

Effects of Initial pH and CuS/ZnS Loading in Rhodamine B Photodegradation Under Visible Light Irradiation

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Copper sulphide doped zinc sulphide (CuS/ZnS) microporous aggregate nanocomposites were synthesised through one-step solid phase thermal decomposition method. This work focused on the effect of initial solution pH and catalyst loading on the degradation of rhodamine B dye using a CuS/ZnS photocatalyst under visible light irradiation. Rhodamine B is a dye widely applied in the textile industry during the colouring process; however, its minute traces in water antagonistically affect the environment and all life forms. The physical and optical properties of the synthesised catalyst were characterised using techniques namely, X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and Brunauer-Emmett-Teller (BET). Optimum rhodamine B dye removal measured 97 % efficiency at 10 gL⁻¹ loading after 2.5 h and complete mineralisation (100 % efficiency) at a pH of 1 after 4 h under visible irradiation. This study reports a promising CuS/ZnS heterogeneous photocatalyst in rhodamine B removal from wastewater.

1. Introduction

There is a rising need for highly concentrated coloured textile wastewater treatment containing perilous industrial chemical effluents (Jain et al., 2007). Access to clean water has become a global concern due to demographic growth, societal development and progress, which leads to increased industrial wastewater discharges which directly affect water quality (Byrappa et al., 2006). These toxic pollutants/ substances constantly circulate in the environment and water bodies thereby continuously threatening the biosphere. Water is vital for all living organisms hence pollution of this water can endanger an entire ecosystem and human health (Xu et al., 2021). Huge amounts of pigments and dye wastes are discharged from textile, cosmetic, pharmaceutical, printing, papermaking and food processing industries. Dyes are a group of organic compounds used mostly in industries such as textile, printing, plastic, paper, food and leather, with huge amounts applied during the colouring process. The dye colours can be clearly observed on water surfaces even when present in very low concentrations thereby contaminating water due to their chemical stability, high aromaticity, low biodegradability, toxic carcinogenic nature and mass production (Ahmad et al., 2021).

Rhodamine B (RhB) is an organic cationic basic dye which represents anthraquinone xanthene dyes used in the stated industrial applications characterised by difficult biochemical degradation, high chromaticity and high organic pollutant concentration (Xu et al., 2021). This results in eye irritation, skin and respiratory tract irritation in humans and animals (Ahmad et al., 2021).

Conventional treatment techniques such as traditional adsorption techniques, biodegradation, ozonation and chlorination, flocculation and membrane processes have been widely applied, but their performance limited due to production of secondary pollutants and nature of recalcitrant new organic pollutants. It is therefore essential to develop methods effective in removal and degradation of organic pollutants before discharge into water bodies. Advanced Oxidation Processes (AOPs) such as photocatalysis have been developed for the degradation of organic water pollutants and their effectiveness in complete mineralization of dyes and pesticides thereby causing a decrease in overall effluent toxicity (Naciri et al., 2018).

Semiconductor photocatalysts are highly effective in the treatment of wastewater due to their easy instrumental procedure, simple controlled operation, cost effective, non-selective oxidation and organic dye complete degradation to harmless products (Ahmad et al., 2021). Photocatalysis is based on the primary production of

unspecific active species like hydroxy radicals (Naciri et al., 2018). When ZnS a semiconductor photocatalyst with a wide band gap of about 3.7 eV (only utilizes UV radiation that account for about 4 % sunlight and has low absorption properties) is illuminated by light, photons excite electrons on the valence band across the band gap into the conduction band whilst leaving holes in the valence band. These holes react with hydroxide ions and water molecules to produce hydroxyl radicals. The generation of hydroxyl radicals is based on the pH of the solution and these radicals oxidise adsorbed pollutants on the catalyst' surface to harmless inorganics such as carbon dioxide, water and mineral acids. Metals, halides, organic aldehydes and inorganic acids are some of the by-products formed in this process depending on initial reagents and extent of decolourisation (Jain et al., 2007). Zinc sulphide (ZnS) and copper sulphide (CuS) are considered prominent metal sulphide nanoparticles due to their environmental friendliness, less toxicity, simple preparation, great optical and light absorbing properties. A p-n heterojunction is created in the photocatalytic system when CuS is doped with ZnS leading to the design of efficient photocatalytic system due to photoexcited electrons and holes that reduce the band gap thus improving its photoactivity (Varghese, 2020).

