

The significance of enhanced photocatalytic degradation of RhB on the synthesis, characterization, and effects of Ag doped CdS-WO₂ Nano composites

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Abstract

A simple and sealing agent-free hydrothermal approach was used to fabricate the very modest Ag/CdS-WO₂ Nano composite in this article. Powder X-ray diffraction (XRD) and UV-vis diffuse reflectance (DRS) spectroscopy was used to characterise the synthesized Ag loaded CdS-WO₂ Nano composite. Under visible light irradiation (VLI), the photocatalytic activity of synthesized photocatalysts was tested for the photodegradation of rhodamine B (RhB). pH, catalyst dose, oxidant dose, and irradiation time were the parameters employed to optimise the photocatalyst. A plausible reaction mechanism for improving Ag/CdS-WO₂ photocatalytic activity has been postulated based on this. As a result, we have an inclination to assume that it could be a promising material for photodegradation of organic contaminants in wastewater.

Keywords: Ag/CdS-WO₂; Rh B; Photocatalyst; Visible light irradiation; Degradation

1. Introduction

Water is extremely crucial in our environment for the regular weather and the co-evolution of life on Earth. Water on the globe is almost entirely salty, rendering it unsafe for drinking and irrigation. Only 0.77% occurs as liquid fresh water and its distribution are very inhomogeneous [1]. Drinking water should be free of pathogenic germs and contamination by toxic compounds like pesticides and industrial chemicals. Drinking water that is both clean and fresh is crucial for human and animal existence [2]. Water pollution is the contamination of aquatic environment, which is most often caused by industrial waste. Deficiently treated wastewater, for instance, can degrade aquatic ecosystems when released onto natural water bodies. The waste-carrying water, or effluent, is dumped into streams, lakes, or seas, where the toxins are spread. Textile colours and other manufacturing dyes mix nicely with freshwater resources from a variety of sources [3]. Furthermore, due to the highly hazardous chemical compounds included in these colours, they can be regarded serious water pollutants. In the current year it is estimated that some 30,000 million liters of pollutants are entering our river systems every day, 10,000 million liters from industrial units alone [4]. Synthetic organic dyes are one of the most widespread contaminants in the environment, and they're utilised in 73 different sectors, including textiles, papers, plastics, pharmaceuticals, and cosmetics [5].

Chemical oxidation techniques, in some kind of a broad sense, are a series of chemical treatment treatments that use hydroxyl radicals ($\cdot\text{OH}$) to oxidise organic and sometimes inorganic compounds in water and waste water [6]. Therefore, in real-world water and wastewater treatment, this phrase mainly refers to a form of ozone (O_3), hydrogen peroxide (H_2O_2) and/or UV light based chemical processes. Photocatalysis is a phrase that might be used to represent any process that uses light to stimulate a material [7]. Photocatalysis holds the potential of resolving issues related to the stochastic nature of sunlight, which is seen as a renewable & ideal source of energy for powering activities on Earth [8]. Homogeneous photocatalysis refers to catalytic reactions in which both the reactants and the catalyst comprises only one phase and the photochemical process takes place in a homogeneous solution. UV/ H_2O_2 , UV/ O_3 and UV/ $\text{O}_3/\text{H}_2\text{O}_2$ systems are the three forms of relatively homogenous photocatalysis. In Heterogeneous photocatalysis, UV/Semiconductor has most common are transition metal oxides and semiconductors, which have unique characteristics. Semiconductor photocatalysis has gotten a lot of attention as a greener way to remove all organic pollutants utilising a freely available solar power source without releasing any harmful emissions [9].

Due to its excellent photoactivity, chemical stability, low price, and safe to the environment and human beings, titanium dioxide (TiO_2) has been widely used as a photocatalyst in numerous environmental and resource applications [10]. TiOS_2 has a low affinity for organic contaminants, especially consisting of organic toxins, when utilised in water purification processes. Probably one of the best semiconductor photocatalysts is cadmium sulphide, a visible-light reactive photocatalyst with the band gap of 2.4 eV [11]. The effects of an Ag/CdS- WO_2 Nano composite on organic contaminant photo - degradation in aqueous medium were examined in this study. Hence, the objectives of this work are, (i) To synthesis Ag doped CdS- WO_2 ternary nanocomposite via hydrothermal method. And prepare the photocatalyst with suitable semiconductor material. (ii) To characterized the synthesized material by using X-ray diffraction (XRD) and UV-vis diffuse reflectance spectra (DRS). (iii) To study the photocatalytic performance of the pure CdS, pure WO_2 , CdS- WO_2 and Ag/CdS- WO_2 photocatalyst by their ability in the photocatalytic degradation of Rhodamine-B (RhB) as a target textile pollutant under visible-light irradiation. (iv) To study the optimization of different process parameters and effects like pH, catalyst concentration, concentration of oxidants (persulphate), and irradiation time. (v) Lastly, To propose a reaction mechanism for the increased photocatalytic degradation of Ag/CdS- WO_2 photocatalyst.

2. Materials and methods

2.1 Chemicals

Cetyl trimethyl ammonium bromide (CTAB), sodium sulfide (Na_2S), ethanol (EtOH) and sodium hydroxide (NaOH), cadmium nitrate [$\text{Cd}(\text{NO}_3)_3$], were purchased from SDFCL, India. Silver nitrate (AgNO_3 , 99%) was obtained from Sigma-Aldrich. Tungstic acid (H_2WO_4 , 99%) and Hydrogen peroxide (30% w/v of H_2O_2) was obtained from Nice chemicals, India. Rhodamine B (98%) was purchased from UNI-CHEM. Throughout the trials, double distilled-water (ddH₂O) water was utilised, which was generated using standard laboratory distillation equipment. All of the chemicals were pure substances and did not require any further purification.

