

Article

CuO-TiO₂-Saponite Ternary Nanocomposite for Efficient Removal of Bromocresol Green Dye

Pollyana Trigueiro ¹, Willams A. Albuquerque ¹, Aimée G. Jerônimo ¹, Monica Sá Rodrigues ²,
Emanoel L. Tavares França ² and Ramón Raudel Peña-García ^{1,*}

¹ Postgraduate Program in Physical Engineering, Academic Unit of Cabo de Santo Agostinho, Federal Rural University of Pernambuco (UFRPE), Cabo de Santo Agostinho 54.518-430, PE, Brazil; pollyanatrigueiro@gmail.com (P.T.); willams.albuquerque@ufrpe.br (W.A.A.); aimeejeronimo@gmail.com (A.G.J.)

² Department of Physics, Federal University of Pernambuco, Recife 50740-540, PE, Brazil; monica.rsa@ufpe.br (M.S.R.); emanoel.laurentan@ufpe.br (E.L.T.F.)

* Correspondence: rraudelp@gmail.com or ramon.raudel@ufrpe.br

Abstract: This study presents the synthesis of a CuO-TiO₂-saponite ternary nanocomposite via a hydrothermal method, designed to efficiently remove bromocresol green dye. Characterization techniques, including X-ray diffraction, Fourier transform infrared spectroscopy, and scanning electron microscopy, confirmed significant interactions between metal oxide nanoparticles and the clay mineral matrix. Diffuse reflectance and photoluminescence analyses revealed a narrow band gap and surface defects, such as oxygen vacancies, enhancing the material's photocatalytic properties. Under UV irradiation, the nanocomposite achieved 83% discoloration of bromocresol green dye within 150 min. The inhibitor studies identified hydroxyl and superoxide radicals as key species in the degradation mechanism. This work underscores the potential of clay-mineral-based nanocomposites, where clay minerals function both as structural support and as enhancers of the semiconductor's photocatalytic activity.

Keywords: saponite; CuO; TiO₂; heterogeneous photocatalysis; environmental research



Citation: Trigueiro, P.; Albuquerque, W.A.; Jerônimo, A.G.; Rodrigues, M.S.; França, E.L.T.; Peña-García, R.R. CuO-TiO₂-Saponite Ternary Nanocomposite for Efficient Removal of Bromocresol Green Dye. *Minerals* **2024**, *14*, 1268. <https://doi.org/10.3390/min14121268>

Academic Editor: Leonid Dubrovinsky

Received: 12 November 2024

Revised: 10 December 2024

Accepted: 11 December 2024

Published: 13 December 2024



Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Population growth and urbanization have significantly intensified industrialization, leading to the contamination of water bodies with organic pollutants. The textile sector, while vital to many economies, stands out as a major contributor to this issue due to its generation of dye-rich wastewater, which poses severe risks to aquatic ecosystems [1,2]. This growing environmental challenge has driven scientific efforts toward innovative solutions for restoring water resources.

Heterogeneous photocatalysis is a promising method for environmental remediation, relying on semiconductors, light sources, and photochemical reactions at the semiconductor-environment interface [3–5]. These reactions generate reactive oxygen species (ROS), which are critical for degrading pollutants. Titanium dioxide (TiO₂) stands out due to its crystalline structure, high oxidation potential, and excellent electronic mobility, which enhance its photocatalytic efficiency [6]. Similarly, copper oxide (CuO) offers complementary properties, such as a narrow band gap, robust electrochemical activity, and high stability in various environments [7].

Enhancing the specific surface area of metal oxides has been shown to improve their photocatalytic activity, as it increases the number of active sites available for chemical degradation [8–11]. A promising strategy for enhancing the photocatalytic potential of metal oxides is immobilizing them onto a solid support. Among various substrates, clay minerals are particularly advantageous due to their low cost, widespread availability, environmental compatibility, high surface area, adsorption capacity, and ion exchange properties [12–17].

Clay minerals enhance the material's dispersibility, stability, electron trapping, and overall functionality [18]. Damaceno et al. [19] developed a ZnO–saponite nanocomposite for the photocatalytic removal of Rhodamine B under visible light irradiation. Their findings revealed that the combination of adsorption and photocatalysis significantly enhanced dye removal, achieving an 85% reduction in 270 min. Similarly, Mylarappa et al. [20] used natural clay from Karnataka to create a ZnO–clay nanocomposite, which exhibited dual functionality as both a biomolecule sensor and a photocatalyst. Under UV light irradiation, the nanocomposite achieved a 90% removal of malachite green dye within 90 min. Talamí et al. [21] synthesized a TiO₂–CuO–clay nanocomposite for the degradation of tartrazine dye, reporting a 62.5% removal efficiency under visible light, surpassing the performance of TiO₂–clay and TiO₂ alone. Pouthika et al. [22] explored the photocatalytic potential of a CuO–SnO₂–halloysite nanocomposite for removing Congo red dye, tetracycline, and atrazine. Their results demonstrated excellent activity under visible light, with removal efficiencies of up to 85% for Congo red, 80% for tetracycline within 90 min, and 74% for atrazine after three hours.

This study aims to synthesize a nanocomposite made up of copper oxide (CuO) and titanium dioxide (TiO₂) nanoparticles, which are immobilized within a matrix of layered clay mineral, specifically saponite. Among clay minerals, saponite is noteworthy for its chemical and thermal stability, surface acidity, and small particle size. It contains silanol and hydroxyl groups that can interact effectively with metal nanoparticles [19,23]. Additionally, saponite's high surface area and notable surface reactivity enhance its ability to adsorb organic pollutants. This improved adsorption promotes diffusion and increases the contact between pollutant molecules and semiconductor surfaces, thereby enhancing the photocatalytic efficiency for degrading bromocresol green dye. This study also examines the influence of the nanocomposite's structural, morphological, and optical properties, as well as the role of scavengers in the photocatalytic process.

2. Materials and Methods

2.1. Synthesis

The synthesis utilized high-purity materials, including titanium isopropoxide (97%, Aldrich) and copper nitrate (98%, Dynamics). Saponite was prepared according to a previously established protocol [19,23], with its ideal half-unit cell formula defined as Na_{0.4}[(Si_{3.6}Al_{0.4})Mg₃O₁₀(OH, F)₂]·nH₂O. Distilled water and ethanol were used for washing and purification. The Ti–Cu molar ratio was fixed at 1:1, and 1 g of raw saponite was added to maintain the optimal colloidal stability of the ternary system. Initially, 1 g of saponite was dispersed in 30 mL of distilled water under constant agitation. Simultaneously, 0.6 mL of titanium isopropoxide was dissolved in 10 mL of isopropanol and stirred for 30 min. The two solutions were then combined and mixed for 2 h, followed by the addition of 0.482 g of copper nitrate, with further stirring for 1 h. The mixture was transferred to a hydrothermal reactor and heated at 120 °C for 15 h. After thorough washing with distilled water and ethanol, the final product was calcined at 500 °C for 2 h under airflow, yielding the TSC500 sample.

2.2. Characterization

The samples were characterized using various techniques. Structural phase confirmation was performed with an X-ray diffractometer (D8 Advance, Bruker) using Cu–K α radiation ($\lambda = 1.5406$ Å) and Bragg–Brentano geometry, with measurements taken between 2° and 80° (2 θ). The samples were analyzed without specific orientation or external agents such as ethylene glycol. Fourier transform infrared spectroscopy (FTIR) was conducted using a Shimadzu IRRXcross spectrometer with an ATR module, employing 45 scans at a resolution of 4 cm^{−1} over the 4000–600 cm^{−1} range.

Morphological analysis was carried out via scanning electron microscopy (SEM) using a TESCAN MIRA3 under 10 kV accelerating voltage, 10 kx magnification, an SE detector, and a 31.6 mm working distance. To improve conductivity and image resolution, samples

were coated with a thin gold layer to prevent surface charging effects. Optical properties were investigated through diffuse reflectance spectroscopy (DRS) with a Shimadzu UV-2700 UV-VIS spectrometer and photoluminescence (PL) analysis using a Horiba-Jobin Yvon Fluorolog-3 spectrofluorometer.

