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RESEARCH PAPER

Enhanced Photocatalytic Degradation of Brilliant Blue Dye by ZnS@ZnO Nanocomposite: An Ecofriendly Solution for Pollutant Removal and Healthy protective

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ABSTRACT

The degradation mechanism is largely driven by the generation of molecular oxygen and other reactive oxygen species (ROS), produced through sequential photochemical reactions, which play a pivotal role in the oxidative breakdown of dye molecules. The synergistic combination of ZnS and ZnO is proposed to further enhance photocatalytic efficiency while minimizing reliance on costly and potentially hazardous sensitizers. In this experimental investigation, ZnO-based photocatalysts were successfully synthesized, doped with transition metals, and characterized using advanced techniques such as X-ray Diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM), and Transmission Electron Microscopy (TEM). The photocatalytic degradation of Brilliant Blue (BB) dye was employed as a model reaction to evaluate the influence of metal dopants on both degradation efficiency and reaction kinetics. Additionally, UV-Visible spectroscopy was utilized to monitor the degradation process. The results demonstrated that the ZnS/ZnO-based photocatalyst achieved complete (100%) degradation of BB dye within 60 minutes, confirming its high efficacy in the treatment of azo dye-contaminated wastewater. Furthermore, it was observed that increasing dye concentrations led to the formation of multiple molecular layers, which hinder light penetration and consequently reduce photocatalytic activity. An optimal photodegradation efficiency of 86.25% was recorded at a dye concentration of 20 $mg{\cdot}L^{-1}$. These findings highlight the potential of ZnS/ZnO nanocomposites as efficient, cost-effective, and environmentally sustainable photocatalysts for the removal of azo dyes from industrial wastewater, thereby contributing to advances in environmental remediation technologies.

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INTRODUCTION

One significant source of environmental contamination is dye pollutants from the textile sector. It is true that these effluents are poisonous, largely non-biodegradable, and impervious to physico-chemical treatment techniques. It is frequently more crucial to remove color from trash than other colorless organic materials since even trace concentrations of dyes (less than one ppm) are noticeable and have a significant impact on the aquatic environment [1-3].

Given their widespread use in various industries, including pharmaceuticals, textile fibers, paper dyeing, and plastics, organic dyes currently represent a substantial source of water pollution. Aquatic ecosystems and human health are seriously threatened by the direct release of untreated dye wastewater into the environment. Additionally, wastewater that has been dyed reduces the amount of light that reaches the surface, thereby lowering photosynthetic efficiency [4-7]. More attention needs to be paid to water scarcity, particularly in light of global warming. For economic, environmental, and health reasons, eliminating dyes from wastewater is recommended. Several methods, including flocculation/coagulation, ozonation/oxidation, membrane separation, and photocatalytic degradation, have been developed to remove dyes from wastewater. However, the majority of these traditional approaches are starting to show themselves as unsuitable for straightforward and efficient treatment. The literature has reported various methods for treating and decontaminating such effluents. Classical procedures, including adsorption, coagulation, ion flotation, and sedimentation, are examples of typical approaches [8-12]. Although all these methods are practical and adaptable, they all generate a secondary waste product that requires further processing. "Advanced Oxidation Processes" (AOPs) are a modern alternative to traditional approaches. They work by producing highly reactive species, such as hydroxyl radicals, which rapidly and non-selectively oxidize a wide variety of organic contaminants. Advanced Oxidation Processes (AOPs), a relatively recent, more potent, and promising collection of procedures, have been developed and utilized to treat wastewater effluents contaminated with dyes. Typically, this process utilizes a potent oxidizing species, such as dot OH radicals, which are generated in situ and initiate a series of events that reduce the macromolecules to smaller, less hazardous forms. Frequently, the macromolecule is entirely [13-17].

