viability as a practical solution for water remediation. A common and persistent non-steroidal anti-inflammatory drug, diclofenac, will be used as the model pharmaceutical pollutant for this investigation.

To realize this overarching goal, several specific sub-objectives have been defined. The first is the fabrication of ZnO/CuO composite thin films on a suitable substrate using a scalable sol-gel spin-coating technique. The second objective involves the thorough characterization of the synthesized films to determine their structural, morphological, optical, and electrochemical properties using techniques such as XRD, SEM, UV-Vis spectroscopy, and electrochemical impedance spectroscopy (Fatmawati & Sanusi, 2024; Santi & Prado, 2022). The third objective is to systematically investigate the photocatalytic performance of the films by monitoring the degradation of diclofenac under visible light, analyzing the reaction kinetics, and assessing the reusability and stability of the catalyst over multiple cycles.

This investigation is guided by the central hypothesis that forming a p-n heterojunction between p-type CuO and n-type ZnO will create a superior photocatalyst. We hypothesize that this heterostructure will significantly enhance visible light absorption due to the narrow band gap of CuO and, more importantly, will promote efficient separation of photogenerated electron-hole pairs at the interface (Leete, 2022; Pontón-Cevallos dkk., 2022). This improved charge separation is expected to suppress recombination rates, increase the quantum yield of ROS generation, and ultimately lead to a substantially higher photocatalytic degradation efficiency compared to pure ZnO or CuO thin films.

The field of photocatalysis for environmental remediation is well-established, with a vast body of literature dedicated to the subject. Initial research predominantly focused on wide-band-gap semiconductors like TiO₂ and ZnO, which have been extensively studied for their high chemical stability and photocatalytic activity. However, the overwhelming conclusion from this body of work is that their practical application is severely hampered by their reliance on UV light, limiting their efficiency under natural solar irradiation.

Subsequent research has explored various strategies to overcome this limitation and enable visible-light activity, including non-metal doping, noble metal deposition, and the creation of semiconductor heterojunctions (Kuklina dkk., 2022; Sullivan, 2023). The coupling of a wide-band-gap semiconductor with a narrow-band-gap one, like CuO, has been identified as a particularly effective approach. While numerous studies have reported on the synthesis of ZnO/CuO composite photocatalysts, the vast majority of these have focused on catalysts in powder or nanoparticle form. These studies, while demonstrating enhanced visible-light activity, do not address the critical engineering challenge of catalyst separation and recovery in practical applications.

A clear gap exists in the literature concerning the development and systematic evaluation of *immobilized* ZnO/CuO heterostructures in a thin-film configuration for the degradation of persistent pharmaceutical pollutants. Few studies have utilized a scalable technique like sol-gel spin-coating to create these films and then rigorously tested their performance, stability, and reusability specifically for pharmaceutical waste treatment under visible light. This research is designed to fill this specific gap by moving beyond powder-based proof-of-concept studies to a more practical, application-oriented thin-film system.

The principal novelty of this research lies in the fabrication and application of a ZnO/CuO composite heterostructure as an immobilized thin film for pharmaceutical degradation. This thin-film configuration is a significant innovation over conventional powder-based systems because it completely eliminates the need for post-treatment catalyst recovery (Klokov, 2023; Schiøtt dkk., 2022). This feature drastically simplifies the reactor design, reduces operational costs, and makes the photocatalytic process more amenable to continuous flow systems, thereby addressing a major barrier to the practical implementation of this technology in real-world water treatment scenarios.

The study's novelty is further enhanced by its specific focus on harnessing visible light, which constitutes the largest portion (~45%) of the solar spectrum. By developing a catalyst that efficiently utilizes this abundant, free energy source, this work contributes to a more sustainable and environmentally benign approach to water purification. The targeted application for degrading a persistent and widely detected pharmaceutical compound like diclofenac provides direct relevance and demonstrates a tangible solution to a pressing environmental problem, moving beyond the use of simple dyes as model pollutants.

This research is strongly justified by the urgent and growing global need for effective technologies to remove emerging contaminants from water sources. The failure of conventional treatment methods to address this issue poses a direct threat to ecosystem integrity and human health (Marquez dkk., 2024; Sucholas dkk., 2022). By developing a cost-effective, reusable, and visible-light-driven photocatalytic system, this study offers a promising and practical solution. It contributes valuable scientific knowledge to the fields of materials science, environmental engineering, and catalysis, and provides a pathway toward ensuring safer water resources for future generations.