2.3. Irradiation Tests

The decolorization of bromocresol green dye was carried out in a borosilicate reactor connected to a thermostatic bath maintained at 24 °C. A 160 W UV lamp served as the light source, and the process was conducted for 150 min. The photocatalyst concentration was 0.5 g L⁻¹, and the initial dye concentration was 30 mg L⁻¹ in a 100 mL model solution. Before turning on the lamp, the system was allowed to reach adsorption–desorption equilibrium in the dark. Samples were collected at regular intervals for analysis. The decolorization rate was monitored by measuring changes in the maximum absorption band of the dye at 616 nm using a spectrophotometer (Shimadzu, Kyoto, Japan, UV-2700) across a wavelength range of 200–800 nm. The dye removal efficiency was calculated using the equation $DR (\%) = ((C_0 - C)/C_0) \times 100$, where C and C_0 represent the concentrations at the time point of irradiation and the initial concentration, respectively. Scavenger tests were performed to identify the primary reactive species involved in the photocatalytic decolorization process. Irradiation experiments were conducted under the same conditions as the photocatalysis tests, using UV light for 150 min. Specific amounts of scavengers were added at the beginning of the reaction, including 0.0086 g of silver nitrate (AgNO₃) as an electron (e⁻) scavenger, 0.0075 g of ethylene diamine tetraacetic acid (EDTA) as a hole (h⁺) scavenger, 406 µL of methanol (MeOH) to scavenge hydroxyl radicals (•OH), and 406 µL of chloroform (CHCl₃) to scavenge superoxide radicals (•O₂⁻).

3. Results

3.1. Structural Analysis

The crystalline phase analyses of the raw saponite and synthesized nanocomposite are shown in Figure 1. Typical reflections for saponite appear at 6.4° ($d = 13.7$ Å), 19.7° ($d = 4.50$ Å), 28° ($d = 3.18$ Å), 35.6° ($d = 2.52$ Å), 53° ($d = 1.73$ Å), and 60.8° ($d = 1.52$ Å), corresponding to the (001), (110), (004), (201), (301), and (060) planes, respectively (Figure 1a). The peak at 60.8° confirms the trioctahedral structure of the clay mineral [23–26]. An additional diffraction peak at 71.6° ($d = 1.32$ Å) is associated with the layered structure typical of smectite-type clay minerals. Other authors have noted this peak in the literature [27,28]. It corresponds to layers of smectites, which have a layered structure and characteristic spacing between their crystalline sheets. This may be related to synthesis conditions, such as reaction time and temperature [27,28]. In contrast, the XRD pattern of the CuO-TiO₂-saponite nanocomposite (Figure 1b) displays a prominent signal at approximately 8.0° ($d = 11.04$ Å), corresponding to the (001) plane of saponite. As observed, there is a noticeable change in the interplanar distance (for the (001) plane) between raw saponite and the CuO-TiO₂-saponite nanocomposite. The integration of TiO₂ and CuO on the surface and potentially within the interlayers of saponite likely induces contractions in the lamellar structure. This effect arises from the interactions between the metal oxides and the functional groups of the clay, such as Si-O and Mg-OH, which may introduce additional attractive forces, resulting in a slight compression of the layers and a reduction in the interplanar spacing. Additionally, the surface charges of the TiO₂ and CuO nanoparticles can alter the interactions between the saponite layers, promoting a closer alignment of the layers. Moreover, the redistribution of charges induced by the oxides further contributes to this structural contraction. Finally, the hydrothermal synthesis process combined with high-temperature calcination likely facilitated the reorganization of the clay structure, leading to a more compact stacking of the layers. Nanoparticles further enhance this effect, which may serve as structural reinforcement agents.

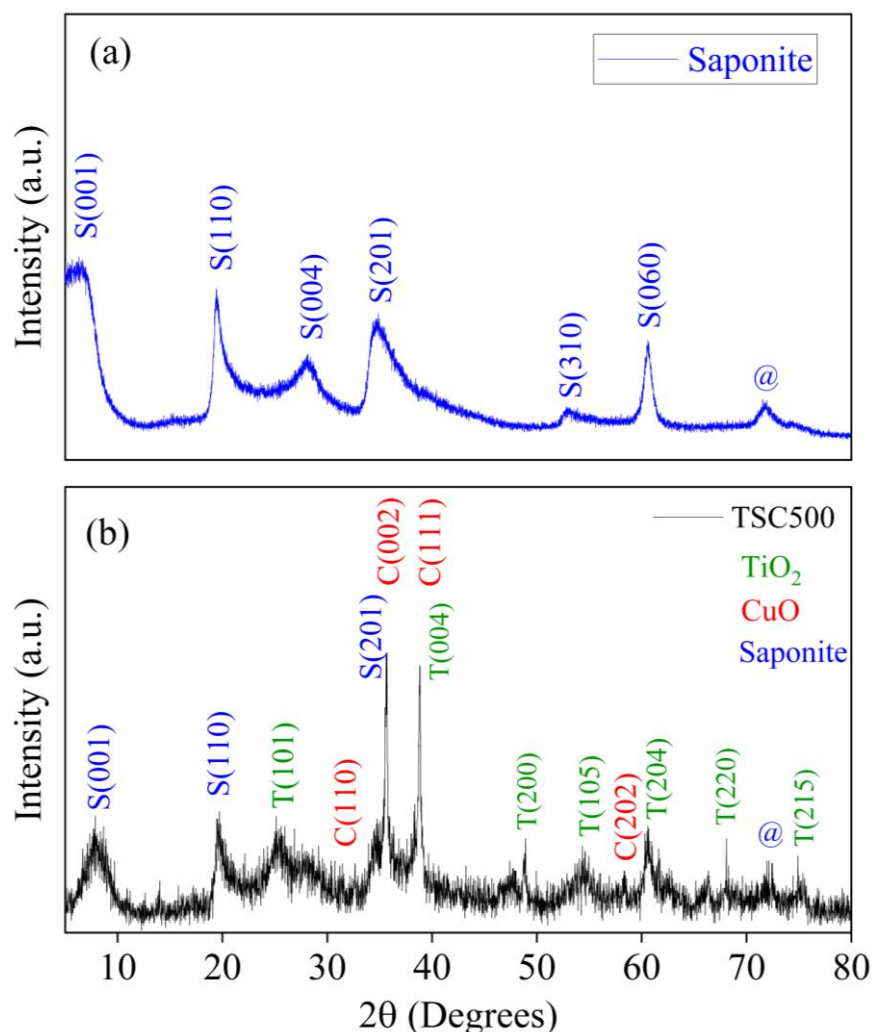


Figure 1. XRD pattern: (a) raw saponite and (b) CuO-TiO₂-saponite nanocomposite obtained by hydrothermal synthesis.

The anatase phase of TiO₂ is identified by diffraction peaks at 25.3°, 38.3°, 48.8°, 54.4°, 60.6°, 68.1°, and 74.9°, corresponding to the (101), (004), (200), (105), (204), (220), and (215) planes, as per ICDD card 21-1272 [29]. Similarly, the CuO phase is confirmed by peaks at 32.5°, 35.6°, 38.3°, 48.0°, 58.3°, and 66.0°, which correspond to the (110), (002), (111), (112), (202), and (310) planes, respectively, as indexed by ICDD card 89-5895 [30]. The results indicate that the sharp and well-defined diffraction peaks demonstrate the good crystallinity of the CuO-TiO₂-saponite nanocomposite. Furthermore, minimal changes in the saponite structure were observed, suggesting that the metal oxide nanoparticles were primarily loaded onto the inner and outer surfaces of the saponite. This finding implies that the hydrothermal method effectively incorporated the nanoparticles onto the saponite surface without disrupting its layered structure.