To the best of our knowledge, this study reports for the first time the use of a visible light activated CuS/ZnS composite photocatalyst synthesized using a facile one-pot method in the degradation of RB dye. This work investigates on the effects of initial solution pH and the as-prepared CuS/ZnS catalyst loading in rhodamine B photodegradation under the condition of visible light irradiation.

2. Experimental

2.1 Materials

Copper (II) nitrate trihydrate [$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$] (CAS: 10031-43-3) and thiourea [$(\text{NH}_2)_2\text{CS}$] (Batch No: 51378) purchased from Sigma-Aldrich (St Louis, MO, United States) and zinc (II) nitrate hexahydrate [$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] (Batch No: GD 19080421) purchased from Glassworld (Johannesburg, South Africa) served respectively as copper, sulphur and zinc precursors in the synthesis of CuS/ZnS nanocomposites. All reagents were used without any purification. Deionised water was used as a solvent in this study.

2.2 Catalyst synthesis

CuS/ZnS nanocomposites was synthesised via a simple one-step solid phase method at a temperature of 400 °C. Apt amounts of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $(\text{NH}_2)_2\text{CS}$ and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ were weighed in the ratio 4 : 1: 0.2, respectively. This mixture was firstly added to a crucible and then thoroughly mixed before calcination for 5 h at 400 °C. A pastel and mortar were used to grind the obtained product achieving a powdered photocatalyst. Pristine ZnS was synthesised using zinc nitrate hexahydrate and thiourea: and CuS using copper II nitrate trihydrate and thiourea following the same method.

2.3 Physicochemical properties

XRD was conducted using a PANalytical X'Pert Pro powder diffractometer in θ - θ configuration with an X'Celerator detector and variable divergence- and fixed receiving slits with Fe filtered Co-K α radiation ($\lambda=1.789$ Å). The phase identification was determined by selecting the best-fitting pattern from the ICSD database to the measured diffraction pattern, using X'Pert Highscore plus software. SEM images were captured on a Zeiss Ultra PLUS FEG SEM and TEM images on a JOEL JEM 2100F TEM. A BET surface area system was used to determine the specific surface area with a liquid nitrogen temperature of 77.350 K on a Micrometrics Tristar II.

2.4 Photodegradation activity

The photocatalytic activity of the synthesised CuS/ZnS photocatalyst was evaluated by monitoring rhodamine B degradation efficacy under visible light irradiation with varied catalyst loadings and different initial solution pH. A batch reactor set-up consisting of a 400 mL beaker loaded with 100 mL of 5 ppm rhodamine B solution with varying catalyst loading ranging 5 - 15 gL⁻¹ catalyst subsequently followed by varying pH in the range of 1 - 13 was used. The experimental procedure involved continuous suspension stirring for 30 min in the dark for adsorption-desorption equilibrium attainment followed by 4 h visible irradiation. The box unit experimental set-up with a cubic size measuring (92 × 70 × 70) cm³ consisted of three 18 W fluorescent day lamps which acted as the visible light irradiation source. 2 mL samples were withdrawn every 30 min, then centrifuged at 10,000 rpm for 10 min and solution filtered through 0.45 μm simplepure filters for particle removal before analysis. Rhodamine B concentration was measured before, during and after degradation using a Labotec UV/Vis Lightwave II spectrophotometer at a wavelength of 554 nm. The efficiency of degradation was evaluated using the expression below.

$$\% \text{ Degradation} = \frac{C_0 - C_t}{C_0} \quad (1)$$

Where C_0 (mgL^{-1}) is the initial concentration and C_t (mgL^{-1}) is the final concentration of rhodamine B.