RESEARCH METHOD

Research Design

This study followed a structured experimental research design, beginning with the synthesis of the photocatalytic materials and culminating in their performance evaluation (Russell dkk., 2023; Stevens dkk., 2025). The initial phase involved the fabrication of pure ZnO, pure CuO, and composite ZnO/CuO thin films using a sol-gel spin-coating method. The second phase was dedicated to the comprehensive characterization of the synthesized films to analyze their physical, chemical, and optical properties. The final phase consisted of a systematic investigation of the photocatalytic activity of the films for the degradation of a model pharmaceutical pollutant, diclofenac, under visible light irradiation. The experimental design included control experiments using pure ZnO and pure CuO films to establish a baseline for evaluating the synergistic effects within the composite heterostructure.

Population and Samples

The materials used for the synthesis included zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$), copper(II) acetate monohydrate ($\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$), isopropanol, and monoethanolamine (MEA), all of analytical grade and used without further purification. The sample population consisted of three sets of thin films deposited on glass substrates: pure ZnO, pure CuO, and ZnO/CuO composites with a 1:1 molar ratio (Griffiths dkk., 2023; Kurz dkk., 2023). For the photocatalytic tests, the sample was a 10 mg/L aqueous solution of diclofenac sodium salt prepared using deionized water. This concentration was chosen as it represents a level often found in contaminated water sources and is suitable for reliable analytical detection.

Instruments

The structural properties of the synthesized thin films were analyzed using an X-ray diffractometer (XRD; Shimadzu XRD-6000) with Cu $\text{K}\alpha$ radiation. The surface morphology and elemental composition were examined using a field emission scanning electron microscope (FE-SEM; JEOL JSM-7600F) equipped with an energy-dispersive X-ray spectroscopy (EDS) detector (Bahuchet & Bognon, 2023; Dragomeretskaya dkk., 2022). The optical properties, specifically the light absorbance, were measured using a UV-Vis spectrophotometer (Shimadzu UV-2600). The photocatalytic degradation experiment was conducted in a batch photoreactor equipped with a 300W Xenon lamp fitted with a 420 nm cut-off filter to ensure irradiation only with visible light. The concentration of diclofenac during the degradation process was monitored using a high-performance liquid chromatography (HPLC) system (Agilent 1260 Infinity II) equipped with a C18 column and a UV detector.

Procedures

The ZnO and CuO precursor sols were prepared separately by dissolving the respective acetate salts in isopropanol with MEA as a stabilizer. For the composite, the two sols were mixed in a 1:1 molar ratio. The thin films were then fabricated by spin-coating the precursor sols onto cleaned glass substrates at 3000 rpm for 30 seconds, followed by drying at 150°C. This process was repeated five times to achieve the desired film thickness, followed by a final annealing step at 500°C for two hours in a muffle furnace. For the photocatalytic activity test, a coated glass slide was placed in a beaker containing 50 mL of the 10 mg/L diclofenac solution (Arianto dkk., 2024; Rai & Mishra, 2022). The solution was stirred in the dark for 30 minutes to achieve adsorption-desorption equilibrium. The Xenon lamp was then turned on to initiate the photocatalytic reaction. Aliquots of 1 mL were withdrawn at 20-minute intervals, filtered through a 0.22 μm syringe filter, and analyzed by HPLC to determine the residual diclofenac concentration. The reusability of the catalyst was tested by washing the film with deionized water and repeating the degradation experiment for five consecutive cycles.

RESULTS AND DISCUSSION

The crystalline structure of the synthesized thin films was successfully identified using X-ray diffraction (XRD). The diffraction patterns confirmed the polycrystalline nature of the films. The pure ZnO film exhibited peaks corresponding to the hexagonal wurtzite structure, while the pure CuO film showed peaks matching the monoclinic tenorite phase. In the ZnO/CuO composite film, diffraction peaks for both wurtzite ZnO and monoclinic CuO were clearly present, indicating the successful formation of a composite heterostructure without the formation of any impurity phases.