The FTIR spectra of the saponite samples are shown in Figure 2, both before and after the metal nanoparticles were incorporated. As shown in Figure 2a, the O-H stretching vibration of saponite is characterized by a weak ν (Mg₃-OH) band located within the range of 3100–3700 cm^{−1}. The primary Si-O stretching vibration of saponite appears at 972 cm^{−1}. Additionally, the band at 654 cm^{−1} corresponds to the perpendicular Mg₃-OH bending vibrations. Lastly, a band between 400 and 600 cm^{−1} is attributed to OH translational and Si-O-Si bending vibrational modes [31,32].

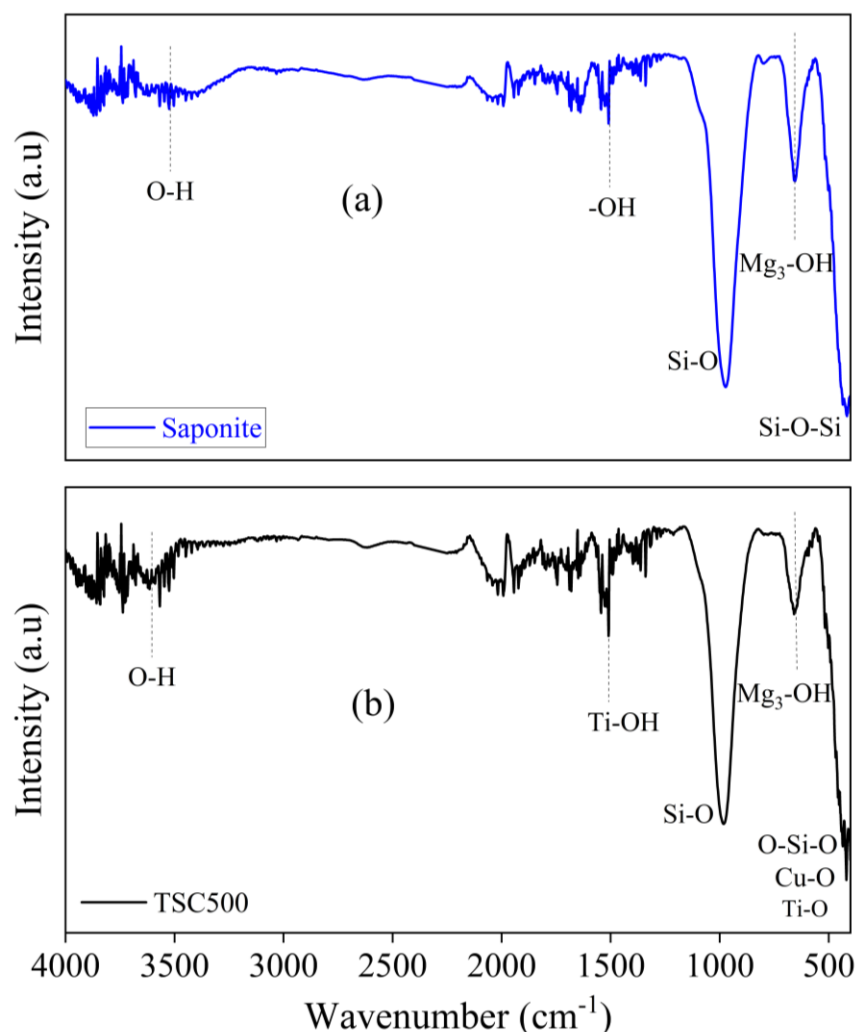


Figure 2. FTIR spectrum: (a) raw saponite and (b) CuO-TiO₂-saponite nanocomposite obtained by hydrothermal synthesis.

In the CuO-TiO₂-saponite nanocomposite (Figure 2b), the vibrational bands of both metal oxides and the Si-O-Si bonds within the 400–600 cm^{−1} range are superimposed, indicating the loading of nanoparticles onto the clay mineral surface [33]. Furthermore, the Si-O band exhibits a slight shift from 972 to 982 cm^{−1}. The band at 3450–3800 cm^{−1}, corresponding to O-H stretching vibrations, appears smaller and broader, suggesting the presence of hydrogen bonding between the CuO and TiO₂ nanoparticles on the saponite surface.

3.2. Morphological Investigation

Microscopic analyses were conducted on the raw saponite and the synthesized nanocomposite to examine their texture and morphology, as illustrated in Figure 3. The image of the raw clay mineral in Figure 3a reveals plate-shaped aggregates, a characteristic feature of smectites. In contrast, the nanocomposite exhibits a distinct morphology, characterized by nodular aggregates embedded within the saponite structure (Figure 3b). The incorporation of TiO₂ and CuO increased particle aggregation, microporosity, and surface roughness in the sample. These observations suggest that the semiconductor nanoparticles are well dispersed across the surface of the clay mineral.

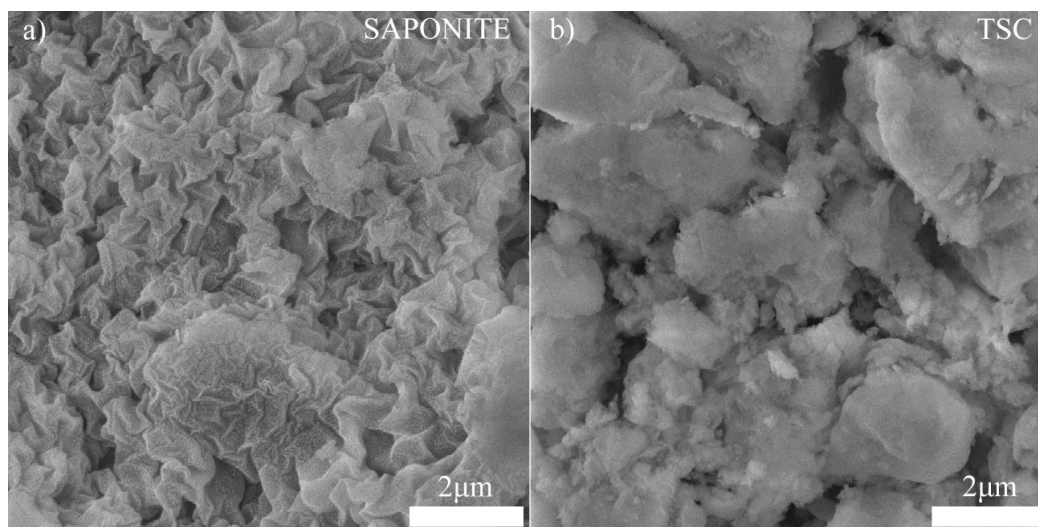


Figure 3. SEM images: (a) raw saponite and (b) CuO-TiO₂-saponite nanocomposite.

3.3. Optical Properties

The diffuse reflectance spectroscopy (DRS) analysis was conducted to evaluate the photo adsorption capacity and band gap energy of the nanocomposite. The results are presented in Figure 4. The Kubelka–Munk function and Tauc plot were applied to estimate the band gap energy (E_g) by plotting $(\alpha h\nu)^2$ against the photon energy ($h\nu$) [34–37]. The calculated energy band gap was found to be 3.21 eV, indicating strong photocatalytic activity in the UV region.

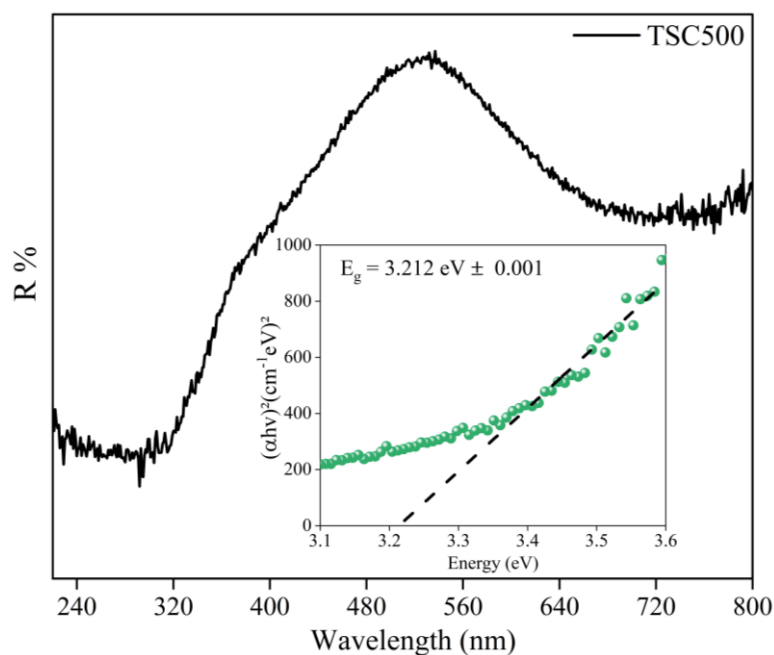


Figure 4. UV-Vis DRS spectrum and the optical band gap for the CuO-TiO₂-saponite nanocomposite. The insert represents the band gap calculation using Tauc's relation.