3. Results and discussion

3.1 Characterisation

Catalyst Phase Analysis

The structure and composition of the synthesised nanocomposites was confirmed by XRD analysis. Figure 1 shows the XRD pattern of the as-synthesised CuS/ZnS. The strong sharp distinct nature of the diffraction peaks confirms the crystalline nature and high purity of the prepared catalyst. The peaks are indexed from ICSD database and are consistent with the XRD pattern reported by Ahn et al. (2021).

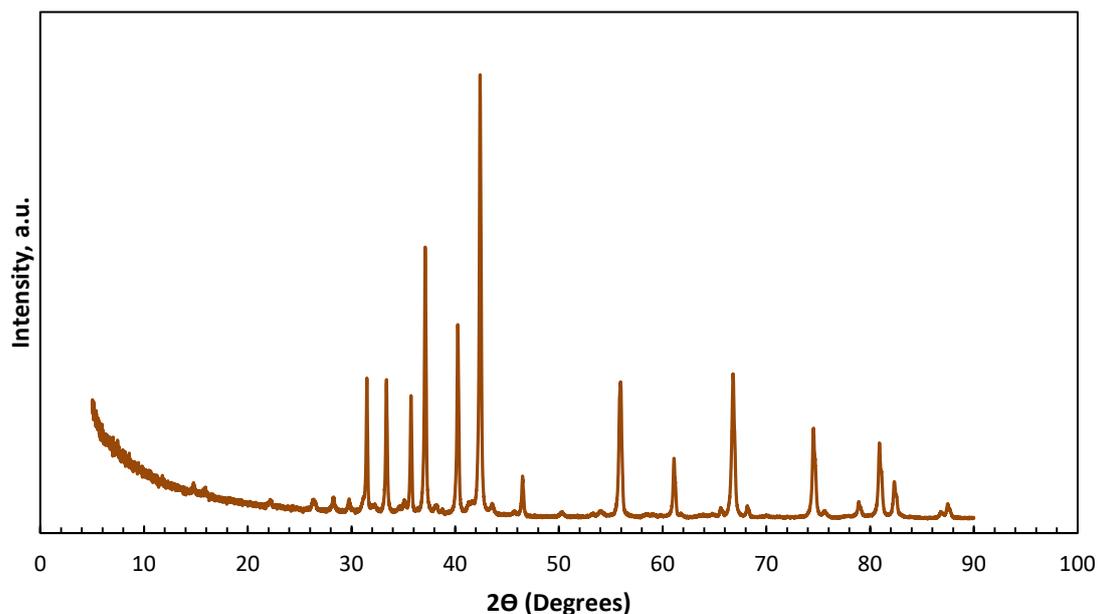


Figure 1: XRD pattern of prepared CuS/ZnS nanocomposites.

Catalyst Surface Characterisation

SEM and TEM were used to capture morphologies of the prepared CuS/ZnS. The synthesis method determines the material's morphological and structural properties (Ichipi et al., 2021). Figures 2(a) and 2(b) show zoomed out and zoomed in SEM images of the synthesised catalyst as having microporous agglomerates covering its surface. Figure 2(c) shows the corresponding TEM image of CuS/ZnS shows the porous structure composed of numerous nanosphere nanoparticles. The clearly observed lattice fringes further confirm the crystal structure (Huang et al., 2015). CuS/ZnS particles morphology is directly related to its photocatalytic properties since different morphologies results in different surface area hence affecting photodegradation efficacy (Moja et al., 2021).