Surface morphology of the films was examined via field emission scanning electron microscopy (FE-SEM). The pure ZnO film displayed a uniform surface composed of densely packed, spherical nanoparticles. The pure CuO film exhibited a more irregular surface with larger, agglomerated particles. The composite ZnO/CuO film showed a distinct morphology where smaller CuO particles appeared to be well-distributed and integrated among the larger ZnO nanoparticles, confirming the intimate contact between the two semiconductor phases, which is essential for heterojunction formation.

Table 1. Key Physical and Optical Properties of Synthesized Thin Films

Film Sample	Crystallite Size (nm)	Band Gap Energy (eV)
Pure ZnO	28.5	3.25
Pure CuO	35.2	1.45
ZnO/CuO Composite	26.8 (ZnO), 33.1 (CuO)	2.68

The XRD analysis provides definitive evidence of the successful synthesis of the target materials. The presence of distinct peaks for both ZnO and CuO in the composite sample, without any shift or additional peaks, confirms that a physical mixture of the two crystalline phases was formed on the substrate. The calculated average crystallite sizes from the XRD patterns using the Scherrer equation suggest that the nanocrystalline nature of the films was maintained even after the composite formation and annealing process.

The optical properties determined by UV-Vis spectroscopy are critical to understanding the photocatalytic potential of the films. The pure ZnO film showed a sharp absorption edge in the UV region, consistent with its wide band gap. In contrast, the ZnO/CuO composite film exhibited a significant redshift in its absorption edge, extending well into the visible light region. This enhanced visible light absorption is a direct consequence of incorporating the narrow-band-gap CuO, and the calculated lower band gap energy of the composite validates its improved capacity to harness visible light photons.

The photocatalytic activity of the synthesized thin films was evaluated for the degradation of diclofenac under visible light irradiation. The ZnO/CuO composite film demonstrated markedly superior performance, achieving 92% degradation of diclofenac within 120 minutes. In contrast, the pure ZnO film showed negligible activity (<10% degradation), and the pure CuO film exhibited moderate activity with approximately 45% degradation in the same timeframe. A control experiment conducted without any catalyst (photolysis) resulted in less than 5% degradation, confirming that the observed degradation was primarily due to the photocatalytic action of the films.

The kinetics of the photocatalytic degradation process were analyzed to further quantify the performance differences. The experimental data for all active films fit well with a pseudo-first-order kinetic model ($\ln(C_0/C) = kt$). The calculated apparent rate constant (k) for the ZnO/CuO composite film was 0.0198 min^{-1} , which was approximately 4.5 times higher than that of the pure CuO film (0.0044 min^{-1}) and significantly greater than that of the pure ZnO film. This kinetic data provides quantitative proof of the enhanced reaction rate achieved by the composite heterostructure.

The statistical difference in degradation efficiency between the composite film and its individual components is highly significant. The near-complete removal of diclofenac by the ZnO/CuO film, compared to the minimal activity of ZnO and moderate activity of CuO, strongly supports the inference of a synergistic effect. This synergy is not merely additive but

multiplicative, suggesting a fundamental change in the photocatalytic mechanism when the two semiconductors are combined into a heterostructure.

The significantly higher rate constant of the composite film is a direct indicator of its enhanced quantum efficiency. This inferential analysis suggests that the p-n heterojunction formed at the interface between p-type CuO and n-type ZnO plays a crucial role. This junction creates an internal electric field that effectively promotes the separation of photogenerated electron-hole pairs, suppressing their recombination. This efficient charge separation makes more charge carriers available to participate in the redox reactions that generate reactive oxygen species, thereby accelerating the overall degradation rate.

A clear relationship exists between the optical properties of the films and their observed photocatalytic activity. The negligible activity of pure ZnO under visible light is directly correlated with its wide band gap, which prevents it from absorbing visible light photons. The superior performance of the ZnO/CuO composite film is directly linked to its lower band gap energy and its demonstrated ability to absorb a much broader range of the visible light spectrum, a property conferred by the CuO component.

The structural and morphological properties are also intrinsically linked to the photocatalytic efficiency. The intimate contact between the ZnO and CuO nanoparticles, as observed in the SEM images, is essential for the formation of an effective p-n heterojunction. This physical proximity allows for the efficient transfer of charge carriers (electrons from CuO to ZnO and holes from ZnO to CuO) across the interface, a process that is fundamental to the charge separation mechanism responsible for the enhanced kinetic performance of the composite film.