On the other hand, a photoluminescence (PL) study was conducted to investigate the structural defects and the nature of electron–hole recombination in the nanocomposite (Figure 5). This technique is valuable in photocatalysis for assessing the separation efficiency of electrons and holes. The synthesized TiO₂-based nanocomposite displays both near-band emission (NBE) and deep-level emission (DLE). The DLE is attributed to various intrinsic structural defects within the TiO₂ lattice [38]. The PL spectrum shows an intense

peak in the range of 339–345 nm, corresponding to the band luminescence of the material attributed to self-trapped excitons, oxygen vacancies, and surface states. Additionally, peaks at 352 nm, 372 nm, and 397 nm are associated with recombination or sub-band gaps caused by oxygen vacancies. The exciton emission corresponding to 466 nm is linked to surface oxygen vacancies, occurring when the charge of Ti^{3+} is transferred to the oxygen vacancy in the TiO_6^{8-} octahedral [29,39]. These defects could result from the combination of compounds in the ternary nanocomposite. Additionally, these defects may reduce electron–hole pair recombination, favoring charge separation and thereby improving the material’s photocatalytic potential [40–43].

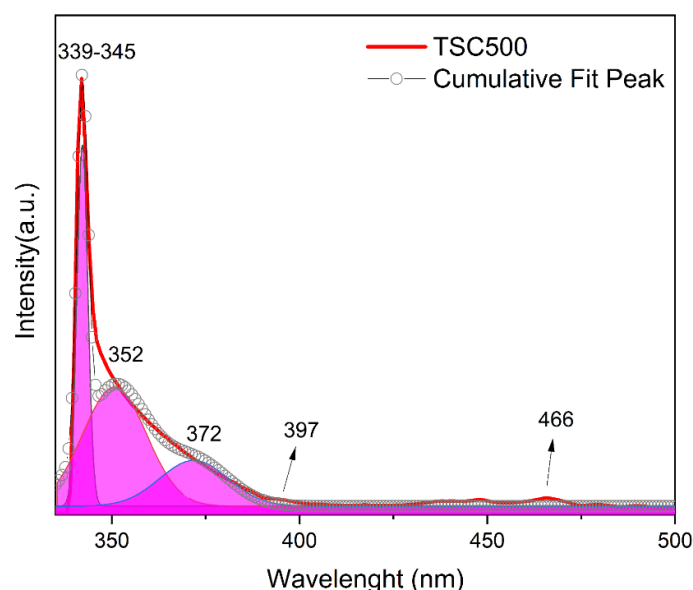


Figure 5. Photoluminescence spectrum of the CuO-TiO₂-saponite nanocomposite.

3.4. Photocatalytic Experiments

The photocatalytic activity of the TSC500 nanocomposite was evaluated by degrading bromocresol green dye under UV irradiation for 150 min, as shown in Figure 6a. The dye’s maximum absorption band at 616 nm decreased significantly during the irradiation process. Figure 6b illustrates that 83% degradation was achieved, demonstrating the nanocomposite’s high photocatalytic efficiency. On the other hand, scavenger tests were conducted to identify the primary reactive species involved in the dye photodegradation mechanism [44,45]. As shown in Figure 7, the silver nitrate (AgNO_3) addition enhanced the photocatalytic capacity by 7%. Silver adsorbs onto the semiconductor surface and acts as an electron acceptor, improving the material’s photocatalytic performance, consistent with previous studies [46,47]. Interestingly, the presence of methyl alcohol (CH_3OH) and chloroform (CHCl_3) significantly reduced the photocatalytic activity, resulting in decolorization rates of 49% and 54%, respectively.

On the other hand, the addition of EDTA ($\text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_8$) resulted in a 7% decrease in the decolorization rate. These findings suggest that while holes play a partial role in the dye degradation mechanism, hydroxyl radicals ($\bullet\text{OH}$) and superoxide radicals ($\bullet\text{O}_2^-$) are critical to the oxidative degradation pathway facilitated by the TSC500 nanocomposite. To evaluate the reusability of the nanocomposite, reuse tests were performed under the same conditions as the photocatalytic experiments (Figure 8). These tests are essential for evaluating the practical applications of the material. The photocatalyst was subjected to three consecutive cycles, with drying performed after each cycle before starting a new test. The results showed moderate stability, with 46% decolorization of bromocresol green achieved in the second cycle and 25% in the third reuse cycle. The lower decolorization rate in the third cycle is likely attributed to material loss during the process [36,37].

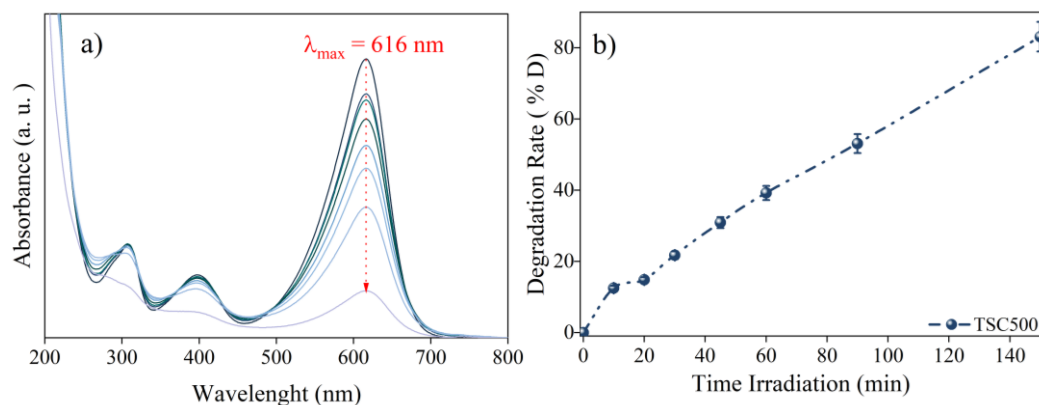


Figure 6. (a) Absorbance spectra and (b) degradation ratio of the bromocresol green dye using the CuO-TiO₂-saponite nanocomposite

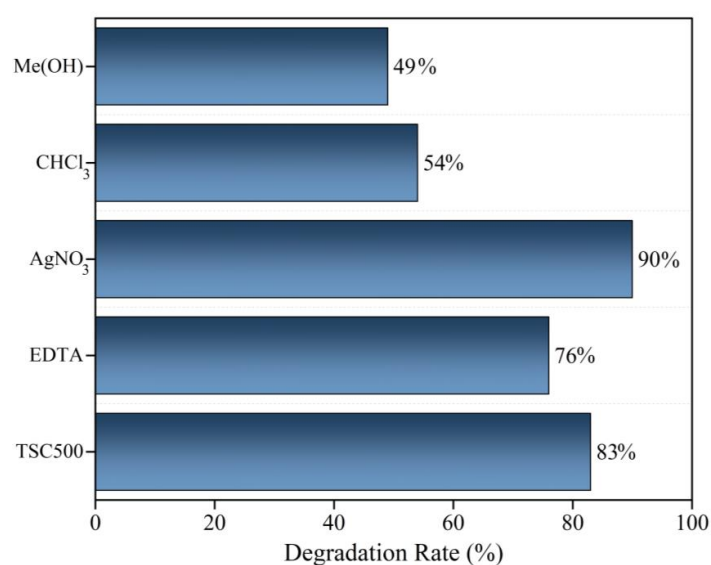


Figure 7. Scavengers' tests of the bromocresol green dye photocatalytic removal using the CuO-TiO₂-saponite nanocomposite under UV irradiation for 150 min.

