Photocatalytic Degradation of MB-Dye by CZTS Catalyst

C.T. Illiyas [a,b], **K.C. Preetha** [a,*]

[a] *Department of Physics, Payyannur College, Payyannur, Kannur University, Kerala, 670327, India*

[b] *Department of Physics, Govt. Arts and Science College Nadapuram, University of Calicut, Kozhikode, Kerala, 673506, India*

Editor’s note: Photocatalysis is an effective method for addressing wastewater issues, particularly in removing organic pollutants from textile industry outputs. Illiyas and Preetha developed copper zinc tin sulfide (CZTS) thin films using the spin coating technique and assessed their photocatalytic activity with a solution of methylene blue (MB) dye. The study found apparent rate constants of 0.00562 min^{-1} for a 2 cm^2 catalyst and 0.00674 min^{-1} for a 4 cm^2 catalyst, with degradation rates of about 46% and 60% after 120 minutes, respectively. These results highlight that photocatalytic degradation efficiency is influenced by both the thin film's surface area and the irradiation time.

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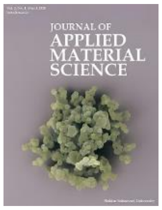

Original Research

Photocatalytic Degradation of MB-Dye by CZTS Catalyst

C.T. Illiyas [a,b], **K.C. Preetha** [a,*]

[a] *Department of Physics, Payyannur College, Payyannur, Kannur University, Kerala, 670327, India*

[b] *Department of Physics, Govt. Arts and Science College Nadapuram, University of Calicut, Kozhikode, Kerala, 673506, India*

Abstract

Copper zinc tin sulfide (CZTS) thin films were prepared by the spin coating technique. The Raman spectrum reveals the kesterite crystal structure of CZTS. Scanning Electron Microscopy (SEM) shows agglomerated surface morphology. The EDAX analysis confirms the presence of all the constituent elements of Cu_2ZnSnS_4. The material with a band gap of 1.92 eV is a promising candidate for the photocatalytic degradation of Methylene Blue (MB)-dye solution, contributing to the eco-friendly wastewater treatment. Photocatalytic activity was studied using a 250 ml MB-dye solution of concentration 10 mg/L. The MB-dye solution containing the CZTS thin-film catalyst placed at the bottom of the beakers was exposed to visible light for irradiation times of 15, 30, 45, 60, 75, 90, 105, and 120 min. The photocatalytic kinetic study showed apparent rate constants of 0.00562 min^{-1} and 0.00674 min^{-1} for 2 cm^2 and 4 cm^2 catalysts, respectively, and about 46% and 60% degradation were observed after 120 minutes of irradiation. The result confirms that photocatalytic degradation strongly depends on both the thin-film area and the reaction time.

Keywords: CZTS; Kesterite; Photocatalysis; Spin Coating.

1. Introduction

The expansion of domestic activities and industries has led to increased water consumption and the generation of large volumes of wastewater, which can cause serious ecological damage when released untreated. In particular, textile industries consume substantial amounts of water for processes such as dyeing and fabric washing, producing effluents rich in dyes that are toxic to living organisms [1]. Photocatalysis has emerged as an effective approach to address these environmental challenges by eliminating organic pollutants from textile wastewater. Among the available methods, semiconductor-based photocatalysis is especially important because it harnesses sunlight to break down harmful organic contaminants. P-type photocatalysts have received comparatively less attention. Materials with a narrow direct band gap and strong solar absorption are gaining interest as efficient photocatalytic [2, 3].

Copper zinc tin sulfide (CZTS) is a quaternary semiconductor material composed of earth-abundant

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* Corresponding author.
Email address: kcpreetha1990@gmail.com (K.C. Preetha)

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and non-toxic elements: copper (Cu), zinc (Zn), tin (Sn), and sulfur (S). Because of its low cost, environmental friendliness, and good optoelectronic properties, CZTS has attracted significant attention in energy-related and environmental applications. CZTS has been successfully applied for the photocatalytic degradation of organic dyes such as Rhodamine B (RhB) and explosive compounds like TNT under visible light irradiation. In addition, its potential for photocatalytic water splitting and hydrogen (H_2) generation has also been demonstrated in earlier reports [4]. CZTS acts as an efficient photocatalyst by absorbing visible light and generating electron–hole pairs due to its suitable band gap. The photo-excited charge carriers participate in redox reactions, enabling degradation of pollutants. CZTS is a sustainable alternative to conventional photocatalysts with repeatability [5, 6].