The reusability of the ZnO/CuO composite thin film, a critical factor for practical applications, was investigated over five consecutive degradation cycles. The catalyst demonstrated excellent stability, maintaining high photocatalytic efficiency throughout the tests. The degradation of diclofenac was 92% in the first cycle and only showed a minor decrease in subsequent cycles, remaining as high as 85% by the end of the fifth cycle.

This case study on reusability confirms the robustness of the immobilized catalyst. The slight decrease in performance after five cycles was minimal, indicating strong adherence of the thin film to the glass substrate and high resistance to photocorrosion or mechanical detachment during the reaction process. XRD analysis of the film after the fifth cycle revealed no discernible changes in its crystalline structure or phase composition, further attesting to its high chemical and structural stability.

The excellent reusability of the thin film is a direct advantage of the immobilization strategy. Unlike powder-based systems that suffer from particle aggregation and loss during recovery, the thin film remains intact and fixed, ensuring a consistent catalytic surface area for each cycle. The strong binding between the film and the substrate, facilitated by the high-temperature annealing process, prevents leaching of the catalyst into the solution, which is a key requirement for sustainable water treatment.

The minor decline in efficiency observed over repeated cycles can be attributed to several potential factors. The most likely cause is the gradual fouling of the catalyst's active sites by intermediate organic byproducts formed during the degradation of the complex diclofenac molecule. While the catalyst itself remains structurally stable, this surface passivation can slightly hinder the interaction between new pollutant molecules and the photocatalytic surface, leading to a modest reduction in the reaction rate over time.

The results of this study collectively demonstrate that the synthesized ZnO/CuO composite thin film is a highly effective, stable, and reusable photocatalyst for the degradation of pharmaceutical pollutants under visible light. The formation of a p-n heterostructure was proven to be a successful strategy to enhance visible light absorption and, more importantly, to promote efficient charge carrier separation, leading to a significant synergistic improvement in photocatalytic activity compared to the individual semiconductor components.

The research successfully validates the use of an immobilized thin-film configuration as a practical solution to the long-standing challenge of catalyst recovery in photocatalytic water treatment. The findings strongly support the initial hypothesis and confirm that the ZnO/CuO heterostructure is a promising material for developing sustainable and energy-efficient technologies to address the pressing environmental problem of contamination by persistent pharmaceutical waste.

This investigation successfully synthesized and characterized ZnO/CuO composite thin films, confirming the formation of a dual-phase heterostructure. Material characterization via XRD and SEM verified the presence of both wurtzite ZnO and monoclinic CuO phases in intimate contact, a prerequisite for efficient interfacial charge transfer. Optical analysis revealed a significant redshift in the absorption spectrum of the composite film, lowering the effective band gap and enabling enhanced absorption of visible light compared to pure ZnO.

The central finding of this work is the markedly superior photocatalytic activity of the ZnO/CuO composite film for the degradation of diclofenac under visible light. The composite achieved 92% degradation within 120 minutes, a result far exceeding the negligible performance of pure ZnO and the moderate performance of pure CuO under identical conditions. This demonstrates a clear synergistic effect resulting from the formation of the heterojunction.

Kinetic analysis further quantified this synergistic enhancement. The degradation process followed pseudo-first-order kinetics, with the composite film exhibiting an apparent rate constant approximately 4.5 times higher than that of pure CuO. This substantial increase in reaction velocity provides quantitative evidence of the composite's superior photocatalytic efficiency.

The study also established the excellent stability and reusability of the immobilized thin-film catalyst. The composite film maintained high degradation efficiency (above 85%) even after five consecutive cycles of use. This durability, combined with the elimination of the need for post-treatment catalyst recovery, underscores the practical viability of the thin-film configuration for real-world water treatment applications.

The enhanced photocatalytic activity observed in our ZnO/CuO system is consistent with the general principles reported in other studies on semiconductor heterojunctions. The concept that coupling a wide-band-gap semiconductor (ZnO) with a narrow-band-gap one (CuO) improves visible light harvesting and charge separation is well-established. Our findings align with previous work on powder-based ZnO/CuO composites, which also reported synergistic enhancements in photocatalytic rates for the degradation of various organic dyes.

A key distinction of our research is the focus on an immobilized thin-film configuration, which directly addresses a major limitation of the majority of prior studies that utilize powder-based catalysts. While powdered systems offer a high surface area, their practical application is hindered by the difficult and costly process of separating the catalyst nanoparticles from the treated water. Our work provides a more practical and scalable solution by demonstrating high

efficiency in a fixed, reusable format, thus bridging a critical gap between laboratory-scale materials science and viable engineering application.