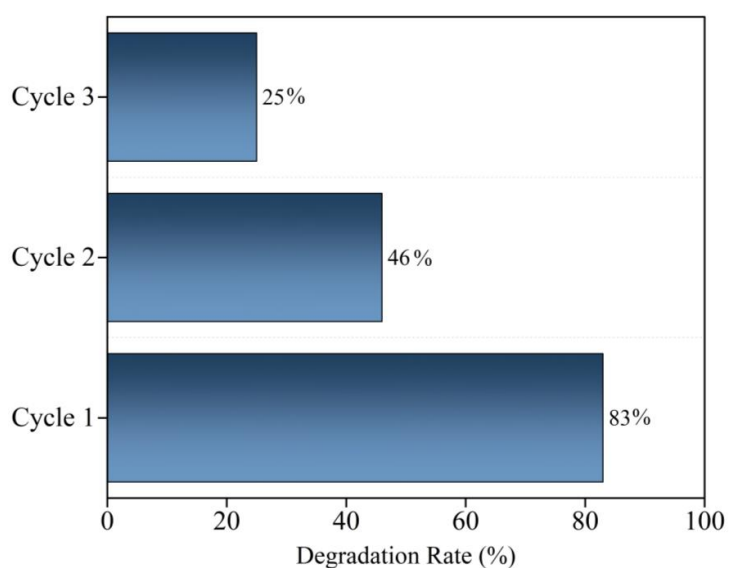
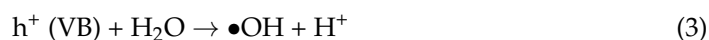
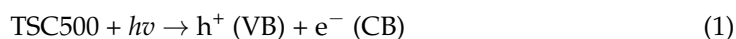


Figure 8. Reuse tests of CuO-TiO₂-saponite for bromocresol green dye decolorization under UV irradiation for 150 min.

4. Discussions

Due to its band structure and charge transfer characteristics, the CuO-TiO₂ heterostructure behaves as a Z-type semiconductor [48–51]. Z-scheme photocatalysts hold significant promise for degrading organic contaminants because of their efficient charge separation and enhanced redox reaction capabilities [49]. Upon light exposure, electrons in both TiO₂ and CuO are excited from the valence band (VB) to the conduction band (CB), leaving holes in their respective VBs. The photogenerated electrons in the TiO₂ CB recombine with the holes in the CuO VB at the interface of the two materials. This charge carrier separation results in optimized redox potential, with electrons possessing high reduction capacity retained in the CuO CB and holes with high oxidation capacity retained in the TiO₂ VB.

The holes in the TiO₂ VB react with water molecules, generating hydroxyl radicals (•OH), while the electrons in the CuO CB react with oxygen molecules to produce superoxide radicals (•O₂[−]). Additionally, saponite, known for its high surface reactivity, can act as an electron trap, reducing O₂ molecules to •O₂[−] radicals [33,52]. With its high surface area and sorption capacity, saponite enhances pollutant–catalyst interactions, promoting photodegradation. Furthermore, it not only supports the dispersibility of the semiconductor but also enhances light absorption, increases the concentration and mobility of charge carriers, and improves the photocatalytic performance of supported materials [19,53]. The reaction mechanism can be summarized through the following Equations (1)–(5). Upon light exposure, the semiconductor generates electron–hole pairs (1). Photogenerated electrons react with oxygen molecules to form superoxide radicals (2). Simultaneously, photogenerated holes react with water molecules to form hydroxyl radicals (3). Finally, these oxidizing species degrade the bromocresol green dye (4) and (5):



The proposed mechanism for the degradation of bromocresol green using the TSC500 nanocomposite is illustrated in Figure 9. Inhibitor experiments revealed that the primary species responsible for dye degradation, in order of importance, are •OH, •O₂[−], h⁺, and e[−].

Various heterostructures have been reported in the literature. For instance, Peng et al. [54] synthesized carbon-doped TiO₂/CuO biochar for degrading ammonia nitrogen. They observed that CuO enhances electron mobility, while carbon biomass introduces intermediate energy levels above the TiO₂ VB, increasing hydroxyl species generation. The biomass also improves ammonia adsorption, thereby enhancing TiO₂ photocatalytic activity. In their study, superoxide radicals were identified as the primary species responsible for pollutant degradation. Similarly, Fahri et al. [55] developed TiO₂/CuO–carbon dots for degrading the pesticide fipronil. The S-scheme heterostructure was shown to enhance electron and hole mobility, while the carbon dots acted as co-catalysts, preventing electron–hole recombination and boosting photocatalytic activity. Hydroxyl and superoxide radicals were identified as key players in the pesticide degradation pathway. Pouthika et al. [33] synthesized a TiO₂–CuO–halloysite heterostructure to photodegrade Congo red dye. Their findings highlighted the importance of the redox potential and high electron mobility at the heterojunction interface in enhancing the photocatalytic process. Clay minerals, with their high surface area, facilitated contaminant adsorption and improved contact between the dye and semiconductors. Scavenger tests revealed significant contributions from hydroxyl and superoxide radicals in the degradation pathway. Zhao et al. [53] developed a CuO–TiO₂–montmorillonite nanocomposite for removing sodium butyl xanthate. They reported

rapid initial adsorption, enhancing overall pollutant removal via photocatalysis. CuO and TiO₂ were identified as active oxidation–reduction sites, with superoxide radicals and holes recognized as primary species in the xanthate degradation mechanism. Moreover, the clay mineral improved light absorption in the visible spectrum and prolonged the lifetime of photogenerated charges.

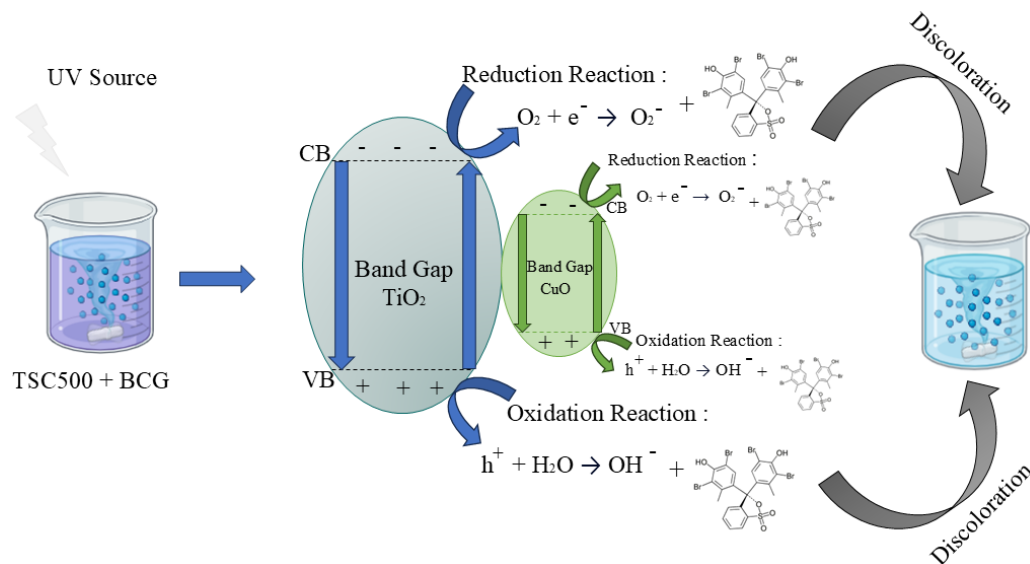


Figure 9. Representation of bromocresol green dye decolorization mechanism over CuO-TiO₂-saponite nanocomposite under UV irradiation.