2.2 Synthesis of CdS

In a typical process, a beaker was filled with 50 mL of 1 M cadmium nitrate, 25 mL of distilled water, 25 mL of ethanol, and 0.34g CTAB. With rapid stirring, 50 mL 1M Na_2S , 25 mL ethanol, and 25 mL

distilled water were added to this solution. Then, with vigorous swirling, 20 mL of 2M NaOH was added, resulting in a light yellow precipitate. This mixture was placed to a Teflon-lined stainless steel autoclave with a capacity of 250 mL, and heated for 2 hours at 100 °C [12]. The mixture was then cooled down to room temperature, and the residue was extracted using centrifugation, distilled water rinsed many times, ethanol and then dried in oven at 40 °C, to get the resulting is the yellow coloured cadmium sulphide.

2.3 Synthesis of WO_2

In 50 mL of distilled water, 2 g of tungstic acid and 0.895 g of CTAB were neutralized. The mixture was then placed in a Teflon-coated autoclave. The hydrothermal reaction was carried out for 12 hours in a hot air oven at 120 degrees Celsius, after which it was allowed to cool to ambient temperature. The yellow colour precipitate was filtered and cleansed many times with deionized water and ethanol to eliminate contaminants, and dried for 6 hours in a hot air oven at 60 degrees Celsius [13].

2.4 Synthesis of $CdS-WO_2$

To make the $CdS-WO_2$ composite, 0.2 g of the above-prepared WO_2 was dissolved in 80 ml ethanol and sonicated for half an hour. 1 g of CdS nanoparticles were combined in 100 ml of water and sonicated for half an hour after being manufactured using a simple hydrothermal process. The WO_2 suspension was then poured to the CdS sample and sonicated for another 30 minutes. The reaction mixture was autoclaved at 200°C for 12 hours in a Teflon-lined stainless-steel autoclave. The filtrates were collected and washed with distilled water and ethanol various times. Finally, the resulting precipitate was dried for 12 hours at 60 degrees Celsius [14].

2.5 Synthesis of $Ag/CdS-WO_2$ Nano composite

The $Ag/CdS-WO_2$ (5 wt %) Nano composite was generated by swirling 0.5 g of $CdS-WO_2$ into a 40 ml ethylene glycol liquid for 20 minutes. After that, the mixture was reheated for 2 hours at 180 degrees Celsius. Then 30 minutes later, 0.025 g (2.7 percent) $AgNO_3$ was added with steady stirring. The resultant mixture was cooled to ambient temperature, rinsed three times with ethanol, and then dehydrated for three hours at 60 °C [15]. The fabrication of $Ag/CdS-WO_2$ nanocomposite is depicted schematically in Figure 1.

2.6 Characterization of photocatalysts

The synthesised photocatalysts' X-ray diffraction (XRD) spectra were recorded through the use of an X-ray diffractometer (Mini Flex II, Japan) with Cu K radiation (1.54 nm) at a scanning rate of 3°/min. The phase purity was ascertained using X-ray diffraction. In the region of 200–800 nm, diffuse reflectance spectra (DRS) were acquired using a Shimadzu 2100 spectrophotometer.

2.7 Photocatalytic degradation studies

The photocatalytic efficiency of the as-synthesised photocatalyst was assessed utilising a photocatalysis chamber and photo degradation of RhB under visible-light irradiation. As a visible-irradiation emitter, a 250W tungsten halogen lamp was used. To get a catalyst concentration of 1.0 g/L, use 75 mL of RhB dye solution. The dispersion was magnetically agitated in the darkness for 60 minutes prior to light irradiation to achieve an adsorption-desorption equilibrium at ambient temperature [16]. During the irradiation, 4 mL serial dilutions were collected at regular intervals and the photocatalyst was centrifuged out. A UV-visible

spectrophotometer (Jasco-630) from Japan was used to track RhB's distinctive absorption wavelength of 554 nm.