In this work, a spin-coated CZTS thin film is used as a catalyst for the degradation of the MB-dye solution. The photocatalytic degradation experiments were conducted using a uniform reaction volume, fixed irradiation distance, and identical light exposure conditions, allowing reliable comparison of degradation kinetics. Furthermore, the immobilized thin-film configuration eliminates catalyst loss during reuse, enhancing repeatability and practical applicability compared to powder-based systems.

2. Experimental

2.1. Materials and methods

Copper (II) chloride dihydrate ($CuCl_2.2H_2O$) 0.8 M, Zinc (II) acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$) 0.5 M, Tin (II) chloride dihydrate ($SnCl_2 \cdot 2H_2O$) 0.4 M and Thiourea ($CS(NH_2)_2$) 3.2 M were used as precursors, 2-Methoxyethanol with drops of Monoethanolamine (MEA) used as solvent. The cationic precursors were mixed and magnetically stirred until complete dissolution was achieved. Thiourea was then added slowly to the solution, followed by stirring for 1 hour, resulting in the formation of a clear yellow sol–gel. CZTS thin film was spin-coated over soda-lime glass at 2000 r.p.m. for 40 sec, dried at 150 °C for 5 minutes. The cycle was repeated two times and post-annealed at 350 °C for 30 minutes in a muffle furnace.

To study photocatalytic activity, 250 ml of aqueous MB-dye solution (10 mg/lit) was used in the presence of CZTS thin film of active areas 2 cm^2 (2 cm X 1 cm) and 4 cm^2 (2 cm X 2 cm) under the visible light irradiation. Before light exposure, the catalyst-containing solution was magnetically stirred and maintained in the dark for 5 hours to establish adsorption-desorption equilibrium. Initially, 10 mL of methylene blue (MB) solution was transferred into nine separate beakers, and a CZTS thin film catalyst was placed at the bottom of each beaker. The beakers were irradiated from the top under visible light for different exposure times of 15, 30, 45, 60, 75, 90, 105, and 120 min, respectively, with time intervals of 15 min. One beaker was kept in the dark to test self-degradation. The experiments were carried out using CZTS thin films with surface areas of 2 cm^2 and 4 cm^2 to investigate the influence of catalyst area on photocatalytic performance, while maintaining a constant reaction solution volume. A 20 W white LED lamp was used as the visible light source. The distance between the light source and the reaction solution was maintained at 20 cm. The reaction beaker containing the catalyst was placed inside an enclosure with mirror-coated walls to effectively collect and redirect the reflected light toward the solution, thereby maximizing light utilization during the photocatalytic process.

2.2. Measurements

Raman spectrum analysis was carried out by a micro-Raman spectrometer (Horiba Plus-Olympus BX43using 532 nm and 100 mW Diode Pump Solid State laser). The morphological and Elemental composition study of CZTS thin films was analyzed by SEM-EDX (Joel 6390 LA/ OXFORD XMX N). The absorption study of the thin film was carried out from 400 nm to 950 nm using a UV-VIS-NIR spectrophotometer (Perkin-Elmer Lambda 365). The thickness was determined by the Stylus-profilometer.

3. Results and discussion

The Raman spectrum of the CZTS sample exhibits a prominent peak centered at 329 cm^{-1} as depicted in Figure 1. This Raman mode arises primarily from the symmetric vibration of sulfur atoms around the metal cations and is widely recognized as a fingerprint peak of kesterite CZTS. The presence of this well-defined A_1 mode confirms the successful formation of the kesterite phase and also indicates good crystallinity of the CZTS nanocrystals. The absence of additional Raman peaks associated with secondary phases such as Cu_2S, ZnS, or

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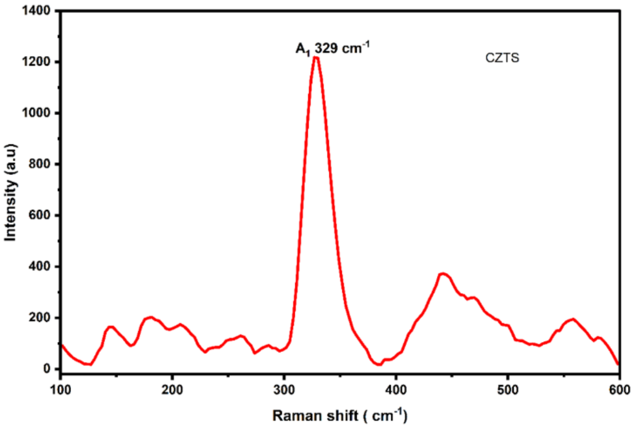

Figure 1. Raman spectrum of CZTS thin film.