5. Conclusions

The CuO-TiO₂-saponite nanocomposite was synthesized successfully using a one-step hydrothermal method, demonstrating outstanding structural, morphological, and photocatalytic properties. The nanocomposite exhibited a high crystallinity degree and strong interaction between the incorporated metal oxide nanoparticles and the saponite matrix, confirmed by X-ray diffraction and Fourier-transform infrared spectroscopy. Microscopic analyses revealed the formation of nodular aggregates well dispersed on the saponite surface, which contributed to an increase in active surface sites. Optical characterizations determined a band gap of 3.21 eV, suitable for UV activation, while photoluminescence studies highlighted structural defects, particularly oxygen vacancies, which enhance charge separation, reduce electron–hole recombination, and boost photocatalytic activity. Under UV irradiation, the nanocomposite achieved an impressive 83% degradation of bromocresol green dye within just 150 min, outperforming many traditional photocatalysts. Mechanistic investigations confirmed that hydroxyl and superoxide radicals are the primary species driving the photocatalytic degradation process. This study underscores the pivotal role of clay minerals, such as saponite, not only as structural supports but also as enhancers of nanoparticle dispersion, light absorption, and charge mobility. The innovative combination of CuO and TiO₂ in a Z-scheme heterostructure effectively maximizes redox potentials, offering a sustainable and efficient solution for environmental remediation. The CuO-TiO₂-saponite nanocomposite presents a cost effective, scalable, and eco-friendly material with significant potential for tackling water pollution through advanced photocatalytic technologies. These findings set the stage for future applications in environmental cleanup and affirm the transformative potential of clay-based nanocomposites in advancing green and sustainable technologies.

Author Contributions: Conceptualization, P.T. and R.R.P.-G.; methodology, W.A.A., P.T., A.G.J., M.S.R., and E.L.T.F.; validation, P.T.; formal analysis, W.A.A., P.T., A.G.J., M.S.R., and E.L.T.F.; investigation, P.T.; resources, P.T. and R.R.P.-G.; data curation, P.T. and R.R.P.-G.; writing—original draft preparation, W.A.A., P.T., and A.G.J.; writing—review and editing, P.T. and R.R.P.-G.; visual-

ization, P.T. and R.R.P.-G.; supervision, P.T. and R.R.P.-G.; project administration, P.T. and R.R.P.-G.; funding acquisition, P.T. and R.R.P.-G. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: Data are available on request from the authors.

Acknowledgments: The authors thank Fundação de Amparo à Ciência e Tecnologia do Estado de Pernambuco (FACEPE), Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES), and Universidade Federal Rural de Pernambuco (UFRPE).

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Sahu, A.; Poler, J.C. Removal and Degradation of Dyes from Textile Industry Wastewater: Benchmarking Recent Advancements, Toxicity Assessment and Cost Analysis of Treatment Processes. *J. Environ. Chem. Eng.* **2024**, *12*, 113754. [\[CrossRef\]](#)
2. Kishor, R.; Purchase, D.; Saratale, G.D.; Saratale, R.G.; Ferreira, L.F.R.; Bilal, M.; Chandra, R.; Bharagava, R.N. Ecotoxicological and Health Concerns of Persistent Coloring Pollutants of Textile Industry Wastewater and Treatment Approaches for Environmental Safety. *J. Environ. Chem. Eng.* **2021**, *9*, 105012. [\[CrossRef\]](#)
3. Fatimah, I.; Fadillah, G.; Yanti, I.; Doong, R. Clay-Supported Metal Oxide Nanoparticles in Catalytic Advanced Oxidation Processes: A Review. *Nanomaterials* **2022**, *12*, 825. [\[CrossRef\]](#) [\[PubMed\]](#)
4. Szczepanik, B. Photocatalytic Degradation of Organic Contaminants over Clay-TiO₂ Nanocomposites: A Review. *Appl. Clay Sci.* **2017**, *141*, 227–239. [\[CrossRef\]](#)
5. Morshedy, A.S.; El-Fawal, E.M.; Zaki, T.; El-Zahhar, A.A.; Alghamdi, M.M.; El Naggar, A.M.A. A Review on Heterogeneous Photocatalytic Materials: Mechanism, Perspectives, and Environmental and Energy Sustainability Applications. *Inorg. Chem. Commun.* **2024**, *163*, 112307. [\[CrossRef\]](#)
6. Eddy, D.R.; Permana, M.D.; Sakti, L.K.; Sheha, G.A.N.; Solihudin, G.A.N.; Hidayat, S.; Takei, T.; Kumada, N.; Rahayu, I. Heterophase Polymorph of TiO₂ (Anatase, Rutile, Brookite, TiO₂ (B)) for Efficient Photocatalyst: Fabrication and Activity. *Nanomaterials* **2023**, *13*, 704. [\[CrossRef\]](#)
7. Raizada, P.; Sudhaik, A.; Patial, S.; Hasiya, V.; Parwaz Khan, A.A.; Singh, P.; Gautam, S.; Kaur, M.; Nguyen, V.-H. Engineering Nanostructures of CuO-Based Photocatalysts for Water Treatment: Current Progress and Future Challenges. *Arab. J. Chem.* **2020**, *13*, 8424–8457. [\[CrossRef\]](#)
8. Jayeola, K.D.; Sipuka, D.S.; Sebokolodi, T.I.; Nkwachukwu, O.V.; Muzenda, C.; Koiki, B.A.; Babalola, J.O.; Zhou, M.; Arotiba, O.A. The Design and Characterisation of a Z-Scheme Bi₂O₃/ZnO Heterojunction Photoanode for the Photoelectrochemical Removal of Ciprofloxacin in Synthetic and Real Wastewater. *Chem. Eng. J.* **2024**, *479*, 147482. [\[CrossRef\]](#)
9. Amir, M.; Fazal, T.; Iqbal, J.; Din, A.A.; Ahmed, A.; Ali, A.; Razzaq, A.; Ali, Z.; Rehman, M.S.U.; Park, Y.-K. Integrated Adsorptive and Photocatalytic Degradation of Pharmaceutical Micropollutant, Ciprofloxacin Employing Biochar-ZnO Composite Photocatalysts. *J. Ind. Eng. Chem.* **2022**, *115*, 171–182. [\[CrossRef\]](#)
10. Goodarzi, N.; Ashrafi-Peyman, Z.; Khani, E.; Moshfegh, A.Z. Recent Progress on Semiconductor Heterogeneous Photocatalysts in Clean Energy Production and Environmental Remediation. *Catalysts* **2023**, *13*, 1102. [\[CrossRef\]](#)
11. Parvin, N.; Hussain, S. Heliyon Fabrication and Synergistically Enhanced Photocatalytic Activity of Ternary Kaolinite, TiO₂, and Al₂O₃ (K65T30A5) Nanocomposite for Visible-Light-Induced Degradation of Methylene Blue and Remazol Red Dye. *Heliyon* **2024**, *10*, e29255. [\[CrossRef\]](#)
12. Feitosa, R.P.; de Lima, I.S.; Guerra, Y.; da Silva-Filho, E.C.; Furtini, M.B.; Almeida, L.; Peña-Garcia, R.R.; Martín, I.B.; Cecília, J.A.; Osajima, J.A. Cerium-Doped TiO₂ and Sepiolite Nanocomposites for Tetracycline Inactivation in Water Treatment. *ACS Appl. Nano Mater.* **2024**. [\[CrossRef\]](#)
13. Freitas, W.; Trigueiro, P.; Marinho, T.; Honorio, L.M.; Silva-Filho, E.C.; Furtini, M.B.; Cecília, J.A.; Fonseca, M.G.; Osajima, J. The Role of Clay Mineral-Derived Photocatalysts in Insights of Remediation. *Ceramics* **2022**, *5*, 862–882. [\[CrossRef\]](#)
14. De Oliveira, W.V.; Maria, L.; Honorio, C.; Almeida, L.C.; Viana, B.C.; Furtini, M.B.; Silva-filho, E.C.; Osajima, J.A. TiO₂ Immobilized on Fibrous Clay as Strategies to Photocatalytic Activity. *Mater. Res.* **2020**, *23*, e20190463. [\[CrossRef\]](#)
15. Miranda, M.O.; Viana, B.C.; Honório, L.M.; Trigueiro, P.; Fonseca, M.G.; Franco, F.; Osajima, J.A.; Silva-Filho, E.C. Oxide-Clay Mineral as Photoactive Material for Dye Discoloration. *Minerals* **2020**, *10*, 132. [\[CrossRef\]](#)
16. Belver, C.; Bedia, J.; Álvarez-Montero, M.A.; Rodriguez, J.J. Solar Photocatalytic Purification of Water with Ce-Doped TiO₂ /Clay Heterostructures. *Catal. Today* **2016**, *266*, 36–45. [\[CrossRef\]](#)
17. Akkari, M.; Aranda, P.; Belver, C.; Bedia, J.; Ben Haj Amara, A.; Ruiz-Hitzky, E. ZnO/Sepiolite Heterostructured Materials for Solar Photocatalytic Degradation of Pharmaceuticals in Wastewater. *Appl. Clay Sci.* **2018**, *156*, 104–109. [\[CrossRef\]](#)
18. Albuquerque, W.; Trigueiro, P.; Silva, B.V.; Neves, L.; Almeida, L.C.; Peña-Garcia, R.R. A Novel RuO₂@ZnO-Alginate-Halloysite Composite for the Effective Degradation of Eosin Yellow Dye and Ciprofloxacin Drug. *Mater. Res. Bull.* **2025**, *182*, 113178. [\[CrossRef\]](#)

