The Performance of Semiconductor Photocatalysts using UV-visible light irradiation– A Comparative Study of CuS and conventional TiO_2

Caressa Munien*, Emmanuel Kweinor Tetteh, and Sudesh Rathilal

Abstract*—Global wastewater remediation requires optimizing the existing photocatalysis wastewater treatment technology efficiency. The primary limitations of photocatalysis include low efficiency in utilizing the solar spectrum, rapid charge recombination, and challenges related to scalability for practical applications. Common photocatalysts, such as conventional titanium dioxide (TiO_2), have a large bandgap and are only activated by ultraviolet (UV) light. Since UV light constitutes only about 5% of the solar spectrum, a large portion of available solar energy, including visible and infrared light, is left unutilized. Hence, developing alternative efficient visible-light-activated photocatalysts is crucial for harnessing more of the abundant solar spectrum to address global environmental and energy challenges like water purification and sustainable fuel production. Therefore, this study aimed to investigate the comparative performance of Copper Sulphide (CuS) and TiO_2 semiconductor photocatalysts under UV-visible irradiation using synthetic wastewater (SW) and raw wastewater (RW). The water quality parameters, chemical oxygen demand (COD), turbidity, and color of the treated effluent were analyzed to evaluate the efficacy at optimum conditions. The optimal solution investigative conditions selected were catalyst load (2 g/L), mixing speed (120 rpm), and exposure time (30 minutes) obtained from Design Expert Software. It was found that the Actual CuS (SW) and CuS (RW) follow the same trend as that of the Predicted CuS (SW). The optimum contaminant removal efficiencies for COD, turbidity, and color using Actual CuS (SW) were 46.8%, 73.4%, and 45.5%, and the optimum efficiencies for CuS (RW) are 45,1%, 90,03%, and 59,58%, respectively. The removal efficiencies obtained for CuS are higher in comparison to those of TiO_2 for both (SW) and (RW). Therefore, the CuS photocatalyst was considered superior.

***Keywords*—copper sulphide; raw wastewater; synthetic wastewater; titanium dioxide; UV-visible**

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I. Introduction

The presence of organic micropollutants (OMPs) in water sources is a significant and growing global concern, as it can lead to water quality degradation, impacting both human and environmental health, and sustainable development [1]. The water-energy crisis in South Africa (SA), particularly due to the disruption in energy supply (load-shedding) for wastewater (WW) treatment, can lead to increased OMPs in WW as inadequate treatment processes discharge these pollutants and contaminate water sources [2]. Conventional treatment technologies suffer from limitations, such as high energy consumption and operational costs, low OMP removal efficiency, transformation into harmful byproducts, and the generation of large volumes of sludge requiring disposal [3, 4]. Hence, exploring the development of advanced, innovative, and eco-friendly water treatment technologies to remove OMPs and mitigate their impact is crucial [5-10]. Photocatalytic degradation (Advanced Oxidation Processes) presents a viable route toward sustainable and affordable water treatment solutions, utilizing sunlight and photocatalysts for addressing OMP challenges in WW by degrading pollutants, often at ambient temperature and pressure, and with minimal chemical requirements [11, 12]. Semiconductor photocatalysis leverages the unique properties of semiconductor materials to generate reactive species that degrade pollutants and inorganic pollutants in WW. The mechanism involves several key steps: (i) Light absorption; whereby the photocatalyst absorbs photons with energy equal to or greater than its bandgap, exciting electrons from the valence band to the conduction band, creating electron-hole pairs (excitons) [13], (ii) Charge separation and transport, whereby the photogenerated electrons and holes must be efficiently separated and transported to the surface of the photocatalyst to participate in redox reactions. This step is crucial as recombination of electron-hole pairs can significantly reduce the efficiency of the photocatalytic process [14], (iii) Surface reactions; at the surface, the electrons and holes drive oxidation and reduction reactions. For instance, holes can oxidize water or organic pollutants to generate reactive oxygen species (ROS) like hydroxyl

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radicals, while electrons can reduce oxygen to superoxide radicals [13, 14], and finally (iv) Reactive species formation; the ROS generated during the photocatalytic process are highly reactive and can degrade a wide range of organic pollutants and microorganisms. This makes photocatalysis an effective method for environmental remediation [13-15].