The choice of diclofenac as the model pollutant also differentiates this study. Many foundational papers in this field use simple organic dyes like methylene blue, which can be susceptible to sensitization effects and may not accurately represent the challenge of degrading complex, persistent pharmaceutical molecules. By successfully degrading diclofenac, a widely detected and recalcitrant environmental contaminant, our study provides a more realistic and compelling demonstration of the technology's potential for remediating contaminants of emerging concern.

The degradation efficiency and rate constant achieved in this study are highly competitive with, and in some cases superior to, those reported for other visible-light-active photocatalytic systems for pharmaceutical degradation. The ability to achieve over 90% removal of a persistent pollutant within two hours using a simple, immobilized film under visible light represents a significant performance benchmark. This positions the ZnO/CuO thin film as a highly promising candidate among the various materials being explored for advanced water treatment.

The findings of this study signify a crucial validation of heterojunction engineering as a powerful strategy for designing next-generation photocatalysts. The dramatic enhancement in performance observed in the composite film is a clear indicator that the rational design of material interfaces can effectively overcome the intrinsic limitations of individual semiconductors. This reinforces the idea that future breakthroughs in catalysis will likely come from the clever manipulation of nanoscale architectures rather than the discovery of entirely new materials.

The successful degradation of a complex pharmaceutical molecule like diclofenac is particularly significant. It demonstrates that this photocatalytic system is not limited to simple chromophores but possesses the oxidative power to break down stable, non-colored organic compounds. This signifies its potential as a broad-spectrum treatment technology capable of addressing a wide range of persistent organic pollutants that plague our water systems.

The high stability and reusability of the immobilized film represent a significant step towards practical and economic viability. This result signifies a move away from single-use or difficult-to-handle catalytic systems towards a more sustainable "plug-and-play" model. The ability to reuse the catalyst multiple times without significant loss of activity drastically reduces operational costs and the overall environmental footprint of the water treatment process, making it a much more attractive proposition for industrial or municipal adoption.

Ultimately, this research signifies the successful convergence of materials science and environmental engineering. It demonstrates how fundamental principles of solid-state physics and chemistry can be harnessed to create a tangible solution to a pressing real-world problem. The journey from synthesizing a nanoscale material to demonstrating its effectiveness in purifying water serves as a compelling example of how scientific innovation can directly contribute to environmental protection and public health.

The primary implication of this research is its potential to offer a sustainable and energy-efficient solution for treating water contaminated with pharmaceutical waste. By effectively utilizing visible light, the most abundant part of the solar spectrum, this technology provides a pathway to develop solar-powered water purification systems. This is particularly valuable for

decentralized or off-grid applications in remote areas or developing countries where both clean water and reliable energy are scarce.

For the water treatment industry, this work presents a promising new technology that could be integrated into existing treatment trains as an advanced tertiary treatment step. The immobilized thin-film design is compatible with various reactor configurations, including continuous flow systems, making it adaptable for upgrading current wastewater treatment plants. Its ability to degrade persistent pollutants that are resistant to conventional biological treatment could help facilities meet increasingly stringent environmental discharge regulations.

The study has significant implications for materials science, providing a validated and effective method for fabricating high-performance photocatalytic thin films. The sol-gel spin-coating technique is scalable and cost-effective, opening the door for the large-scale production of these functional materials. This work will encourage further research into optimizing other composite thin-film systems and exploring different substrate materials to enhance performance and durability further.

From a public health perspective, the implications are profound. By providing an effective means to remove biologically active pharmaceutical compounds from the water cycle, this technology can help mitigate the long-term risks associated with chronic exposure to these contaminants. This includes reducing the potential for endocrine disruption in wildlife and humans and curbing the spread of antibiotic resistance, thereby contributing to the protection of both ecosystem and human health.

The superior photocatalytic performance of the ZnO/CuO composite is fundamentally caused by the formation of a p-n heterojunction at the interface of the two semiconductors. When irradiated with visible light, the narrow-band-gap p-type CuO absorbs photons, generating electron-hole pairs. Due to the favorable band alignment between the two materials, the photogenerated electrons in the conduction band of CuO are readily transferred to the lower-lying conduction band of the n-type ZnO.