SnS_x suggests high phase purity of the synthesized CZTS material [7].

The UV-Vis-NIR absorption spectrum of the CZTS thin film, shown in Figure 2(a), exhibits strong and broad absorption throughout the visible region, indicating efficient utilization of visible light. This high absorption behavior is attributed to the intrinsic optical properties of CZTS, which possesses a direct band gap and a high absorption coefficient. The optical band gap of 1.9 eV was determined using the Tauc plot as presented in Figure 2(b). This band gap lies within the visible range, confirming the suitability of CZTS as an efficient visible-light-active material for photocatalytic and optoelectronic applications [8, 9].

The SEM image in Figure 3 shows a densely packed granular morphology, where the surface is composed of closely agglomerated grains. The grains appear irregular to quasi-spherical in shape, indicating polycrystalline growth of CZTS. Such grain agglomeration is due to solution-processed deposited CZTS films and suggests successful nucleation and growth of the material. The presence of grain boundaries throughout the film can facilitate charge separation by acting as trapping sites for photogenerated charge carriers, which is beneficial for photocatalytic reactions. The film surface appears compact with minimal large cracks or pinholes, indicating good surface coverage of the substrate. This uniform coverage is advantageous for photocatalytic applications, as it ensures continuous interaction between light, the catalyst surface, and reactant molecules.

The EDAX spectrum in Figure 4 confirms the presence of all constituent elements - Cu, Zn, Sn, and S with atomic percentages of 25.63%, 14.91%, 15.12%, and 44.34%, respectively. The detection of these elements without any extraneous peaks indicates the successful formation of CZTS with good compositional purity. The elemental ratios are close to the stoichiometric composition of CZTS, suggesting effective incorporation of metal cations and sulfur into the lattice during film deposition. The relatively higher sulfur content may be attributed to sulfur-rich growth conditions or surface enrichment, which is often beneficial in suppressing sulfur vacancies and reducing non-radiative recombination centers. The slight deviation in metal ratios is commonly observed in chemically synthesized

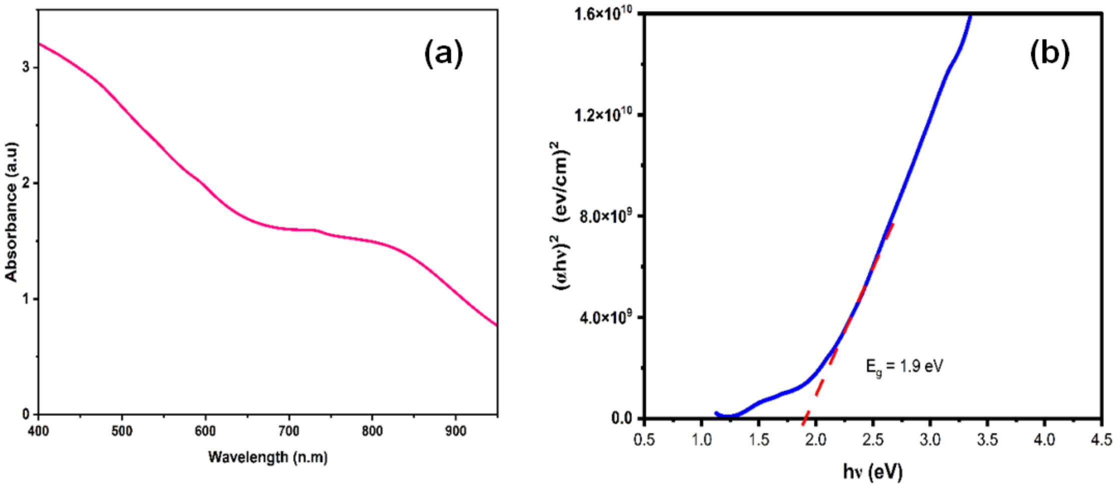

Figure 2. (a) Absorption spectrum and (b) Tauc plot of CZTS thin films.