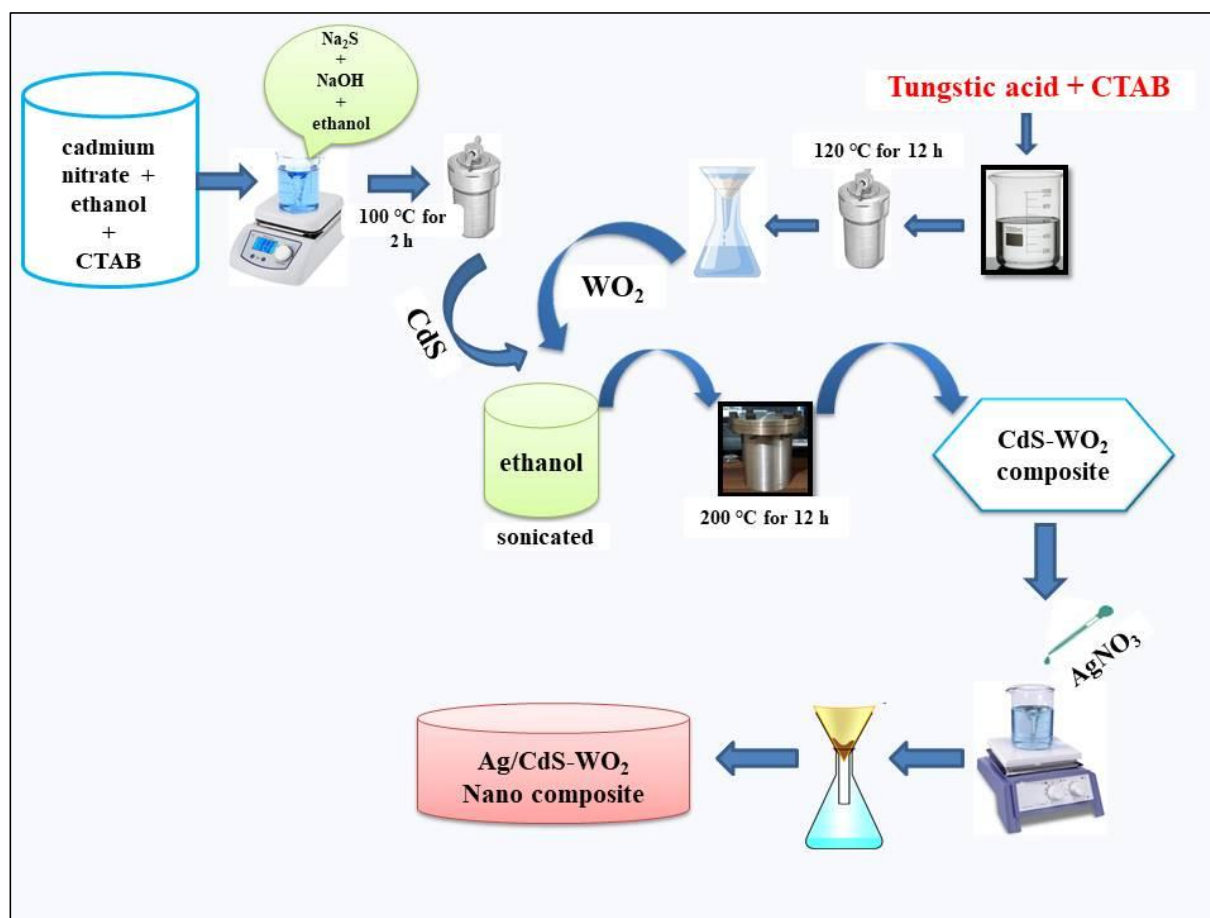


FIG 1. The synthesis of Ag/CdS-WO₂ nanocomposite is depicted schematically.

3. Results and discussions

3.1 XRD studies

XRD results in Fig. 2. were used to analyse the crystalline phase and purity of the as-synthesised bare CdS, bare WO₂, CdS-WO₂, and Ag/CdS-WO₂ nanocomposites. XRD was used to analyse the phase and structure of CdS semiconductor. The hexagonal phase structure was closely matched (JCPDS File no. 10-0454) by the powder XRD pattern of CdS nanoparticles. The (101), (102), (110), (103), (201), (004), and (104) planes had diffraction peaks at 20.93°, 35.04°, 43.52°, 48.8°, 52.02°, 55.97°, and 61.09°, respectively. No impurity peak was observed. Furthermore, peak broadening was observed implying either the amorphous nature of the compound or the nano crystalline behavior of the sample [12]. At 2θ = 21.02°, 24.47°, 26.85°, 27.94°, and 42.03°, the XRD pattern of pure WO₂ revealed monoclinic crystal structure corresponding to the (002), (200), (120), (112), and (222) diffractions (JCPDS no. 43-1035). Only monoclinic WO₂ peaks appear in the XRD patterns of Ag/CdS-WO₂ Nano composites, with no additional CdS peaks. Due to less available content of CdS nanoparticles may be the reason for absence of

CdS peaks. In the Ag/CdS-WO₂ Nano composites, however, the peak intensity of WO₂ did rise as the quantity of CdS increased [17].