MATERIALS AND METHODS

Chemicals

The following chemical reagents were utilized (Sigma-Aldrich): MB (99% the chemical structure shown in Fig. 1), methanol (CH_3OH, 995%), hydrogen peroxide (H_2O_2, 23%), ethanol

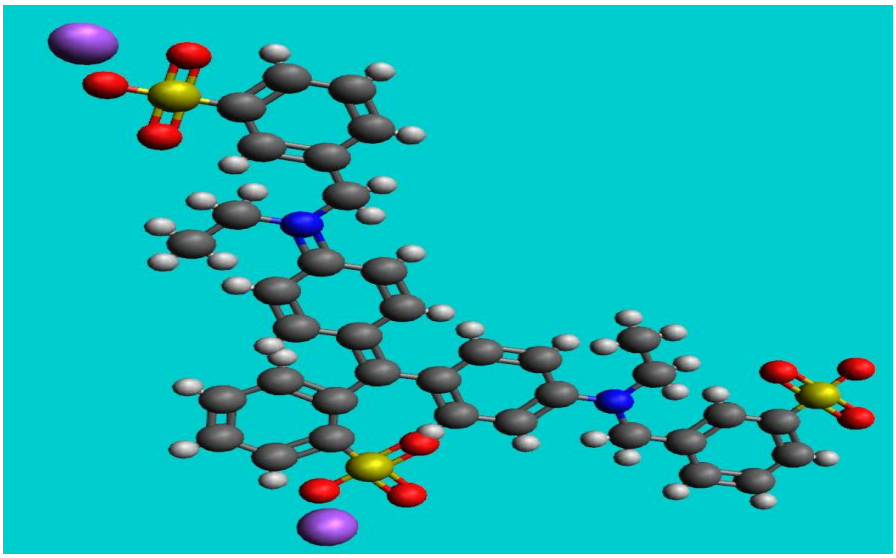

Fig. 1. Chemical structure of BB dye in 3D view.

(CH_3CH_2OH, 98.5%), sodium sulfide (Na_2S, 95%), reducing agents, cadmium acetate dehydrate ($Cd(CH_3COO)_2{\cdot}2H_2O$, 99.5%), and zinc acetate ($Zn(CH_3COO)_2{\cdot}4H_2O$, 99.5%).

Preparation of ZnS/ZnO Nanomaterial by the hydrothermal method

Pure ZnS nanoparticles were synthesized using zinc acetate and sodium sulfide as precursors.

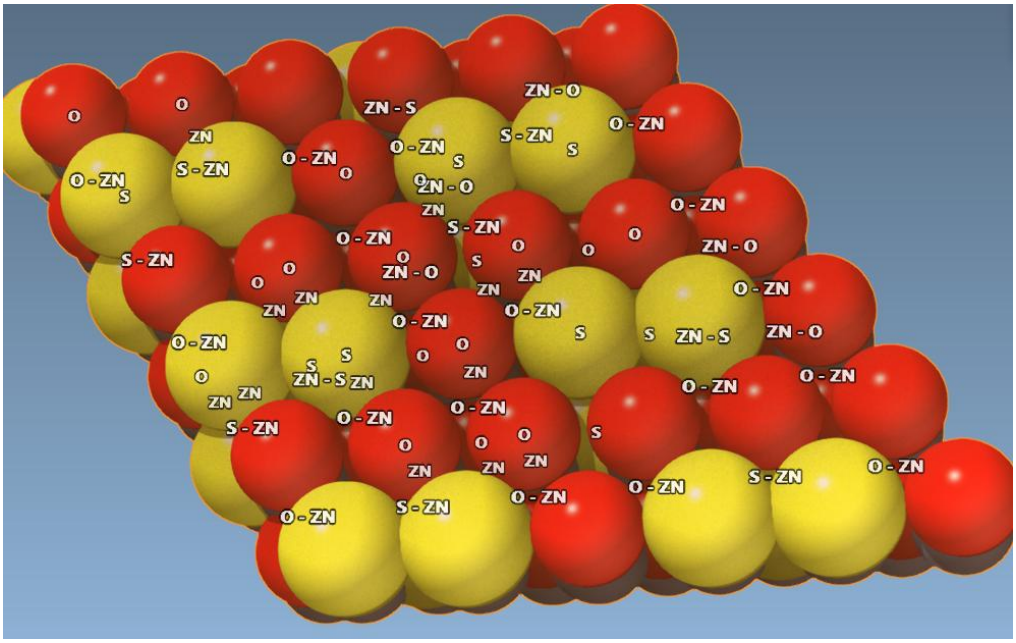

Fig. 2. CIF file generated by VMD software for Crystal structure of nanocomposite ZnO/ZnS nanocomposite surface.