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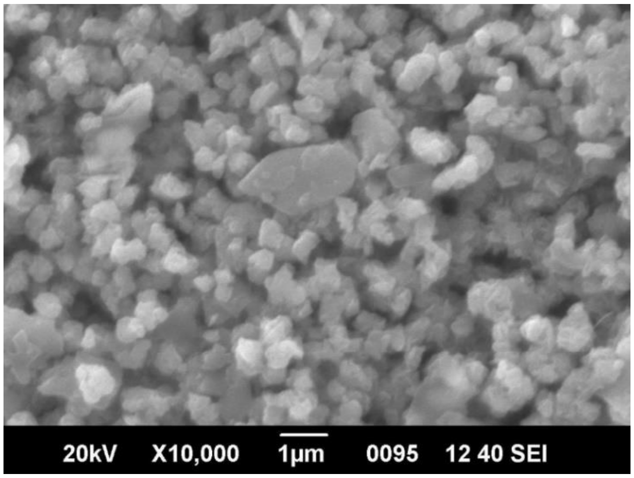

Figure 3. SEM image of CZTS thin film.

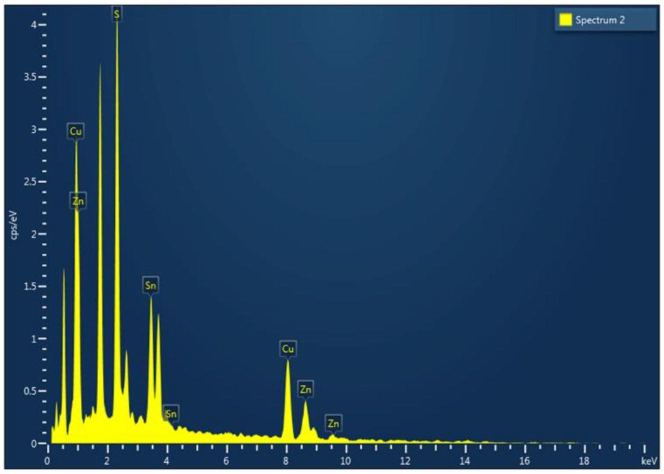

Figure 4. EDAX spectrum of CZTS.

CZTS thin films and can influence defect chemistry, particularly the formation of copper vacancies and antisite defects. Such compositional characteristics are known to favor p-type conductivity and can enhance photocatalytic performance by promoting efficient charge separation [10].

AFM analysis, as depicted in Figure 5, provides quantitative information about the surface morphology and roughness of the CZTS thin film. The root mean square roughness (R_q) of 33.7 nm represents the standard deviation of surface height variations, indicating a moderately rough surface with noticeable height fluctuations. The average roughness (R_a) value of 27.0 nm corresponds to the mean deviation of surface heights from the average plane, further confirming a non-uniform but reasonably homogeneous surface morphology.

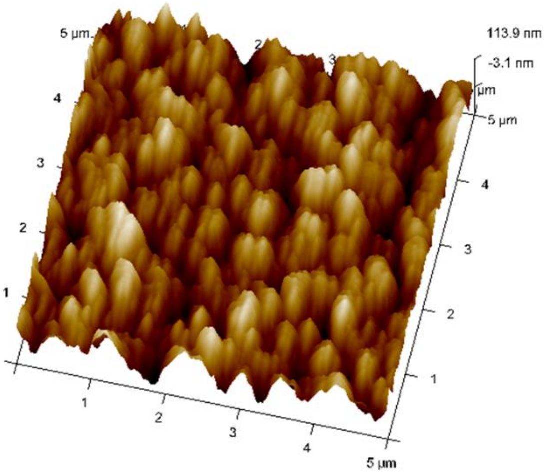

Figure 5. Surface roughness of thin film by AFM analysis.

A moderately rough surface with well-developed grains can enhance light trapping and surface activity. The presence of height variations and surface features promotes light scattering and multiple reflections at the film surface. This improves light harvesting by increasing the interaction time between incident photons and the photocatalyst, leading to enhanced generation of electron-hole pairs under visible light. Surface roughness also contributes to the formation of surface defects and grain boundaries, which can act as trapping sites for charge carriers. These traps help to suppress the rapid recombination of photogenerated electrons and holes, thereby increasing their lifetime and improving photocatalytic efficiency.