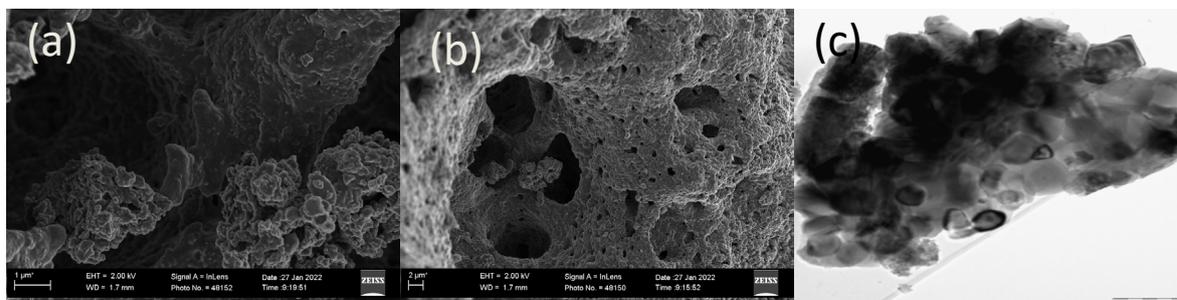


Figure 2: (a) Zoomed out SEM image of CuS/ZnS, (b) Zoomed in SEM image of CuS/ZnS and (c) CuS/ZnS TEM image

Surface area and pore size analysis

The surface area and pore size of CuS/ZnS nanocomposites was analysed using BET method. The photocatalyst specific surface area and porosity greatly impact photocatalytic activity (Shen et al., 2016). The nanocomposites surface area is also drastically enhanced by the presence of nanospheres (Varghese, 2020). The BET surface area analysis measured $3.0 \text{ m}^2\text{g}^{-1}$ which is relatively low; however, the existence of a microporous (mesoporous) structure is indicated by the average pore size of 9.0 nm. Micropores proved essential in absorption of pollutants such as rhodamine B and solar energy due to exposure of more photocatalytic active sites and thus further accelerates pollutant flow within the catalyst. Thus, microporous CuS/ZnS nanocomposites are an excellent photocatalyst candidate.

3.2 Photodegradation study

The photocatalytic performance of the synthesised CuS/ZnS nanocomposites was investigated and analysed under solar irradiation in the degradation of an organic pollutant (rhodamine B) for a duration of 4 h. Figure 3 illustrates the effect of catalyst loading in rhodamine B photodegradation. The reactor was allowed to run for initial 30 min in the dark before exposure to visible light for the whole 2.5 h duration. This was to reach an adsorption-desorption equilibrium. After 30 min in the dark, a removal of 24 %, 33 %, 60 % and 53 % for catalyst loadings of 5 gL^{-1} , 7.5 gL^{-1} , 10 gL^{-1} and 15 gL^{-1} was reported with a loading of 10 gL^{-1} (60 %) showing the highest rhodamine B removal. This pollutant degradation efficiency was calculated using Eq (1).