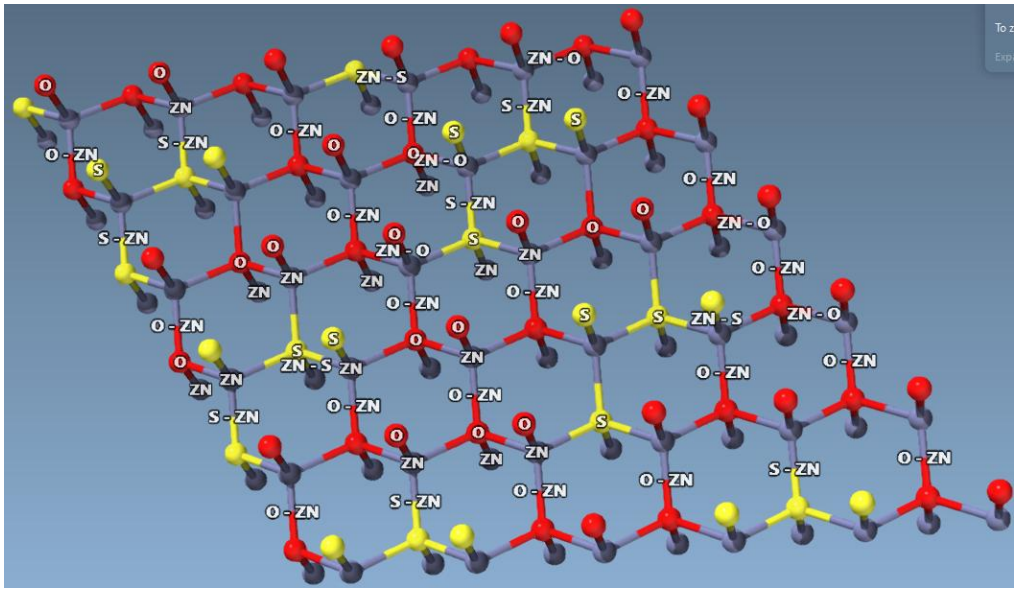

Fig. 3. CIF file generated by SAMSON software for Crystal structure of nanocomposite ZnO/ZnS nanocomposite surface.

First, 3.2 g of zinc acetate was added to 50 mL of distilled water and stirred with a magnetic stirrer for 25 minutes. Next, a 50 mL solution of 0.5 M sodium sulfide was prepared by dissolving 1.56 g of Na_2S in distilled water. The sodium sulfide solution was then added drop-wise to the zinc acetate solution using a burette, while maintaining continuous stirring. After stirring the mixed solution for another 25 minutes, it was transferred to a 150 mL Teflon-lined stainless steel autoclave. The autoclave was placed in an oven at 120 °C for 24 hours and then allowed to cool to room temperature. The resulting sample was washed twice with distilled water and ethanol, followed by drying overnight in an oven at 95 °C, the crystal structure view shown in Figs. 2 and 3.

Procedures

A solution with a known dye concentration was made for the photo-degradation of BB dye. It was then left to equilibrate in the dark for 15 minutes. After that, 200 milliliters of the suspension were moved to a 300-ml beaker. After making the necessary adjustments, the dye's pH value was 6.8. The reaction was then started by turning on the lamp. The suspension was kept homogeneous during irradiation by maintaining agitation, and it was sampled following the proper illumination duration. Using a calibration curve and a spectrophotometer (UV-Vis Spectrophotometer) set to λmax=663 nm, the amount of dye in each deteriorated sample was measured. The conversion percentage of BB dye can be obtained at various intervals using this procedure. The following provides the photo-degradation efficiency (E%):