Common semiconductor photocatalysts such a titanium dioxide (TiO_2), bismuth-based materials, graphene-semiconductor nanocomposites, silver-based photocatalysts, and Indium Vanadate ($InVO_2$) are favored for their stability, efficiency, and ability to harness visible light. Their effectiveness is further enhanced through the creation of heterojunctions and optimization of surface properties. Copper Sulphide (CuS) combined with Graphene-nanosheets (GNs), (CuS-GNs), showed enhanced photocatalytic activity due to a larger specific surface area and lower band gap, leading to 100% and 99.8% efficient degradation of Rhodamine B (RhB) and Methylene Blue (MB), respectively, in 30 mins [16]. Cu metal organic frameworks (Cu-MOFs) exhibited high photocatalytic activity for degrading various antibiotics, with superoxide radicals playing a dominant role in the degradation mechanism, leading to 91.45% efficient degradation of oxytetracycline in 60 mins [17]. CuS quantum dots were incorporated into an iron-based MOF (CuS QDs@Fe MIL101), which enhanced visible light absorption and charge separation, leading to 96% degradation efficiency of meloxicam in 45 min [18].

However, the current TiO_2 photocatalytic degradation has limitations. These limitations include physicochemical, engineering, and practical limitations. The physicochemical limitations include (i) Wide bandgap: TiO_2 's bandgap (around 3.0-3.2 eV) restricts its absorption to UV light, which makes up only a small percentage of the solar spectrum, limiting its performance under natural sunlight; (ii) Electron-hole recombination: photogenerated electrons and holes quickly recombine, reducing the number of reactive species (like hydroxyl radicals) available to degrade pollutants and thus decreasing photocatalytic efficiency and (iii) Catalyst separation and recovery: TiO_2 's stable colloidal dispersion in water makes it difficult to separate and recover from treated water, posing practical challenges for reuse and commercial application. The engineering and practical limitations include (i) Low kinetics for unsupported catalysts: while heterogeneous photocatalysis is efficient, the degradation kinetics can be lower when the catalyst is supported, and removing pollutants requires longer treatment times, impacting overall process viability; (ii) Catalyst deactivation: over time, catalysts can become deactivated, reducing their ability to break down pollutants, which is a key challenge for long-term applications and (iii) Energy requirements: to overcome the limited solar response, artificial UV light sources are often needed, which increases the energy demand and cost of the photocatalytic process. These limitations hinder its effectiveness under sunlight and make large-scale application challenging [19].

Thus, additional research assessing alternative visible-light photocatalysts is required to utilize the freely available solar energy for water treatment, to meet the future growing demands for clean water, environmental, and energy technologies (photocatalytic technology) powered by solar energy. Subsequently, this is significant for WW reclamation and to minimize adverse environmental effects [20, 21]. Likewise, addressing OMPs requires integrated approaches that promote advancements in sustainable water technologies, renewable energy efficiency, and pollution prevention for sustainable development [22, 23].

Therefore, this study aimed to investigate the comparative performance of (CuS) and TiO_2 semiconductor photocatalysts under UV-visible irradiation using synthetic wastewater (SW) and raw wastewater (RW). Chemical Oxygen Demand (COD) is a widely used parameter to measure the amount of organic matter in WW, indicating the degree of organic pollution [24-26]. COD measures the amount of organic pollutants in WW, which is crucial for understanding the extent of contamination and the effectiveness of treatment processes [27]. High COD levels indicate the presence of significant organic matter, which can deplete dissolved oxygen in water bodies, adversely affecting aquatic life [28]. Therefore, the water quality parameters, COD, turbidity, and color of the treated effluent were analyzed to evaluate the efficacy of the photocatalysts under UV-visible irradiation at optimum conditions. The optimal solution investigative conditions selected were from the current study's predecessor, a published paper titled "Response Surface Optimization of CuS Photocatalytic Process Using UV-vis Irradiation for Wastewater Treatment," which offered the optimal conditions for the investigation [29] obtained from Design Expert Software.

Moreover, this research aligns with the United Nations' Sustainable Development Goals (SDGs), which involve a commitment to ensure universal and equitable access to safe, affordable, and reliable drinking water (SDG#6: Water Sustainability) [30] and energy services (SDG#7: Energy Sustainability) [31, 32] for all by 2030. Additionally, Africa Agenda 2063 is a strategic framework developed by the African Union (AU) that aligns with the UN's SDGs, aiming to optimize the use of Africa's resources for sustainable growth [33]. Subsequently, this research also aligns with the African Agenda 2063 goals for healthy and well-nourished citizens (#3), blue/ocean economy for accelerated economic growth (#6), and environmentally sustainable and climate resilient economies and communities (#7). Mitigating these challenges as well as achieving the envisioned UN's 2030 Agenda, its SDGs, and the AU's 2063 Agenda is essential. The subsequent sections provide a detailed description of the methodology (section II), experimental setup (section III), results and discussion (section IV), and conclusions (section V).