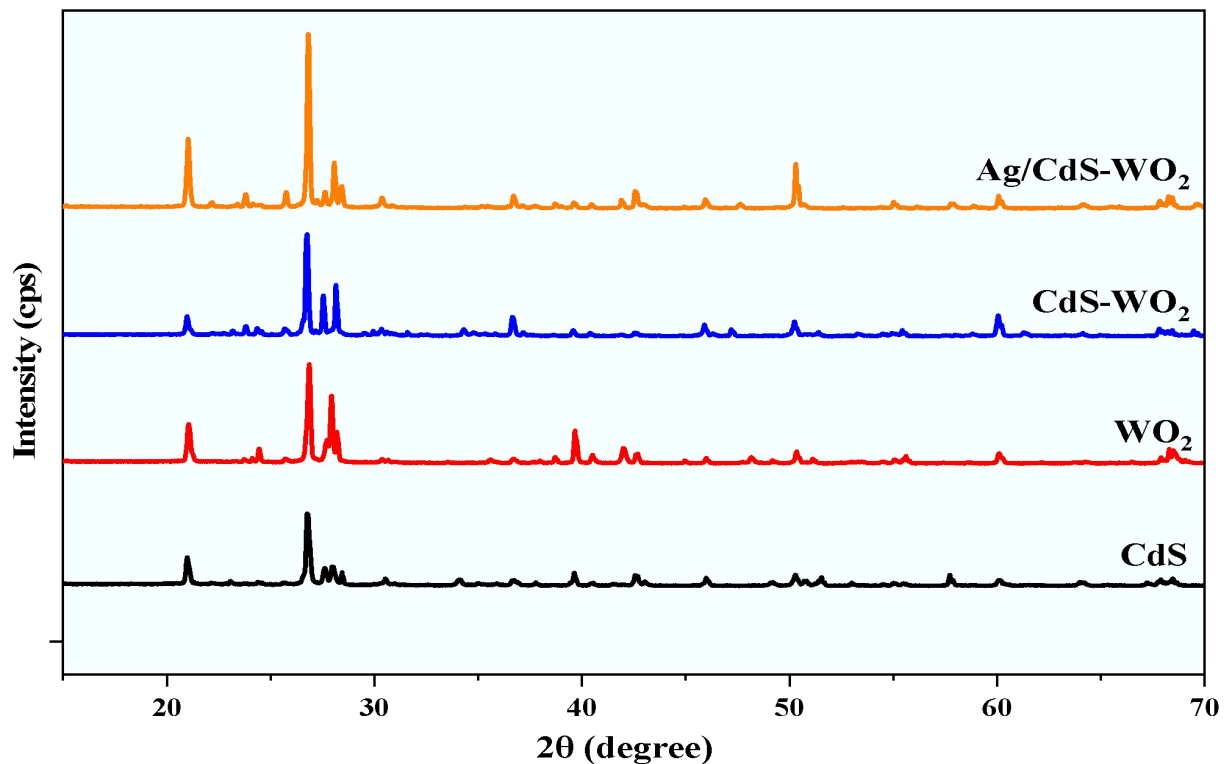


FIG 2. XRD spectrum of (a) CdS, (b) WO₂, (c) CdS-WO₂ and (d) Ag/CdS-WO₂

3.2 Optical absorption studies

The light absorption properties of CdS, WO₂, CdS-WO₂ and Ag/CdS-WO₂ photocatalysts were investigated by UV-vis diffuse reflectance spectroscopy and the spectral characteristics are displayed in Fig. 3. The optical peaks of absorbance for synthesised CdS, WO₂, CdS-WO₂, and Ag/CdS-WO₂ are 423, 510, 525, and 485 nm, correspondingly and 2.93, 2.43, 2.36, and 2.55 eV are the computed band energy gap values, accordingly. It should be mentioned that the addition of WO₂ increases the visible light absorption capability of CdS. As shown in Figure 4, the photocatalytic activity of CdS photocatalysts in the degradation of RhB was limiting, with efficiencies of 82.5, 93.2, 95.0, and 96.5 percent after 90 minutes of irradiation, respectively [18-20]. Adsorption and photo catalysis work together to degrade RhB dye. It should be noted that a significant improvement of RhB degradation can be found in the presence of both catalyst and light.

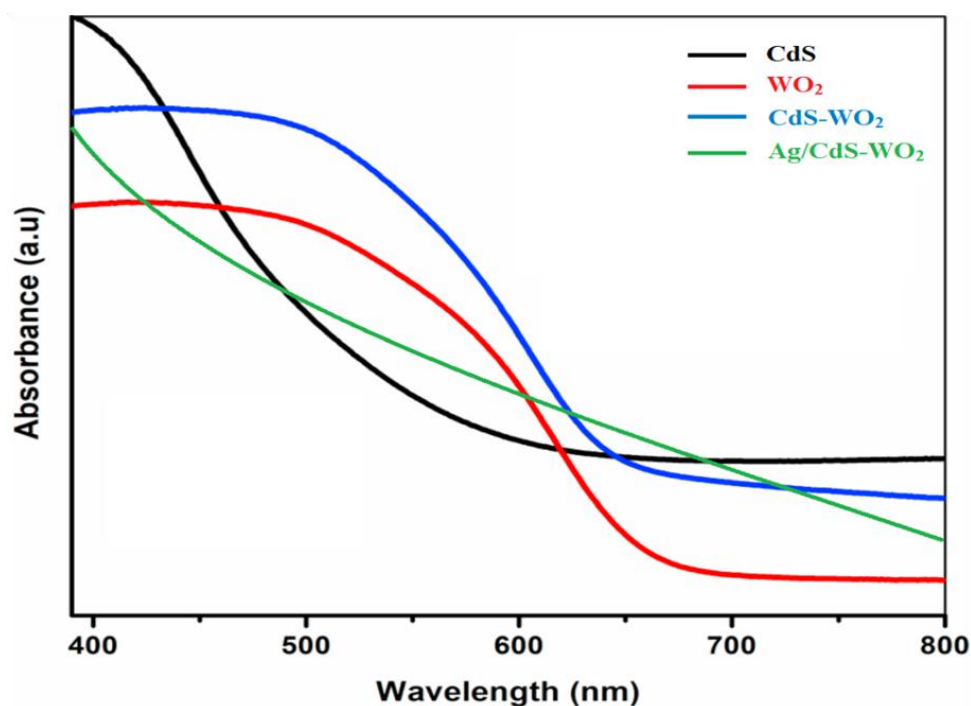


FIG 3. UV-DRS of CdS, WO₂, CdS–WO₂ and Ag/CdS–WO₂ Nanocomposites.

3.3 Photocatalytic degradation studies

3.3.1 Effect of pH

At different pH values (3–9), the photocatalytic activity of produced catalysts was studied. The production of aromatic hydroxylated species slowed the degradation of rhodamine B at higher pH (> 8) due to the formation of aromatic hydroxylated species that occurs in the form of anions and competes with dye molecules for adsorption, resulting in a reduction in degradation efficiency. As a result, maintaining an optimal pH level is essential to avoid wasting extra catalyst; It also aids in the maximal assimilation of visible light for better photodegradation [21]. The pH trend of catalysts is shown in graph (a) in Figure 4. At neutral pH = 7, CdS degrades at a max of 65 percent. Because of the increased active sites on 75 percent of WO₂ at neutral pH, it degrades more quickly (i.e., 7). Likewise, at neutral pH = 7, the CdS–WO₂ catalyst exhibited maximal degradation of 76 percent. Ag/CdS–WO₂ had a higher final degradation rate of 90% than that of the other two catalysts. The opportunities of dye molecules have increased as a result of the injection of Ag on the CdS–WO₂ interface, because there are more active sites available, adsorption on the catalyst's surface improves.