Figure 6(a) and (b) show characteristic peaks at a wavelength of 662 nm of the MB-dye solution and the effect of the addition of CZTS catalyst of 2 cm^2 and 4 cm^2 for different reaction times. The peak intensity was observed to decrease with time, with a faster reduction for the solution of 4 cm^2 catalyst compared to the 2 cm^2. No degradation was observed under dark condition showing that MB-dye is stable and cannot be degraded itself as depicted in Figure 7(a). After the addition of the CZTS catalyst to the MB-dye solution and irradiation, a reduction in the peak intensity was observed. The catalytic degradation efficiency (%) for CZTS thin film was calculated as [11]:

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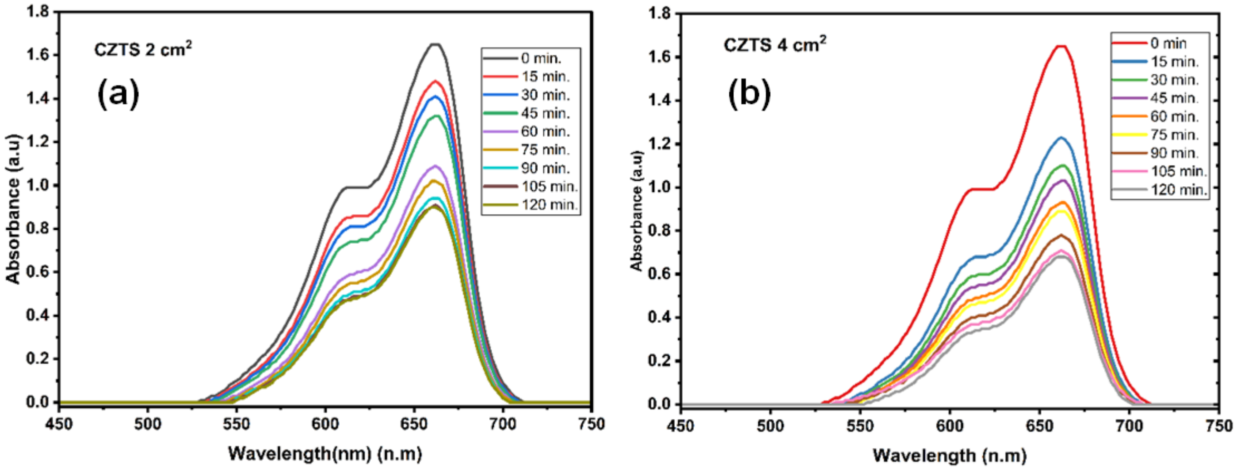

Figure 6. Absorption spectra of MB solution under visible light in the presence of (a) CZTS 2 cm², (b) CZTS 4 cm² for different time intervals.

$$Degradation\ Efficiency = 100\left(\frac{C_0 - C_t}{C_0}\right) = 100\left(\frac{A_0 - A_t}{A_0}\right) \quad (1)$$

where 'C_0' is the initial concentration after equilibrium adsorption, 'C_t' is the concentration after irradiation time 't', 'A_0' is the initial dye solution absorbance in the absence of catalysis, and 'A_t' is the dye solution absorbance in the presence of the catalyst after a time 't'. Plot of $[A_t]/[A_0]$ against reaction time was shown in Figure 7(b), which indicates that the self-degradation of MB-dye in the presence of light is negligible after 120 min.

The apparent rate constant(k_{app}) calculated by the pseudo-first-order reaction model- photodegradation kinetics (Eq. 2) to estimate the degradation rate of MB-solution from the slope of the linear plot of ln(C_0/C) versus irradiation time, as indicated in Figure 8 [3].

$$ln\left(\frac{C_0}{C_t}\right) = k_{app}t \quad (2)$$

The MB-solution with CZTS thin film catalyst of active area of 4 cm² exhibited a higher apparent rate constant (k_{app} = 0.00674 min^{-1}) compared to the 2 cm² thin film catalyst, which showed a slightly lower value (k_{app} = 0.00562 min^{-1}). The enhanced photocatalytic performance of the larger-area film can be attributed to its greater effective active surface area, improved light absorption, and increased availability of catalytic sites. This allows for more efficient generation of photogenerated electron-hole pairs and their