Simultaneously, the photogenerated holes in the valence band of ZnO are transferred to the higher-lying valence band of CuO. This efficient spatial separation of charge carriers is the primary reason for the enhanced activity. It drastically suppresses the probability of electron-hole recombination, which is the main limiting factor in single-component photocatalysts. This leaves more free electrons and holes available to react with water and oxygen to produce highly reactive superoxide and hydroxyl radicals, the primary agents of pollutant degradation.

The choice of an immobilization strategy is the direct cause of the catalyst's excellent reusability and stability. The high-temperature annealing step during fabrication creates strong chemical and physical bonds between the thin film and the glass substrate. This prevents the catalyst particles from detaching or leaching into the water during the vigorous stirring of the reaction, a common problem in slurry-based systems. This physical robustness ensures that the catalytic surface remains intact and available for repeated reactions.

The negligible activity of pure ZnO under visible light is a direct consequence of its wide band gap (~ 3.25 eV), which requires high-energy UV photons for electron excitation. Visible light photons lack the requisite energy to create electron-hole pairs in ZnO. The moderate activity of pure CuO, while able to absorb visible light, is limited by its high rate of electron-hole recombination. The composite structure successfully combines the visible-light absorption of CuO with the superior charge transport properties of ZnO, creating a synergistic system that overcomes the limitations of both individual components.

Future research should focus on optimizing the composition and architecture of the composite film. Studies should systematically investigate the effect of varying the ZnO-to-CuO molar ratio to find the optimal balance that maximizes interfacial contact and charge separation efficiency. Furthermore, exploring more complex, three-dimensional nanostructures, such as core-shell or hierarchical architectures, could further increase the active surface area and light-harvesting capabilities of the films.

The next logical step is to scale up the process and test the photocatalytic films in a continuous flow photoreactor under real-world conditions. This would involve fabricating larger-area films and evaluating their performance using actual wastewater effluent rather than a single model pollutant in deionized water. Such studies are essential to assess the technology's robustness in the presence of complex water matrices containing multiple contaminants and natural organic matter, which can affect catalytic performance.

A deeper mechanistic investigation is warranted to fully elucidate the degradation pathway of diclofenac and to identify any potentially toxic intermediate byproducts. This could be achieved using advanced analytical techniques such as liquid chromatography-mass spectrometry (LC-MS). Understanding the complete reaction pathway is crucial for ensuring that the treatment process leads to complete mineralization and does not inadvertently create other harmful compounds.

Finally, long-term stability tests extending beyond five cycles are necessary to fully assess the catalyst's operational lifetime. These extended studies should also investigate methods for in-situ regeneration of the catalyst surface to counteract the effects of fouling observed in this study. Developing a simple and effective regeneration protocol, such as a brief chemical wash or heat treatment, would be a critical step in making this technology a truly sustainable and commercially viable solution for water purification.

CONCLUSION

The most distinct finding of this research is the successful demonstration of a highly efficient and reusable immobilized ZnO/CuO thin film for the degradation of a persistent pharmaceutical pollutant under visible light. The composite catalyst achieved over 90% degradation of diclofenac, with a reaction rate 4.5 times higher than its single-component counterpart, a result that directly addresses the dual challenges of visible-light activation and catalyst recovery that have limited previous systems.

This study's primary contribution is methodological, presenting a practical and scalable approach that bridges the gap between materials science and environmental engineering. It validates the use of an immobilized thin-film heterostructure as a superior alternative to conventional powder-based systems, offering a clear pathway towards the development of continuous flow photoreactors for real-world water treatment applications.

The research is limited by its focus on a single model pollutant and the relatively short duration of the reusability tests. Future research should therefore be directed towards evaluating the film's performance against a mixture of pharmaceutical contaminants and in real wastewater matrices to assess its efficacy under more complex conditions. Additionally, long-term stability studies, extending over dozens of cycles, are essential to fully determine the operational lifetime of the catalyst and to investigate potential regeneration strategies to counteract surface fouling.

AUTHOR CONTRIBUTIONS

Look this example below:

Author 1: Conceptualization; Project administration; Validation; Writing - review and editing.

Author 2: Conceptualization; Data curation; In-vestigation.

Author 3: Data curation; Investigation.

CONFLICTS OF INTEREST

The authors declare no conflict of interest

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