A. Effluent sample

The raw municipal wastewater effluent samples were obtained from a local eThekwini municipality WWTP located

in Durban, KwaZulu-Natal, South Africa, which was sampled in 25L drums and utilized to conduct this study. Before every experiment, the samples were carefully agitated to guarantee a homogeneous feed combination.

B. Synthetic municipal wastewater

The synthetic wastewater was simulated using 15 L of distilled water, which contained the synthetic water chemical makeup, and 5 L of raw wastewater, which was then homogenized into a solution. This synthetic wastewater solution represents the typical composition for the wastewater treatment plant, as the organics are increased with the addition of chemicals found within the synthetic water makeup. The composition of the chemicals used was adapted from Munien et al. (2023) [34].

C. Effluent sample and characterization

The raw and synthetic wastewater was characterized by the following characteristics, presented in Table I. The critical performance criteria were assessed based on the OMP's removal efficiency concerning the water quality characteristics: pH, turbidity (NTU), COD (mg/L), and color (Pt. Co).

TABLE I
PROPERTIES OF SYNTHETIC AND RAW WASTEWATER BEFORE TREATMENT

Water Quality Parameter	Raw Wastewater	Synthetic Wastewater
pH	7.24	6.98
COD (mg/L)	855.33	8960
Turbidity (NTU)	48.33	307
Color (Pt. Co)	569	2724

D. Chemicals and reagents

All chemicals, reagents, and photocatalysts used in this study were of analytical grade and were supplied by Sigma Aldrich, Durban. The photocatalysts used in this study were Titanium (IV) Oxide (TiO_2) and Copper Sulphide (CuS). The physicochemical characteristics of the semiconductor photocatalysts considered are presented in Table II [35-39].

TABLE II
TITANIUM (IV) OXIDE AND COPPER SULPHIDE PHYSICOCHEMICAL CHARACTERISTICS

Semiconductor Photocatalyst	Band Gap (eV)	Absorbance Wavelength (nm)	Purity
TiO_2	3.2	275-405	ReagentPlus®, ≥99%
CuS	1.6-2.2	380-800	≥99% trace metals basis

E. Analytical Methods

The pH and the turbidity were analyzed using the pH meter HI98130 and the turbidity meter HI98703-02, respectively (HANNA instruments). The COD and color were analyzed by the Spectrophotometer DR 3900 (HACH). The degradation efficiency was monitored according to COD, turbidity, and color removal (responses) percentages, and determined using Equations (1), respectively:

$$\text{Removal \%} = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

Where C_i and C_f are the initial and the final concentrations (mg/L) before and after treatment, respectively [40].

II. EXPERIMENTAL SETUP

A. UV-visible irradiation

The experimental investigation was conducted to assess the comparative performance of semiconductor photocatalysts (CuS and conventional TiO_2) using UV-visible irradiation. The experiments utilizing a UV-visible light source were carried out using a laboratory-scale photochemical reactor (Lelesil Innovative Systems), shown in Figure 1 [34]. The photochemical reactor consists of a reaction vessel that has a 1.5 L capacity and an immersion well made of quartz, which houses the UV lamp. A cold-water circulating tank was used to cool down the immersion well that contains the lamp. A 250 W, 365 nm mercury UV and UV-visible lamp was used. The light intensity (LUX) under UV-vis irradiation was recorded as 1910x100 (191 000) LUX, using an MT940 handheld Lux Meter.

The water quality parameters, chemical oxygen demand (COD), turbidity, and color of the treated effluent were analyzed to evaluate the effectiveness of the UV-visible light source at optimum conditions. The optimal solution investigative conditions selected were (Solution No. 1, Table III): catalyst load (2 g/L); mixing speed (120 rpm), and exposure time (30 minutes) [41] obtained from the experimental Box-Behnken design (BBD) matrix adapted from the response surface methodology (RSM) obtained from the Design Expert Software (version 13.0.5.0). The three (3) input parameters investigated were: Catalyst Load, Exposure Time, and Mixing Speed. The three (3) response outputs (COD, Color, pH) were the treatability performance indicators, which were modeled as a function of the input parameters, whereby the numerical optimization technique was used to ascertain the optimum conditions. Refer to the current study's predecessor, a published paper titled "Response Surface Optimization of CuS Photocatalytic Process Using UV-vis Irradiation for Wastewater Treatment," which offered the optimal conditions for the investigation [29].