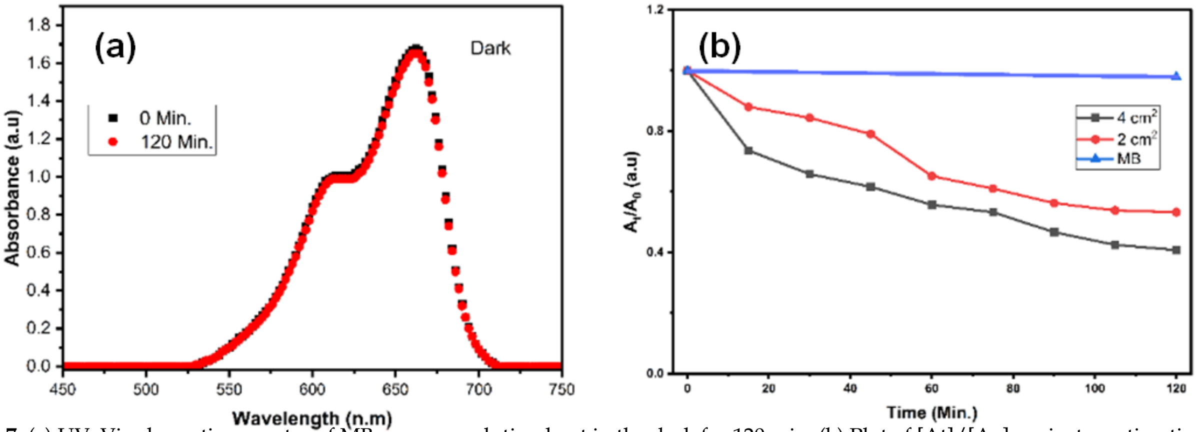

Figure 7. (a) UV–Vis absorption spectra of MB aqueous solution kept in the dark for 120 min. (b) Plot of [At]/[Ao] against reaction time t, for a catalyst of dimensions 4 and 2 cm².

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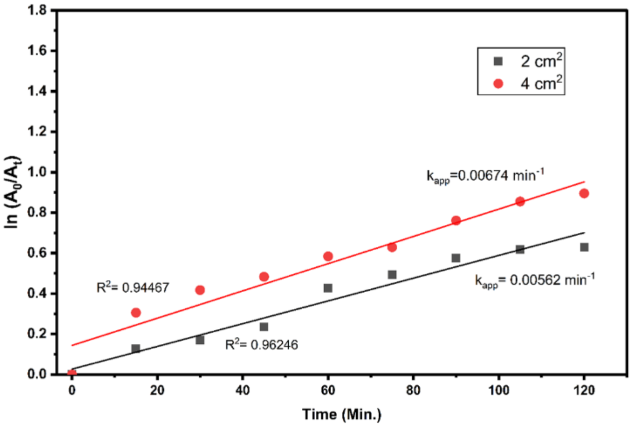

Figure 8. Rate of the reaction against irradiation time t.

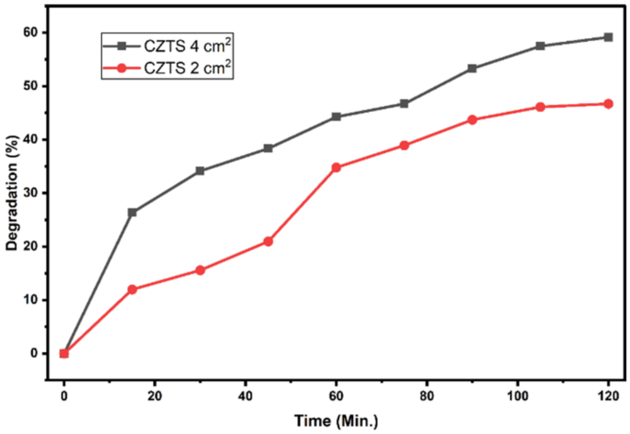

Figure 9. Degradation % of two catalysts of different dimensions against reaction time t.

participation in redox reactions responsible for MB degradation. Figure 9 shows the variation of degradation (%) with reaction time of the catalysts, and 46% degradation was observed for 2 cm² and 60 % degradation for 4 cm² thin films within 120 minutes. The degradation curve and rate constant indicate that the degradation strongly depends on the area of the CZTS catalyst-thin film and reaction time.