$$E\ (\%) = ((C_0 - C_t)/C_0) \times 100 \quad (1)$$

RESULTS AND DISCUSSION

Morphology of the surface

Fig. 4 shows the FESEM images of the ZnS/ZnO

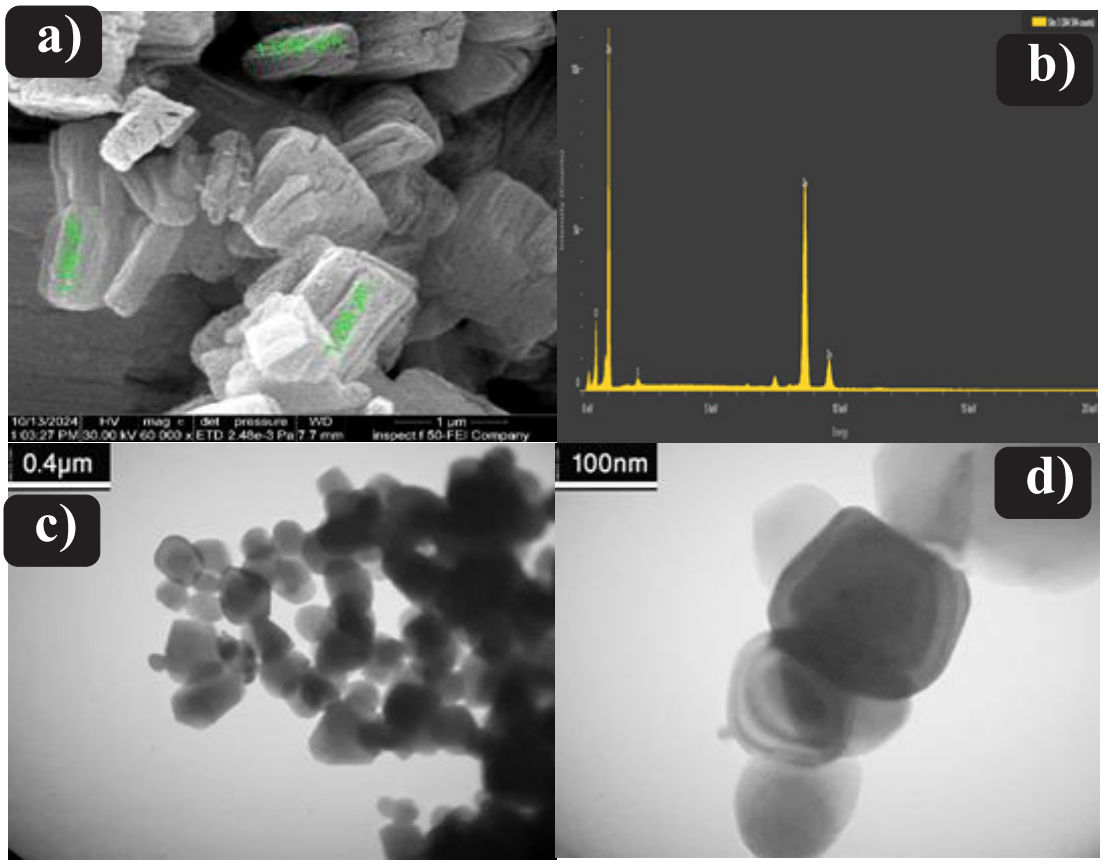

Fig. 4. FESEM images of a) ZnS/ZnO ;b) EDX of ZnS/ZnO; TEM c), d) of ZnS/ZnO NPs.

NPs sample after two hours of heat treatment at 300°C. Fig. 4a shows the spherical 3D structure, which is approximately 1 nm in diameter. As can be observed in Fig. 4a, which was obtained at a magnification of 1 nm, the ZnS/ZnO particles exhibit a shape resembling nanosheets that are