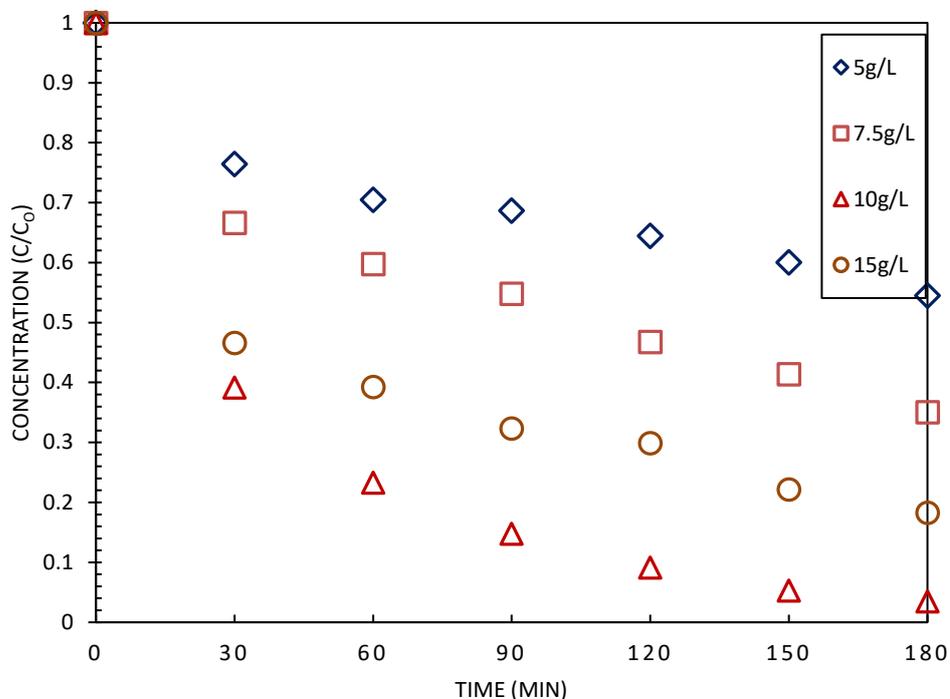


Figure 3: Photocatalytic activity of CuS/ZnS with different catalyst loading.

Figure 4 clearly depicts CuS/ZnS degradation efficiency in the removal of rhodamine B using different catalyst loadings at 30 min intervals throughout the study. Degradation efficacy can be deduced from the figure below, which clearly shows increase in degradation with time. At every interval, the photocatalytic degradation increases from a loading of 5 gL^{-1} to 10 gL^{-1} before decreasing at a higher loading of 15 gL^{-1} . The maximum rhodamine B removal after 180 min reported 45 %, 65 %, 97 % and 82 % for loadings of 5 gL^{-1} , 7.5 gL^{-1} , 10 gL^{-1} and 15 gL^{-1} . A conclusion can be stated that the efficiency of pollutant degradation increases with a catalyst loading from 5 gL^{-1} to 10 gL^{-1} however gradually decreases with further loading increase to 15 gL^{-1} . An increase in catalyst loading increases the number of active sites on the surface of the catalyst which consequently increases the number of superoxide and hydroxyl radicals. The degradation rate decreases above optimum dosage due to light interception by the suspension thereby primary oxidant hydroxyl radical decrease in the photocatalytic system; furthermore, as a result of catalyst particle agglomeration which restricts photon absorption on catalyst surface (Hameed and Akpan, 2009).

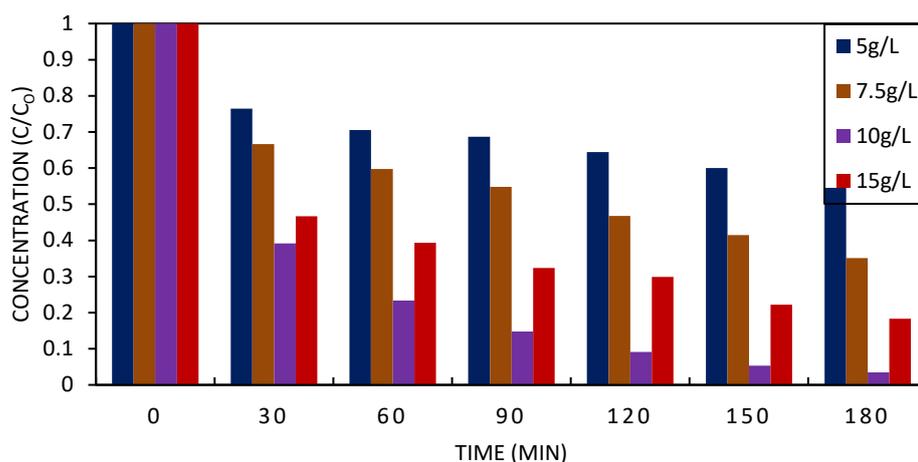


Figure 4: Effect of catalyst loading on CuS/ZnS degradation efficacy.