3.3.2 Effect of catalyst concentration

The amount of CdS, WO₂, CdS–WO₂, and Ag/CdS–WO₂ used to optimise the catalyst dosage for degrading rhodamine B dye was changed from 10 to 90 mg/100 ml. Figure 5 illustrates that as the catalyst dose is increased, the degradation becomes more intense due to the increased availability of catalytic site. Up to a certain point (Ag/CdS–WO₂ = 75, 150, 225, 300 mg/100 ml), the trend continued the results demonstrated that rhodamine B degradation was slowed due to the formation of agglomerates. [22].

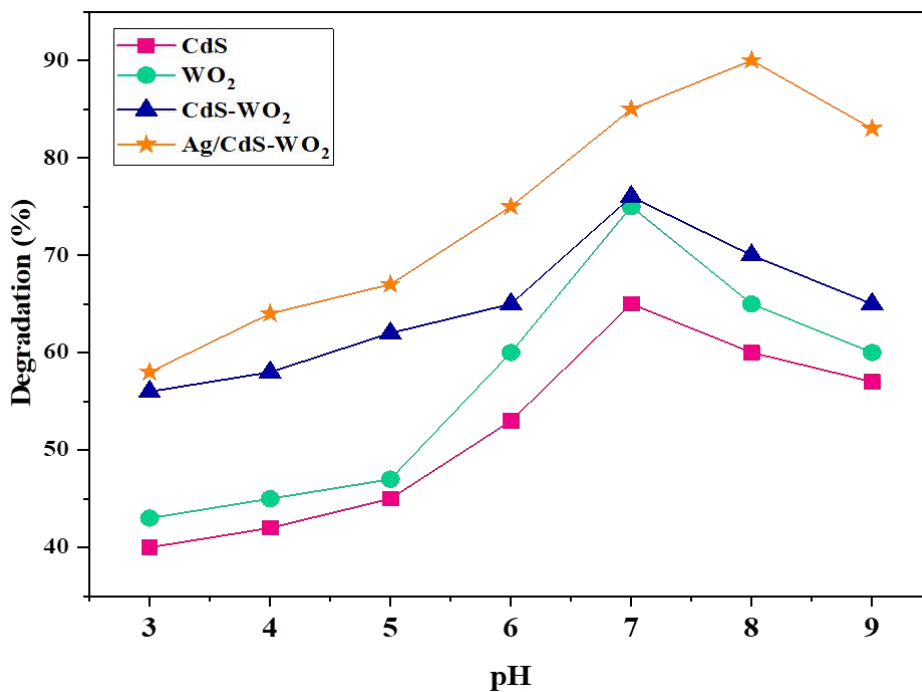


FIG 4. CdS, WO₂, CdS-WO₂, and Ag/CdS-WO₂ were used to optimise pH reaction parameters.

As a result, with the above-mentioned catalyst loading of certain catalysts, the maximal degradation is obtained.

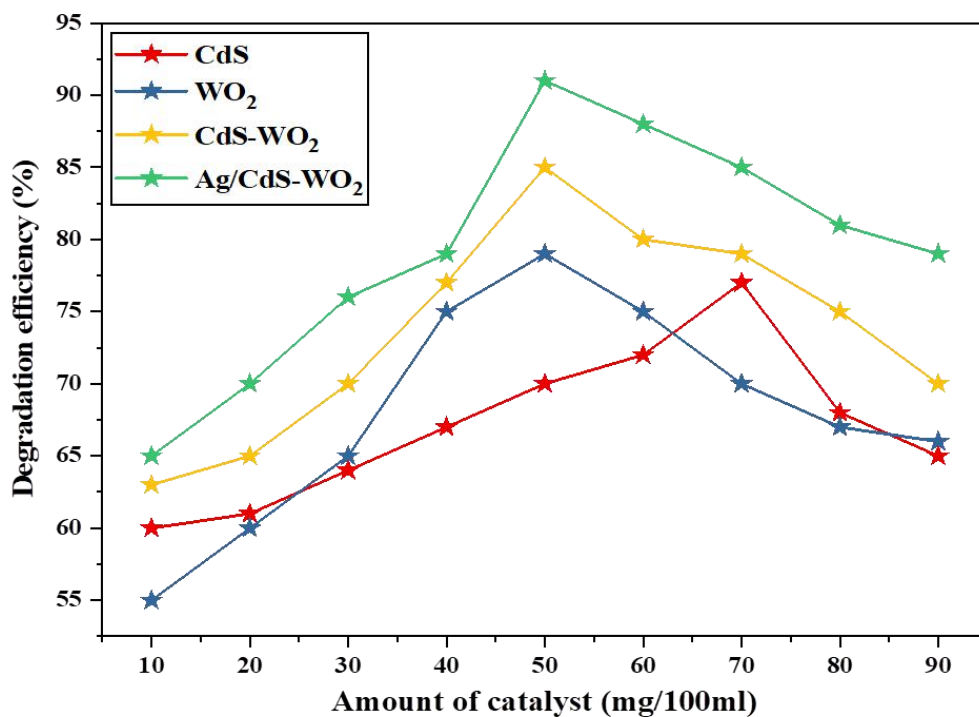


FIG 5. Optimization of reaction parameter of catalyst dose using CdS, WO₂, CdS–WO₂ and Ag/CdS–WO₂

3.3.3 Effect of oxidant concentration

Experiments on the photocatalytic degradation of RhB were carried out to investigate the role of S₂O₈²⁻, using oxidant concentrations ranging from 3 to 13 mM as a starting point. For three distinct catalysts CdS, WO₂, CdS–WO₂, and Ag/CdS–WO₂, the effect of oxidant dosage on dye degradation was determined. And the results are depicted in Figure 6. Under the reaction conditions examined, it is clear that the deterioration significantly improved as the concentration of S₂O₈²⁻ increased. With an increasing in the initial per sulphate concentration, the rate of decolorization increases to 43.41, 72.40, 74.40, and 79.32 percent. The capability of persulfate to behave like an electron acceptor is responsible for the improvement [23].