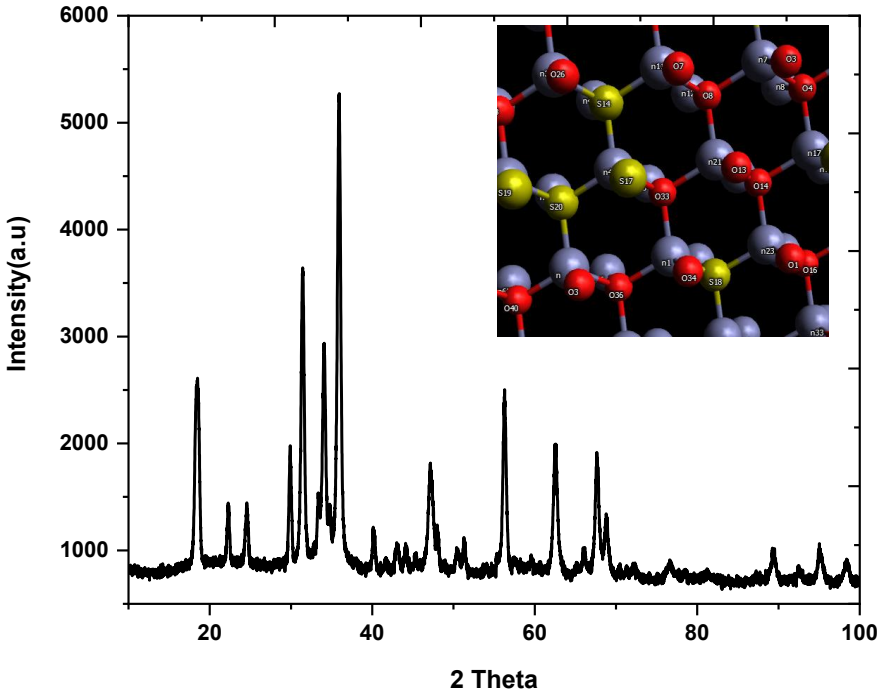

Fig. 5. XRD structure of ZnS/ZnO nanocomposite.

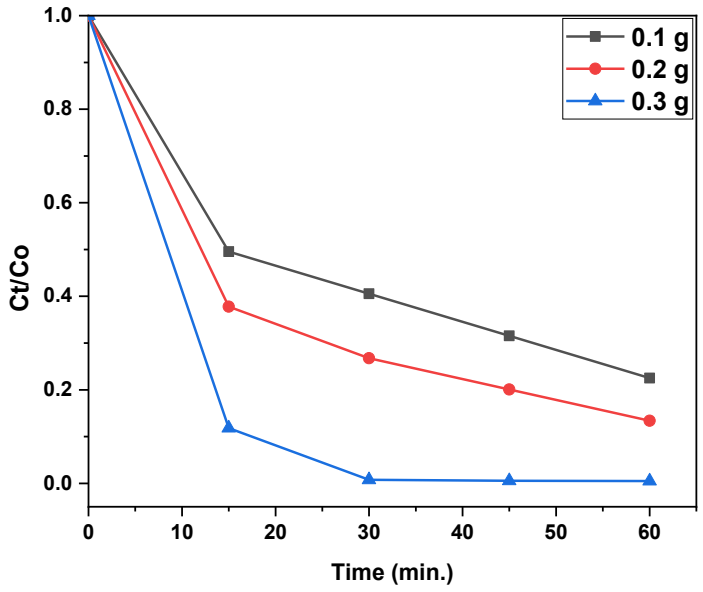

Fig. 6. Effect of the weight of ZnS/ZnO nanoparticles on photocatalytic degradation BB dye.

joined together to form a three-dimensional structure. This successful loading reassures us of the effectiveness of our process [18]. The EDX of the ZnS/ZnO NPs confirms the presence of Zn, O, and S, as shown in Fig. 4b

The crystal structure, particle size, and shape were found to be constrained by the TEM image. The average size of ZnS/ZnO NPs at 0.4 and 100 nm, as shown in Figs. 4c and 4d. The surface morphology and crystal structure of ZnS/ZnO NPs