19. Damaceno, D.H.; Trigueiro, P.; Lima, L.C.B.; Honório, L.M.; Peña-García, R.; Furtini, M.B.; Guerra, Y.; Fonseca, M.G.; da Silva-Filho, E.C.; Jaber, M.; et al. ZnO-Saponite Nanocomposite: Input of Adsorption and Photocatalysis for Removal of Rhodamine B Dye. *Water Air Soil Pollut.* **2024**, *235*, 656. [\[CrossRef\]](#)
20. Mylarappa, M.; Raghavendra, N.; Bhumika, N.R.; Chaithra, C.H.; Nagalaxmi, B.N.; Shravana Kumara, K.N. Study of ZnO Nanoparticle-Supported Clay Minerals for Electrochemical Sensors, Photocatalysis, and Antioxidant Applications. *ChemPhysMater* **2024**, *3*, 83–93. [\[CrossRef\]](#)
21. Talami, B.; Zeghioud, H.; Dalhatou, S.; Bonnet, P.; Caperaa, C.; Ligny, R.; Assadi, A.A.; Massai, H.; Kane, A. A New Sunlight Active Photocatalyst Based on CuO-TiO₂-Clay Composite for Wastewater Remediation: Mechanistic Insights and Degradation Optimization. *Water. Air. Soil Pollut.* **2024**, *235*, 104. [\[CrossRef\]](#)
22. Pouthika, K.; Roopan, S.M.; Madhumitha, G. Green Engineered CuO/SnO₂/HNT Composites: Illuminating the Photocatalytic Path for Organic Pollutant Remediation and Zebrafish Embryo Toxicity Evaluation. *Langmuir* **2024**, *40*, 23337–23355. [\[CrossRef\]](#) [\[PubMed\]](#)
23. Cavalcanti, G.R.S.; Souprayan, C.; Guillermin, D.; Rodrigues, F.; Fonseca, M.G.; Jaber, M. Designing Photochromatic Pigments Based on Clay Minerals and Spiropyran. *Dye. Pigment.* **2022**, *204*, 110358. [\[CrossRef\]](#)
24. Bisio, C.; Gatti, G.; Boccaleri, E.; Marchese, L.; Superti, G.B.; Pastore, H.O.; Thommes, M. Understanding Physico-Chemical Properties of Saponite Synthetic Clays. *Microporous Mesoporous Mater.* **2008**, *107*, 90–101. [\[CrossRef\]](#)
25. Sato, K.; Zhao, Y.; Kamaya, M. Structural Reconfigurations of Nanosheet Arrays in Layered Minerals Caused by Wave Irradiation: Desorption Mechanism of Cs from Nanosheet Edges. *Phys. Chem. Chem. Phys.* **2019**, *21*, 16345–16352. [\[CrossRef\]](#)
26. Nityashree, N.; Price, C.A.H.; Pastor-Perez, L.; Manohara, G.V.; Garcia, S.; Maroto-Valer, M.M.; Reina, T.R. Carbon Stabilised Saponite Supported Transition Metal-Alloy Catalysts for Chemical CO₂ Utilisation via Reverse Water-Gas Shift Reaction. *Appl. Catal. B Environ.* **2020**, *261*, 118241. [\[CrossRef\]](#)
27. Besselink, R.; Stawski, T.M.; Freeman, H.M.; Hövelmann, J.; Tobler, D.J.; Benning, L.G. Mechanism of Saponite Crystallization from a Rapidly Formed Amorphous Intermediate. *Cryst. Growth Des.* **2020**, *20*, 3365–3373. [\[CrossRef\]](#)
28. Baldermann, A.; Dohrmann, R.; Kaufhold, S.; Nickel, C.; Letofsky-Papst, I.; Dietzel, M. The Fe-Mg-Saponite Solid Solution Series—A Hydrothermal Synthesis Study. *Clay Miner.* **2014**, *49*, 391–415. [\[CrossRef\]](#)
29. Kao, L.H.; Chen, Y.P. Characterization, Photoelectrochemical Properties, and Surface Wettabilities of Transparent Porous TiO₂ Thin Films. *J. Photochem. Photobiol. A Chem.* **2017**, *340*, 109–119. [\[CrossRef\]](#)
30. Ali, K.; Sajid, M.; Abu Bakar, S.; Younus, A.; Ali, H.; Zahid Rashid, M. Synthesis of Copper Oxide (CuO) via Coprecipitation Method: Tailoring Structural and Optical Properties of CuO Nanoparticles for Optoelectronic Device Applications. *Hybrid Adv.* **2024**, *6*, 100250. [\[CrossRef\]](#)
31. Theo Klopogge, J.; Ponce, C.P. Spectroscopic Studies of Synthetic and Natural Saponites: A Review. *Minerals* **2021**, *11*, 112. [\[CrossRef\]](#)
32. Madejová, J.; Gates, W.P.; Petit, S. IR Spectra of Clay Minerals. In *Developments in Clay Science*; Elsevier: Amsterdam, The Netherlands, 2017; Volume 8, pp. 107–149. ISBN 9780081003558.
33. Pouthika, K.; Madhumitha, G. Tailoring Interfacial Charge Separation in Z-Scheme CuO@TiO₂@halloysite Heterostructure for Efficient Photocatalytic Removal of Congo Red. *J. Taiwan Inst. Chem. Eng.* **2024**, 105752. [\[CrossRef\]](#)
34. Silva, M.; Trigueiro, P.; Jerônimo, A.; Barbosa, R.; Lins, A.; Albuquerque, W.; Araujo, F.P.; Osajima, J.A.; Peña-García, R.R. Eco-Friendly Synthesis of Zn_{0.97}La_{0.03}O Compound with Natural Polysaccharide and Its Application in Methylene Blue and Eosin Dyes Discoloration. *Mater. Lett.* **2024**, *363*, 136256. [\[CrossRef\]](#)
35. Soares, A.; Trigueiro, P.; Jerônimo, A.; Guerra, Y.; Castro-Lopes, S.; Albuquerque, W.; Peña-García, R.R. Enhanced Ciprofloxacin Degradation, Fe³⁺/Fe²⁺ and Oxygen Vacancy Detection in the Zn_{0.98}Fe_{0.02}O Compound Synthesized at Different PH Values. *Mater. Lett.* **2024**, *372*, 137023. [\[CrossRef\]](#)
36. Martins, E.; Trigueiro, P.; Jerônimo, A.G.; Barbosa, R.; Neves, L.; Sales, D.A.; Almeida, L.C.; Viana, B.C.; Soares, A.S.; Peña-García, R.R. Efficient Photocatalytic Degradation of Diclofenac Drug Using the Zn_{1-x}YPrxAl_yO Photocatalyst under UV Light Irradiation. *Environ. Sci. Pollut. Res.* **2024**, *31*, 53074–53089. [\[CrossRef\]](#) [\[PubMed\]](#)
37. Martins, E.; Jerônimo, A.G.; Barbosa, R.; Neves, L.; Santos, E.; Meira, T.; Osajima, J.A.; Trigueiro, P.; Soares, A.S.; Peña-García, R.R. Influence of Al Cations Insertion on the Structural, Morphological, Optical Properties, and Methyl Orange Photocatalytic Removal of Pr-Doped ZnO System. *Mater. Chem. Phys.* **2024**, *318*, 129300. [\[CrossRef\]](#)
38. Karunakaran, C.; Magesan, P.; Gomathisankar, P.; Vinayagamoorthy, P. Absorption, Photoluminescence and Photoelectron Transfer Resistance of Sol-Gel Synthesized Core/Shell CuO/TiO₂ Nanoparticles. *Optik* **2016**, *127*, 3013–3017. [\[CrossRef\]](#)
39. Alias, S.H.; Mohamed, N.N.; Loon, L.W.; Chandren, S. Synthesis of Carbon Self-Doped Titanium Dioxide and Its Activity in the Photocatalytic Oxidation of Styrene under Visible Light Irradiation. *Malays. J. Fundam. Appl. Sci.* **2019**, *15*, 291–297. [\[CrossRef\]](#)
40. Silva, M.C.R.; Castro-Lopes, S.; Jerônimo, A.G.; Barbosa, R.; Lins, A.; Trigueiro, P.; Viana, B.C.; Araujo, F.P.; Osajima, J.A.; Peña-García, R.R. Green Synthesis of Er-Doped ZnO Nanoparticles: An Investigation on the Methylene Blue, Eosin, and Ibuprofen Removal by Photodegradation. *Molecules* **2024**, *29*, 391. [\[CrossRef\]](#)
41. Lins, A.; Jerônimo, A.G.; Barbosa, R.; Neves, L.; Trigueiro, P.; Almeida, L.C.; Osajima, J.A.; Pereira, F.A.; Peña-García, R.R. Facile Synthesis of Ni-Doped ZnO Nanoparticles Using Cashew Gum: Investigation of the Structural, Optical, and Photocatalytic Properties. *Molecules* **2023**, *28*, 7772. [\[CrossRef\]](#)