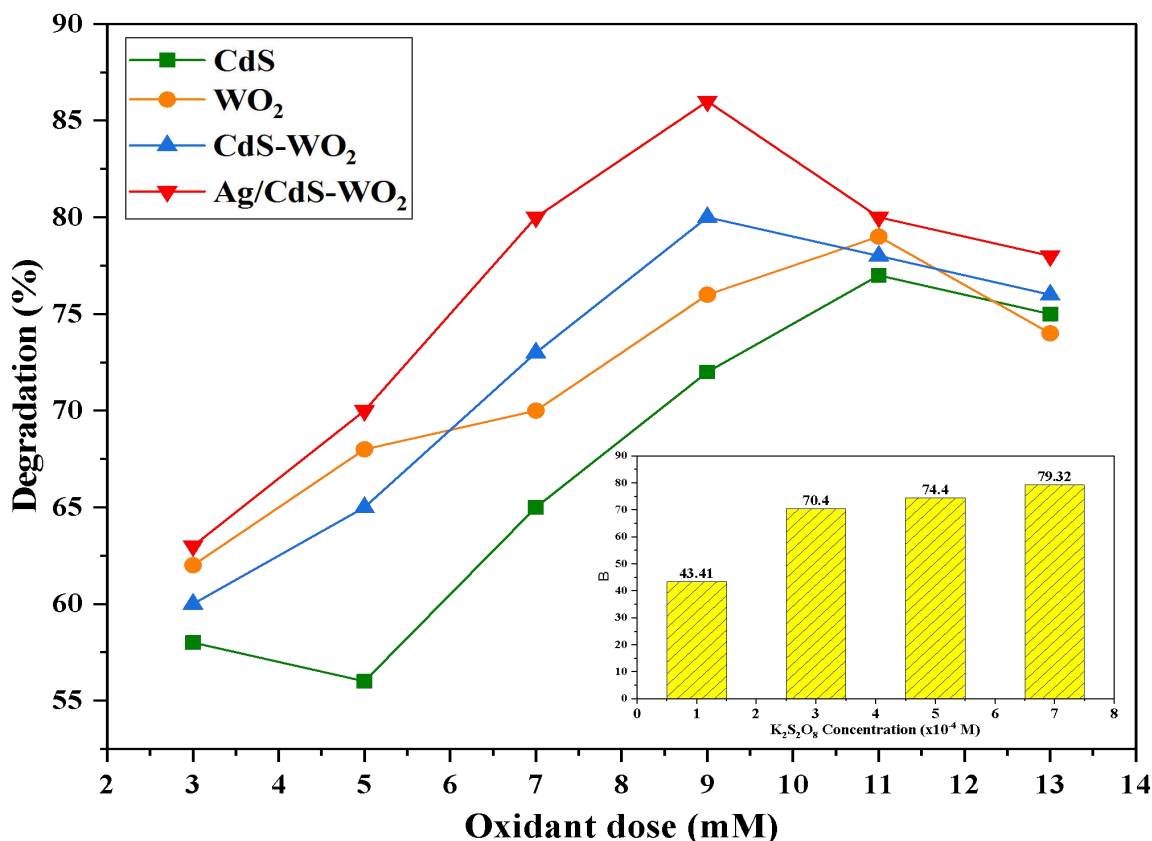
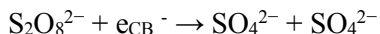
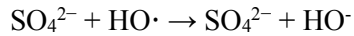
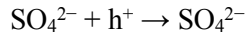


FIG 6. Optimisation of the oxidant dose reactivity parameter using CdS, WO₂, CdS–WO₂ and Ag/CdS–WO₂

Sulphate radicals, which have a significant potential (2.6 eV), are a powerful oxidant that can contribute in RhB breakdown. This is why the rate has decreased [24].





3.3.4 Effect of irradiation time

By holding the above three variables (pH, oxidant dose, and catalyst amount) constant while changing the time (10–90 minutes), the time can be optimised. The degradation of four distinct catalysts, including CdS, WO₂, CdS-WO₂, and Ag/CdS-WO₂, was studied. The catalysts were removed from the precursor solution and their absorbances have been measured using only a spectrophotometer just after time intervals were completed. In the presence of the Ag/CdS-WO₂ photocatalyst, the UV–visible spectra of RhB irradiated with visible light at different time intervals are shown in Fig 7. In Fig. 8, the collected data are displayed as percentage degradation. The statistics clearly show that the proportion of degradation grows over time. With the catalysts, the maximum efficiency were recorded after 70 minutes, as a result of the best performance of individual catalysts under corresponding optimal conditions, 70 minutes was chosen as the ideal time.