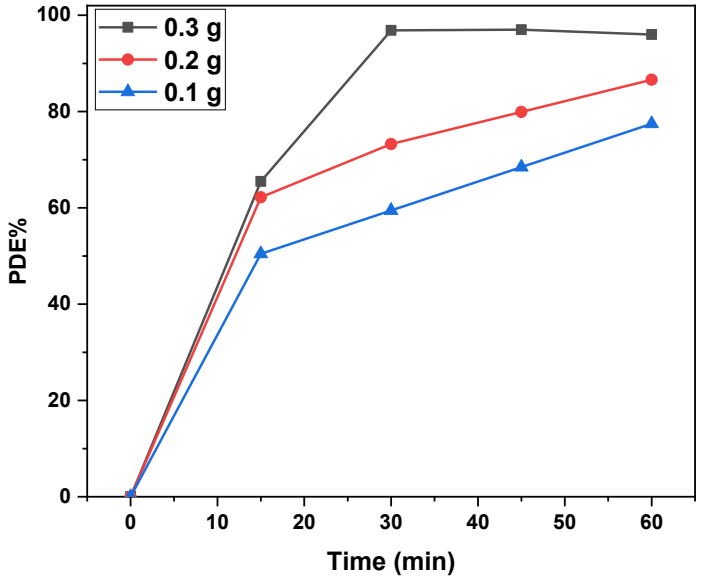

Fig. 7. Removal percentage of BB dye by ZnS/ZnO nanoparticles.

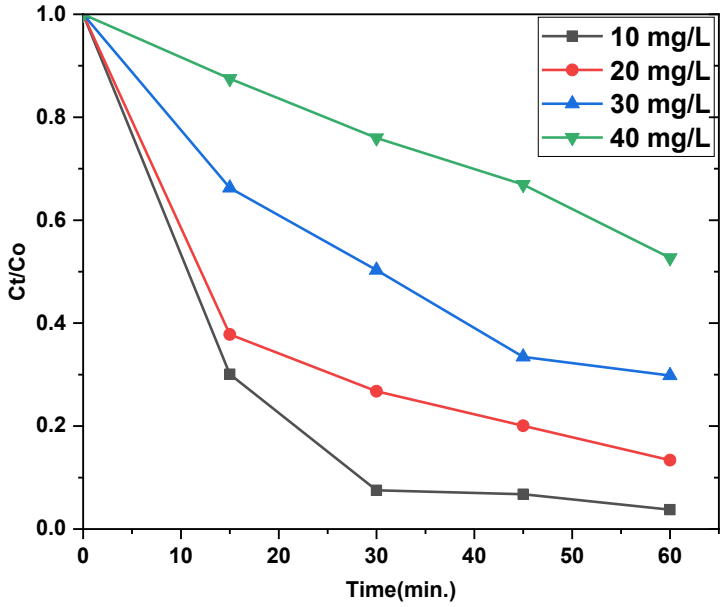

Fig. 8. Photocatalytic degradation at different concentration of BB dye onto ZnS/ZnO nanoparticles.

were characterized. Fig. 4c shows the ZnO/ZnS surface as a spherical, white structure. Additionally, the result was a dark spherical structure [19-21].

X-ray diffraction (XRD)

X-ray diffraction (XRD) analysis to estimate the crystalline phase and purity of the prepared ZnO and ZnS/ZnO nanocomposite. The results showed that the samples possess a high degree of crystallinity and purity, as evidenced by the sharp peaks in their appearance. In the XRD pattern of zinc oxide (Fig. 5) the XRD pattern of ZnS/ZnO nanocomposite (Fig. 5) showed reflections at 2θ values of (18.81 °, 22 .02°, 24.41 °,28.94 °, 32.06 ° 35.06 ° , 38.06 ° and 55.51 °) for ZnS/ZnO nanocomposite, which correspond to reflections from crystal planes. (111), (100), (002), (101), (102,220), (110,311), (103), and (112), respectively. Clearly and distinctly, the position of the ZnO peaks was slightly shifted towards higher 2θ values compared to pure ZnO [22, 23].