The optimal solution investigative conditions were applied to the experimental methodology for each respective photocatalyst (CuS and TiO_2) and using the respective wastewater (synthetic & raw). The experimental methodology includes 2 g/L of the semiconductor photocatalyst introduced into the reactor/immersion well containing 1000 mL (1 L) of wastewater. The reactor was placed in a closed chamber to allow uniform irradiation exposure. The magnetic stirrer speed was set to 120 rpm, and the timer was set to 30 minutes for each run. The left controller was used for the suitable UV-vis lamp. Thereafter, the photochemical reactor start switch was

then initiated. After each run was completed, the samples were collected with a syringe and filtered through a vacuum pump filter (Model: LAB-440; Power: AC220V50HZ). The above procedure was then repeated under identical conditions for each respective photocatalyst (CuS / conventional TiO_2) using the respective wastewater (synthetic/raw).

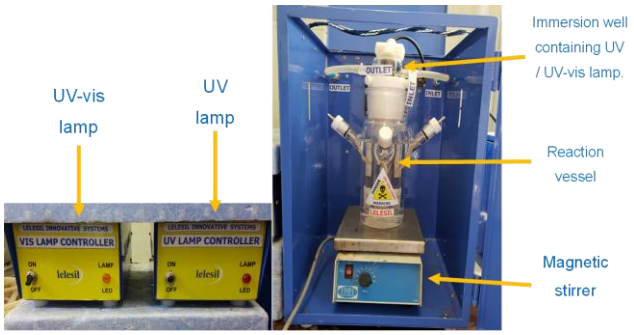

Fig. 1 (L-SPR) Laboratory-scale photochemical reactor

TABLE III
SOLUTIONS GENERATED

No	Cat Load	Mixing Speed	Exposure Time	COD	Turbidity	Color	Desirability	
1	**2**	**119.999**	**29.557**	**47.172**	**75.062**	**48.323**	**0.963**	✓
2	2	119.998	29.762	47.172	75.017	48.257	0.963	
3	2	120.000	30.263	47.174	74.909	48.099	0.963	

III. RESULTS AND DISCUSSION

A. Comparative study of CuS and conventional TiO_2 semiconductor photocatalyst under UV-visible light irradiation

Finally, once the optimal operating parameters were verified, a comparative study was performed whereby the experiment was conducted for CuS and TiO_2 using synthetic wastewater (SW) and raw wastewater (RW). As shown in Figure 2, the Actual CuS (SW) follows the same trend as that of the Predicted CuS (SW). The optimum Predicted CuS (SW) values were 47.2%, 75.1%, and 48.2% for COD, turbidity, and color, respectively. The Actual values for CuS (SW) were 46.8%, 73.4%, and 45.5% for COD, turbidity, and color, respectively, with a minimal difference as discussed in section B, which correlates with that of the predicted results. Finally, once the optimal operating parameters were verified, a comparative study experiment was performed for CuS and Conventional TiO_2 Photocatalyst under UV-visible Light Irradiation using synthetic wastewater (SW) and raw wastewater (RW), with the average contaminant (COD, turbidity, and color) removal efficiency represented respectively as shown in the Figure. 2. The optimum Predicted CuS (SW) contaminant removal efficiencies were 47.2%, 75.1%, and 48.2% for COD, turbidity, and color, respectively (refer to the legend). The optimum Actual CuS (SW) contaminant removal efficiencies were 46.8%, 73.4%, and 45.5% for COD, turbidity, and color, respectively, which correlates with the same trend as that of the Predicted CuS (SW) results, with a minimal difference, as the difference between the Predicted and Actual values was minimal (<5%). This suggests the model's predictability was consistent ($p < 0.05$) at 95% confidence levels. The optimum CuS (RW) contaminant removal efficiencies were 45.10%, 90.03%, and 59.58%, for COD, turbidity, and color, respectively, and correlated to a similar trend to that of the Predicted CuS (SW) and Actual CuS (RW). The COD removal of 45.10% for CuS (RW) is similar to that of Actual CuS (SW) at 46.8% and is in good agreement.

Finally, the Cus removal efficiencies obtained are higher in comparison to those of the conventional TiO_2 for both synthetic wastewater (SW) and raw wastewater (RW). Therefore, with desirable contaminant removal performance at 40%, among CuS and TiO_2 catalysts examined, CuS was considered superior to the conventional TiO_2.