42. Gurylev, V.; Perng, T.P. Defect Engineering of ZnO: Review on Oxygen and Zinc Vacancies. *J. Eur. Ceram. Soc.* **2021**, *41*, 4977–4996. [[CrossRef](#)]
43. Rezaei, M.; Nezamzadeh-Ejhieh, A.; Massah, A.R. A Comprehensive Review on the Boosted Effects of Anion Vacancy in the Heterogeneous Photocatalytic Degradation, Part II: Focus on Oxygen Vacancy. *ACS Omega* **2024**, *9*, 6093–6127. [[CrossRef](#)] [[PubMed](#)]
44. Araujo, F.P.; Honorio, L.M.C.; Lima, I.S.; Trigueiro, P.; Almeida, L.C.; Fachine, P.B.A.; Santos, F.E.P.; Peña-Garcia, R.; Silva-Filho, E.C.; Osajima, J.A. New Composite TiO₂/Naturals Gums for High Efficiency in Photodiscoloration Process. *Ceram. Int.* **2020**, *46*, 15534–15543. [[CrossRef](#)]
45. Jerônimo, A.G.; Barbosa, R.; Neves, L.; Trigueiro, P.; Guerra, Y.; Santos, E.; Almeida, L.C.; Osajima, J.A.; Araujo, F.P.; Peña-Garcia, R.R. Simultaneous La³⁺ and Cu²⁺ Cations Insertion in the ZnO Crystal Structure and Its Effect on the Structural, Optical, and Photocatalytic Properties. *J. Mater. Sci.* **2024**, *59*, 1280–1297. [[CrossRef](#)]
46. Teixeira, A.R.F.A.; de Meireles Neris, A.; Longo, E.; de Carvalho Filho, J.R.; Hakki, A.; Macphee, D.; dos Santos, I.M.G. SrSnO₃ Perovskite Obtained by the Modified Pechini Method—Insights about Its Photocatalytic Activity. *J. Photochem. Photobiol. A Chem.* **2019**, *369*, 181–188. [[CrossRef](#)]
47. Honorio, L.M.C.; de Oliveira, A.L.M.; da Silva Filho, E.C.; Osajima, J.A.; Hakki, A.; Macphee, D.E.; Santos, I.M.G. Supporting the Photocatalysts on ZrO₂: An Effective Way to Enhance the Photocatalytic Activity of SrSnO₃. *Appl. Surf. Sci.* **2020**, *528*, 146991. [[CrossRef](#)]
48. Pouthika, K.; Madhumitha, G. Synergistic Synthesis of Carrisa Edulis Fruit Extract Capped Heterogeneous CuO-ZnO-HNT Composite for Photocatalytic Removal of Organic Pollutants. *Inorganica Chim. Acta* **2023**, *551*, 121457. [[CrossRef](#)]
49. Qi, K.; Cheng, B.; Yu, J.; Ho, W. Review on the Improvement of the Photocatalytic and Antibacterial Activities of ZnO. *J. Alloys Compd.* **2017**, *727*, 792–820. [[CrossRef](#)]
50. Kubiak, A.; Bielan, Z.; Kubacka, M.; Gabała, E.; Zgoła-Grześkowiak, A.; Janczarek, M.; Zalas, M.; Zielińska-Jurek, A.; Siwińska-Ciesielczyk, K.; Jesionowski, T. Microwave-Assisted Synthesis of a TiO₂-CuO Heterojunction with Enhanced Photocatalytic Activity against Tetracycline. *Appl. Surf. Sci.* **2020**, *520*, 146344. [[CrossRef](#)]
51. Zhu, H.; Zhen, C.; Chen, X.; Feng, S.; Li, B.; Du, Y.; Liu, G.; Cheng, H.-M. Patterning Alternate TiO₂ and Cu₂O Strips on a Conductive Substrate as Film Photocatalyst for Z-Scheme Photocatalytic Water Splitting. *Sci. Bull.* **2022**, *67*, 2420–2427. [[CrossRef](#)]
52. Low, J.; Jiang, C.; Cheng, B.; Wageh, S.; Al-ghamdi, A.A. A Review of Direct Z-Scheme Photocatalysts. *Small Methods* **2017**, *1*, 1700080. [[CrossRef](#)]
53. Zhao, S.; Xiao, H.; Chen, Y.; Qi, Y.; Yan, C.; Ma, R.; Zhao, Q.; Liu, W.; Shen, Y. Photocatalytic Degradation of Xanthates under Visible Light Using Heterogeneous CuO/TiO₂/Montmorillonite Composites. *Green Smart Min. Eng.* **2024**, *1*, 67–75. [[CrossRef](#)]
54. Peng, X.; Wang, M.; Hu, F.; Qiu, F.; Dai, H.; Cao, Z. Facile Fabrication of Hollow Biochar Carbon-Doped TiO₂/CuO Composites for the Photocatalytic Degradation of Ammonia Nitrogen from Aqueous Solution. *J. Alloys Compd.* **2019**, *770*, 1055–1063. [[CrossRef](#)]
55. Fahri, A.N.; Ilyas, S.; Anugrah, M.A.; Heryanto, H.; Azlan, M.; Ola, A.T.T.; Rahmat, R.; Yudasari, N.; Tahir, D. Bifunctional Purposes of Composite TiO₂/CuO/Carbon Dots (CDs): Faster Photodegradation Pesticide Wastewater and High Performance Electromagnetic Wave Absorber. *Materialia* **2022**, *26*, 101588. [[CrossRef](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.