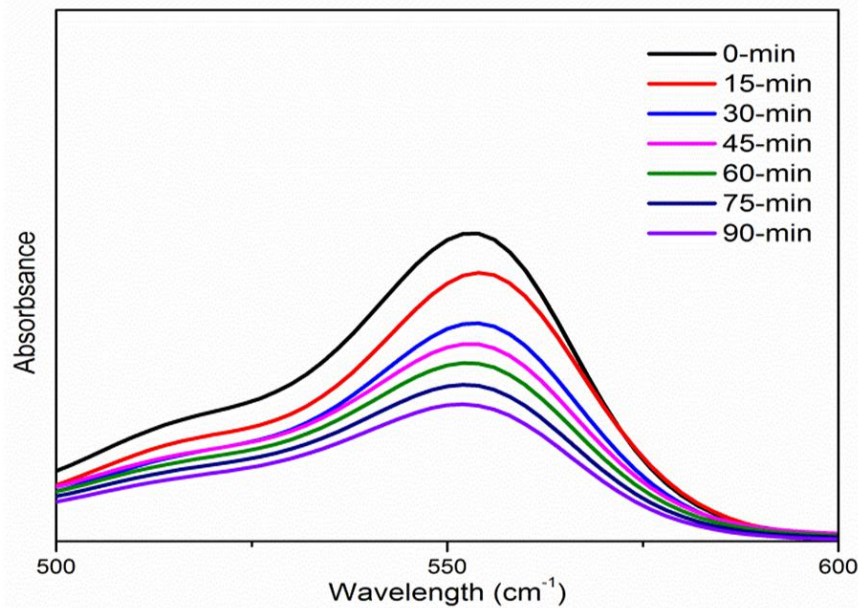


FIG 7. UV–visible spectra of RhB at different time intervals of Ag/CdS-WO₂.

3.4 Reaction Kinetics

The pseudo first-order kinetic model was used to examine the experimental results for the quantitative analysis of RhB degradation. When the contaminant concentration is in the mill molar range, the equation is specifically designed for photocatalytic experimental studies.

$$\ln \frac{C_o}{C} = - kt$$

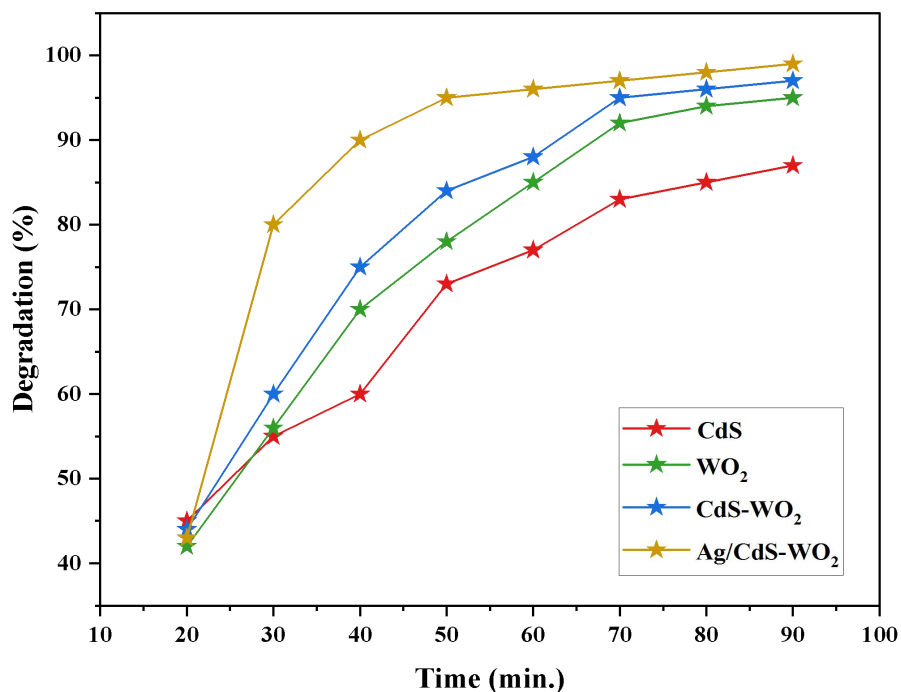


FIG 8. Optimization of reaction parameter of irradiation time using CdS, WO₂, CdS–WO₂ and Ag/CdS–WO₂

Where C_0 denotes the starting concentration and C denotes the RhB concentration at time t . The value of k can be calculated from the slope of the pseudo first-order reaction and represented in figure 9 by plotting $\ln(C_0/C)$ over time. The results show that different dye concentrations of 75, 150, and 225 g/L of Ag/CdS-WO₂ have distinct K (rate constant) values for the degradation of RhB. The 75 g/L Ag/CdS-WO₂ concentration was higher than that of the 150 and 225 g/L Ag/CdS-WO₂ concentrations, indicating that the integration of both catalysts improves degrading ability over the individual catalysts. Lastly, among many other composites, Ag/CdS-WO₂ was really a new nanocomposite with unique properties.

3.5 Photocatalytic degradation mechanism

By absorbing light energy and generating a hole (h^+) in the valence band, an electron in the valence band (VB) is excited to a higher energy [25]. The electron - hole pairs migrate to the CdS surface and interact with molecular oxygen (O_2) and H_2O to form the superoxide radical anion ($\bullet-O_2^-$) and the hydroxyl radical ($\bullet-OH$), respectively, which act as the active center and strong oxidizing agent for the photo catalytic activity [18, 19, 23, 24]. So under influence of enhanced visible light, RhB degrades due to two reactions: de-ethylation and disintegration of the RhB chromophore structure. These processes can be characterized by the shift of the maximum absorption band (λ_{max}) and change in the absorption maximum C_{max}/C_{max}^0 respectively [26]. Thus the process of producing photo excited e^- can be used to generate more $\bullet-O_2^-$ from O_2 , subsequently accelerating reaction with organic dyes. Simultaneously, holes in the valence band (h^+) have had the capable of degrading RhB. Combined with two active species $\bullet-O_2^-$ and h^+ , photo catalyst can degrade organic dyes in a short time [27].