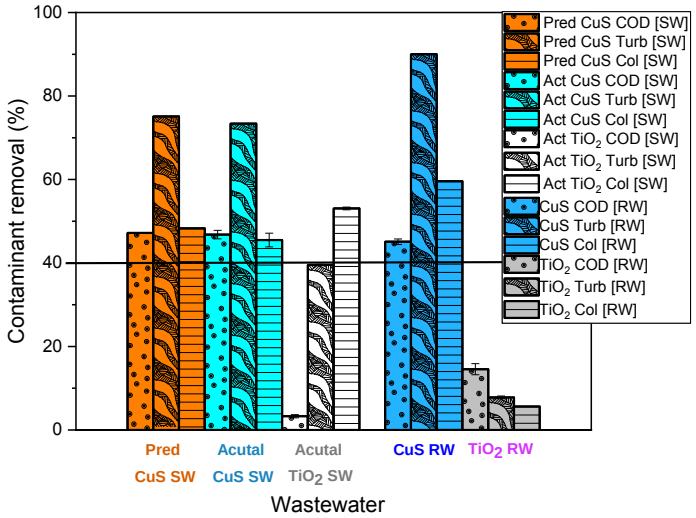

Fig. 2 Comparative study between CuS and TiO_2 using synthetic (SW) and raw wastewater (RW) for contaminant removal efficiency (%)

The primary focus of this research was to degrade the organics, and the results showed an optimum COD removal efficiency at 47% which equates to 4749 mg/L remaining and therefore met the maximum permitted discharge limits of <5000 mg/L (Table VI) [42]. However, the turbidity and color removal efficiency at 73% and 46% equated to 83 NTU and 1471 Pt.Co, which did not meet the maximum permitted discharge limits of <5 NTU and <15 Pt.Co for turbidity and color, respectively, according to the South Africa Bureau of Standards [43] for drinking water (Table IV). This is due to the vacuum pump not being able to completely filter all photocatalyst nanoparticles. Consequently, a post-treatment process is required to enhance the improvement of the water quality (color and turbidity).

TABLE VI
MAXIMUM LIMITS OF PERMITTED DISCHARGES IN SOUTH AFRICA

Parameter	South Africa		Ref.
	Not less than	Not to exceed	
pH (value at 25°C)	5.5	12	[42]
COD	-	5 000 mg/L	[42]
Turbidity	-	5 NTU	[43]
Color	-	15 Pt.Co	[43]

IV. CONCLUSION

A comparative study was performed, whereby the same experiment was conducted for CuS and TiO_2 using synthetic wastewater and raw wastewater. The Actual CuS (SW) and raw wastewater for CuS (RW) follow the same trend as that of Predicted CuS (SW). The optimum contaminant removal efficiencies for COD, turbidity, and color using Actual CuS SW were 46.8%, 73.4%, and 45.5%, and the optimum efficiencies for CuS RW are 45,1%, 90,03%, and 59,58%, respectively. The removal efficiencies obtained for CuS are higher in comparison to those of TiO_2 for both synthetic wastewater (SW) and raw wastewater (RW). Therefore, with desirable performance at 40%, among CuS and TiO_2 catalysts examined, CuS was considered superior to the conventional TiO_2.

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AUTHORS' CONTRIBUTIONS

Conceptualization, C.M., and E.K.T.; methodology, C.M.; software, C.M., and E.K.T.; validation, C.M., and E.K.T.; formal analysis, C.M., and E.K.T.; investigation, C.M..; resources, S.R. and E.K.T.; data curation, C.M.; writing—original draft preparation, C.M., and E.K.T.; writing—review and editing, C.M., S.R. and E.K.T.; visualization, C.M.; supervision, S.R., and E.K.T.; project administration, S.R. and E.K.T. All authors have read and agreed to the published version of the manuscript.

DECLARATION OF COMPETING INTERESTS

We have no financial or personal affiliations that could have influenced this paper's findings.

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Recently, Ms Caressa was honored with the prestigious Research Excellence Award for Next-Generation Researchers (NRF Awards 2025) in recognition of outstanding academic performance and research impact. Additionally, she was also invited to present at the NRF Next Generation and Emerging Researchers Symposium, where she showcased her work to a national audience of scholars and policymakers. She was honored to be invited as a role model and a guest speaker at the NRF science engagement. Similarly, she was also pleased to be invited as a Guest Speaker at the Horticultural Research Colloquium (HRC) event at DUT, where she was acknowledged for her essential contributions towards invaluable knowledge exchange and inspiration. Furthermore, she was the Famelab

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Ms. Caressa's research vision aims to continue making significant contributions towards water, energy, environmental and societal sustainability, targeting the African Union (AU) and the United Nation's Sustainable Development Goals for an efficient and sustainable future for all, making a lasting impact on both the scientific community, society, and the world as a whole, towards nourishing Mother Nature and her beautiful creations, both human and animal.