Effect of the weight of ZnS/ZnO

The study investigated the effect of nanocomposite weight on the removal of methylene blue dye via photocatalytic degradation. The dye concentration was set at 20 mg/L, with an air flow rate of 10 ml/min at a temperature of 25 °C. Fig. 6 illustrates the range of nanocomposite weights (0.1g to 0.3 g) used in the photocatalytic degradation process. The results indicated that as the surface weight of the nanocomposite increased, the rate of dye degradation also increased, reaching a peak of 0.3 g per 200 mL solution. Initially, the photodegradation of the dye increased gradually, resulting in higher photocatalytic efficiency. This effect can be explained by the limited light absorption that occurs in the upper layers of the dye, while the deeper layers of the solution do not receive sufficient light photons. Ultimately, a nanocomposite weight of 0.2 g yielded the highest photodegradation efficiency at 86.25%.[24, 25], as shown in Fig. 7.

Effect of concentration of dye

The effect of various concentrations of BB dye (10-40 mg/L) on its photodegradation was investigated using 0.3 g of ZnS/ZnO nanocomposite in 200 mL of solution, with a light intensity of 1.3 mW/cm² at 25 °C. It was observed that the photodegradation rate significantly decreased as the dye concentration increased. The optimal concentration identified for maximizing the coverage area of the nanocomposite was 20 mg/L. This phenomenon can be attributed to the higher light absorption by the BB dye at this concentration, which enhances the photocatalytic process

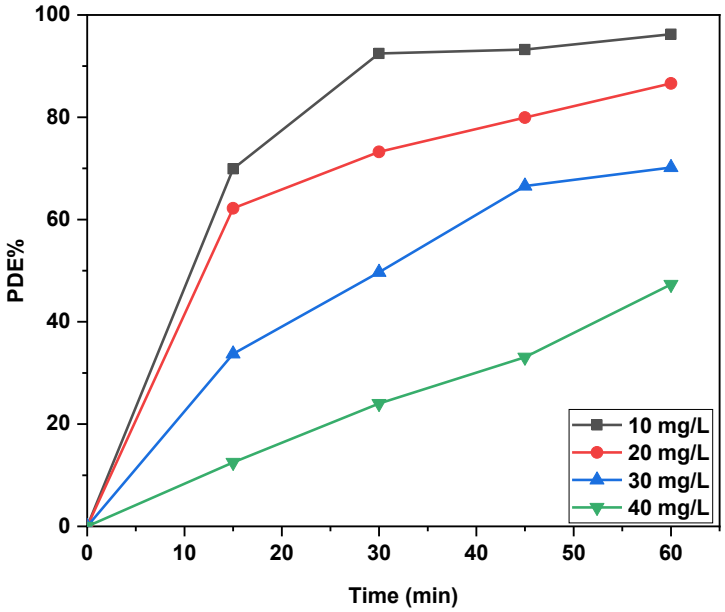

Fig. 9. removal percent BB dye at different initial concentration.

occurring on the surface of the nanocomposite [26, 27]. As the dye concentration increases, it creates multiple layers that hinder light penetration to the surface of the solution. At a concentration of 20 mg/L, the system achieves an optimal photolysis efficiency of 86.25%, as illustrated in Figs. 8 and 9.

CONCLUSION

One possible approach to addressing the wastewater treatment problem is photocatalysis, which primarily utilizes ZnO nanoparticles as a catalyst. This work investigates how the addition of ZnS as a selective metal dopant can enhance the photocatalytic activity of ZnO nanoparticles. The goal of incorporating ZnS into the ZnO NPs lattice is to improve its photocatalytic capabilities, including surface reactivity and bandgap engineering. It is anticipated that the unique mix of ZnS and ZnO nanoparticles will enhance the degradation efficiency and reduce the need for expensive and potentially hazardous sensitizers. ZnO NPs -based photocatalysts are synthesized and characterized as part of the experimental study. Brilliant blue (BB) photocatalysis is being used to investigate how metal dopants affect the rate and effectiveness of degradation. The results facilitate an understanding of the fundamental concepts that underpin the photocatalytic process and provide valuable guidance for advancing and improving advanced photocatalytic systems. Ultimately, this study contributes to the development of efficient and sustainable methods for removing azo dyes from various wastewater sources, thereby enhancing both human welfare and environmental preservation.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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