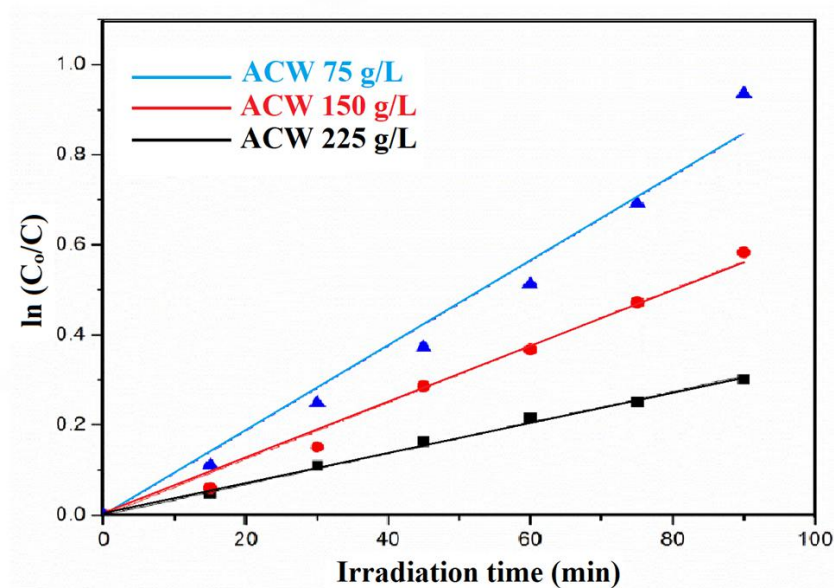
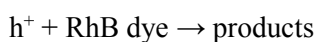
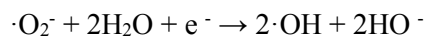
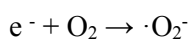
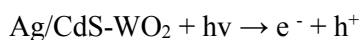


FIG 9. Pseudo-first-order kinetic fitting curves of Rh B over Ag/CdS-WO₂ composite.

As a result, the following is a feasible reaction mechanism incorporating RhB dye photodegradation:



The likely photocatalytic degradation mechanism in the presence of nanocomposite photocatalyst is represented schematically in Fig. 10 based on the foregoing calculations.

4 Conclusion

A simple and sealing agent-free hydrothermal approach was used to make the very stable Ag/CdS-WO₂ nanocomposite. The effect of photocatalyst amounts; initial dye concentration and K₂S₂O₈ become studied. In all circumstances, RhB degradation following pseudo-first order kinetics. The findings of the present study shown that the existence of oxidants can have a serious influence on the source compound's photocatalytic degradation efficiency as well as the rate of conversion of organic intermediates. The concentration levels of S₂O₈²⁻ were discovered to have a significant impact on degrading efficiency. The initial concentration of S₂O₈²⁻ had a clear favourable effect on the degradation process, significantly increasing RhB photodegradation efficiency. The effect of S₂O₈²⁻ on the breakdown of RhB was perhaps the most significant. The addition of a minute amount of oxidant is an inexpensive way to greatly improve the degradation rate of a photocatalyst. The unique Ag/CdS-WO₂ nanocomposite has important potential in degradation of organic pollutants.

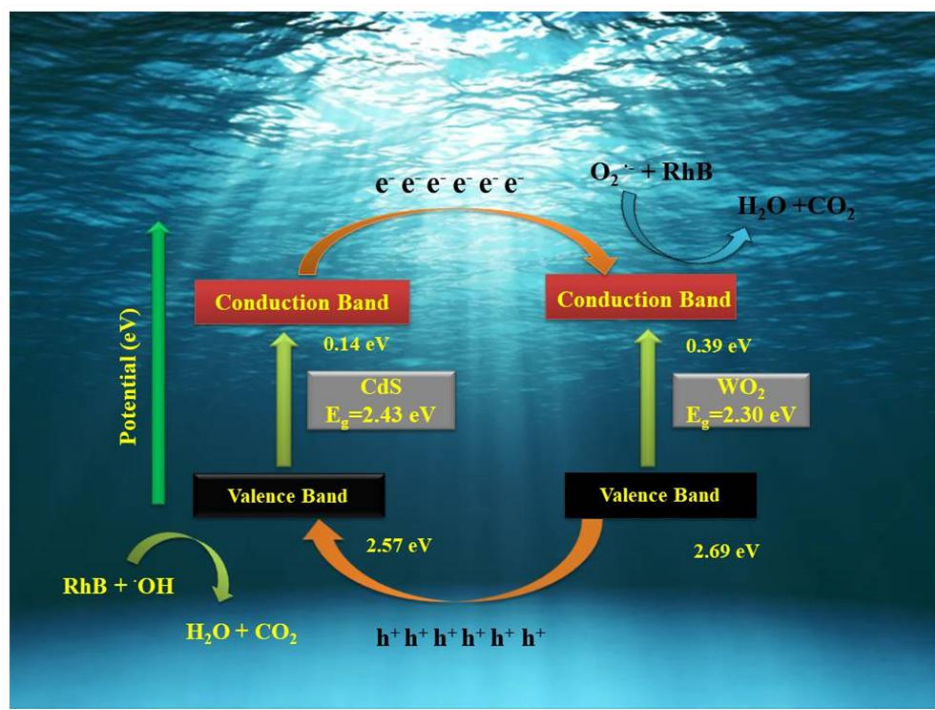


FIG 10. Under VLI, the Ag/CdS-WO₂ nanocomposite photocatalyst for the degradation of RhB is shown schematically.

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