Figure 5 shows the effect of initial rhodamine B pH on the photocatalytic degradation of 5 ppm of RhB using the synthesised CuS/ZnS under visible light irradiation for 4.5 h. The initial rhodamine B solution pH is adjusted by adding an appropriate amount of NaOH or HNO₃. The photocatalytic performance of the prepared CuS/ZnS nanocomposites is investigated at pH 1, 3, 5, 7, 9, 11 and 13. The highest degradation was achieved at pH 1 with complete (100 %) rhodamine B removal. The pH of 11 had the next best degradation (98 %) followed by pH 13 (91 %), then pH 3, pH 5 and pH 7 having the same degradation (89 %) and pH 9 achieving the least removal. This shows how H⁺ and HO⁻ ions are directly and effectively involved in RhB degradation. pH is an intricate parameter in photocatalytic and adsorption processes that occur on the photocatalysts surface as a result of its effect on the catalysts' surface charge properties. Photocatalysis can be described as surface phenomenon initiated mostly through adsorption followed by catalysis under light irradiation (Anjum et al., 2017). Depending on the pollutant net surface charge, adsorption can either be low due to repulsion between the surface of the catalyst and pollutant with the same polarity or high due to opposite charges attraction (Tichapondwa et al., 2020). More H⁺ radicals are formed in acidic conditions due to H⁺-electron interaction thereby leading to highly reactive HO⁻ radicals formation due to hydrogen peroxide dissociation. These highly reactive hydroxyl radicals yielded outstanding effective RhB degradation. The hydroxyl ion concentration increases in basic conditions thereby reacts with h⁺ (positively charged holes) to form highly reactive HO. The presence of these hydroxyl radicals directly affects RhB removal (Varghese, 2020). The results obtained and illustrated in Figure 5 suggests significant retardation of rate of electron-hole recombination.

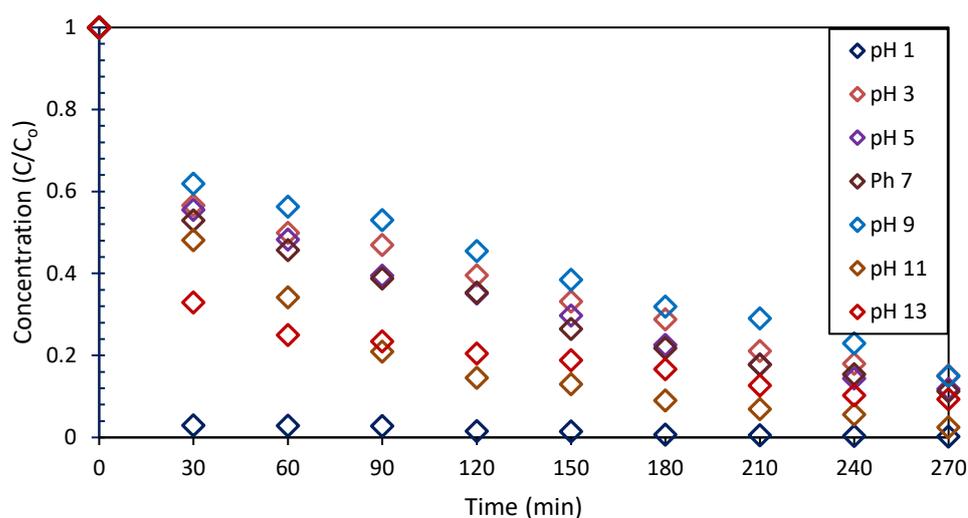


Figure 5: Effect of pH on photocatalytic degradation of rhodamine B

4. Conclusions

CuS/ZnS nanocomposites were successfully synthesised, and the main physicochemical properties characterised by XRD, BET, SEM and TEM. The catalyst achieved significant photocatalytic performance with an excellent rhodamine B removal no less than 85 %. The positive results collected under visible light irradiation imply that sustainable abundant solar light can potentially be employed in wastewater remediations such as organic pollutant removal. The innovative method of synthesis yielded this promising catalyst that can be commercialized consequently providing solutions in water treatment. This process can be further optimized by varying other extrinsic factors that may likely affect the degradation efficiency such as the effect catalyst recovery and reuse, degree of mineralization achieved by the catalyst and potential for use in a continuous reactor setup.

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