The MB-dye solution degradation mechanism in the presence of CZTS, which acts as a catalyst on exposure to the light, is explained and schematically shown in Figure 10(a). The possible reaction mechanism of dye degradation is shown below [11]. The degraded solutions after 120 min. of irradiation are shown in Figure 10(b), (c), and (d).

$$CZTS + hv \rightarrow CZTS\,(e_{CB}^{-} + h_{VB}^{+}) \tag{3}$$

$$H_2O + h_{VB}^{+} \rightarrow OH^{\bullet} + H^{+} \tag{4}$$

$$O_2 + e_{CB}^{-} \rightarrow O_2^{\bullet}- \tag{5}$$

$$O_2^{\bullet}- + H_2O \rightarrow H_2O_2 \tag{6}$$

$$H_2O_2 \rightarrow 2OH^{\bullet} \tag{7}$$

$$OH^{\bullet} + Dye \rightarrow Degraded\ Product \tag{8}$$

4. Conclusions

The structural analysis revealed the kesterite crystal structure. The SEM analysis confirms that the CZTS thin

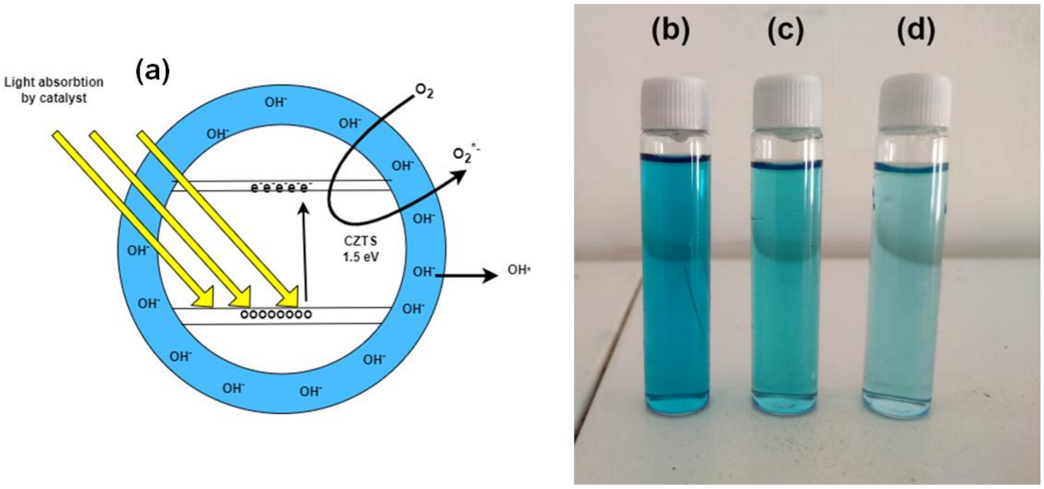

Figure 10. (a) Schematic representation of the degradation of MB-dye by CZTS catalyst on exposure to light. (b) Photographs of the MB dye solution after 120 min: without catalyst (c), degraded by CZTS catalyst 2 cm², and (d) degraded by CZTS catalyst 4 cm².

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film possesses a uniform, granular, and rough morphology, which is favorable for enhanced photocatalytic performance under visible light irradiation. The observed surface roughness and particle clustering enhance light scattering and increase the effective surface area, promoting improved light absorption and adsorption of pollutant molecules during photocatalysis. The EDAX results confirm the successful synthesis of CZTS with near-stoichiometric composition, making the thin film suitable for optoelectronic and photocatalytic applications. Increasing the catalyst surface area leads to improved degradation kinetics of MB-dye under visible light illumination. A densely packed granular morphology with sub-micrometer-sized grains and uniform surface coverage enhances light scattering and provides abundant active sites for photocatalytic reactions. The photocatalytic kinetic study showed apparent rate constants of 0.00562 min^{-1} and 0.00674 min^{-1} for 2 cm^2 and 4 cm^2 catalysts, respectively, and about 46% and 60% degradation were observed after 120 minutes of irradiation. The result indicates that the photocatalytic degradation of MB-aqueous solution depends on the area of the CZTS thin film and reaction time.

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Conflict of Interest

The authors declare no conflict of interest.

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