

Full Length Article

Novel silver vanadate coupled semiconductor nanocomposites for effective removal of toxic organics

S. Sasikruba^a, R. Siranjeevi^b, I. Muthuvel^{a,c}, G. Thirunarayanan^c, T. Rajachandrasekar^{a,*}^a Photocatalysis Laboratory, Department of Chemistry, M.R. Govt. Arts College (Affiliated to Bharathidasan University, Tiruchirappalli-24), Mannargudi 614 001, Tamil Nadu, India^b Department of Chemistry, Saveetha School of Engineering, Saveetha Institute of Medical and Technical Sciences, Saveetha University, Chennai 602 105, Tamil Nadu, India^c Advanced Photocatalysis Laboratory, Department of Chemistry, Annamalai University, Annamalai Nagar 608 002, Tamil Nadu, India

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ABSTRACT

One of the world's most important challenges is the lack of access to clean water, and researchers are working tirelessly to find a solution. Nanotechnology-treated water is superior to conventionally treated water since it contains no hazardous microorganisms or organic dyes. In this study, the influence of light on Ag₃VO₄ nanocomposites doped with synthesized ZnO nanoparticles was analyzed. SEM, FTIR, XRD, XPS, and UV-vis spectroscopy were just some of the methods used to characterize the as-prepared nanocomposites. An Ag₃VO₄/ZnO nanocomposite was used to successfully adsorb and photodegrade Acid Green-16 (AG-16), and Acid Red-72 (AR-72) from an aqueous solution. Visible light dramatically accelerates the adsorption and photodegradation of the Ag₃VO₄/ZnO nanocomposite compared to complete darkness. 77.52 %, 82.86 %, and 89.56 % of AG-16 and 77.11 %, 82.74 %, and 87.91 % of AR-72 were removed by the ZnO, Ag₃VO₄, and Ag₃VO₄/ZnO nanocomposites, respectively, in less than 60 min. However, visible-light photodegradation is more successful than adsorption alone in removing AG-16 and AR-72. In this pioneering study, we assess the catalytic performance of newly synthesized ZnO incorporated Ag₃VO₄ nanocomposites for the UV-assisted degradation of organic dyes. Our study presents an innovative catalyst system that exhibits improved efficiency and holds promise for implementation in environmentally sustainable wastewater treatment methods.

1. Introduction

Most of the world's rivers, lakes, and seas are composed of water, which is a chemical liquid that is tasteless, odourless, and practically colourless. Water also makes up the majority of the fluids found within the bodies of most living creatures. Even though it does not contain any calories or organic nutrients, water is known as a universal solvent due to its capacity to dissolve a wide range of substances. This is despite the fact that water itself does not supply any of these things. Water is an essential component of all known forms of life [1]. The lack of access to clean water is already a big problem that is only expected to become worse in the years to come as a result of heavy global industrialization and rising human population [2]. The primary cause of pollution in the atmosphere is the introduction of unprocessed, raw waste into the environment [3]. This is accomplished mostly via the emissions produced by various forms of industrial activity. The discharge of untreated

or poorly treated effluent into the environment by industries results in the contamination of both the water and the soil. A high potential to cause cancer in people, as well as in animals and aquatic environments, and that they have a low rate of biodegradability [4]. In addition to this, it is neurotoxic, which means that it causes persistent damage to both animals and people. The dyes and pigments that are found in textile effluents may potentially contaminate water sources. The requirement for dyes for industrial uses is essential for society, despite the fact that they have an effect on the surrounding environment [5]. Because of its ease of use and modest power needs, adsorption is the most pragmatic method of pollution control currently available. The photocatalytic degradation of catalysts is an approach that seems to have more potential. The one tried-and-true strategy for enhancing the efficiency of degradation is to couple photocatalysts with photosensitizers or co-catalysts in order to form multi-component composite photocatalysts [6,7]. A potential photocatalyst is zinc oxide (ZnO), which has a higher

* Corresponding author.

E-mail address: proftrchem1966@gmail.com (T. Rajachandrasekar).<https://doi.org/10.1016/j.chphi.2024.100630>

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photocatalytic effectiveness for the breakdown of organic contaminants [8].

In recent years, ZnO has become a lot of popularity, and it is now utilized in a wide variety of applications, such as solar cells, transparent conductive contacts, light-emitting devices, spintronic devices, laser deflectors, paints, antibacterial agents, biosensors, piezoelectric transducers, and gas sensors. ZnO is also used in a variety of paints, which are used to protect against bacteria. [9,10,11]. Recently, it was revealed that the small bandgap energy of silver vanadate (Ag_3VO_4), which is around 2.1 eV and significantly lower than that of silver halides, makes it a good candidate for visible-light-driven photocatalysis. This discovery was made possible by the fact that silver halides have substantially higher bandgap energies. After that, the nanocomposite was put through a series of tests to determine whether or not it has the capacity to eliminate Acid Green-16 dye from water when exposed to visible light. After 120 min of irradiation, the findings indicated that $\text{Ag}_3\text{VO}_4/\text{ZnO}$ nanocomposite was very successful at removing the dye. The removal effectiveness of the nanocomposite was over 95 % after the dye was removed.

The purpose of this investigation was to create one-of-a-kind $\text{Ag}_3\text{VO}_4/\text{ZnO}$ hybrid photocatalysts with a range of Ag_3VO_4 wt. Acid Green-16(AG-16) served as a model pollutant that was used in the experiment that investigated the photocatalytic activity of the $\text{Ag}_3\text{VO}_4/\text{ZnO}$ nano combination when exposed to UV light. When compared to pure ZnO and Ag_3VO_4 , the generated $\text{Ag}_3\text{VO}_4/\text{ZnO}$ composites displayed remarkable photodegradation, photostability, and antibacterial activity [12]. This was achieved despite the removal of Acid Green-16 (AG-16). In this article, we discuss how the hydrothermal dispersion process may be used for the synthesis of oxide-wrapped ZnO silver vanadate. In addition, investigated whether or not Ag_3VO_4 and ZnO are effective as catalysts for the breakdown of AG -16 and AR-72 when exposed to UV and solar irradiation [13].

The field of advanced nanomaterials for environmental remediation has seen a notable advancement with the creation of a novel nanocomposite known as Highly Visible Light Driven $\text{Ag}_3\text{VO}_4/\text{ZnO}$. The use of a new nanomaterial combining Ag_3VO_4 and ZnO demonstrates the potential for a unique approach in effectively eliminating Acid Green-16 dye from aqueous solutions. This composite material harnesses the improved photocatalytic properties resulting from visible light, thereby presenting new opportunities in the pursuit of sustainable and efficient wastewater treatment. It effectively tackles a pressing environmental issue while also demonstrating the significant capabilities of nanotechnology in the realm of water purification.

2. Materials and methods

2.1. Materials

Commercially accessible reagents, such as Acid Green-16 and Acid Red-72, Zinc nitrate hexahydrate, silver nitrate, oxalic acid dihydrate (Merck), ceric ammonium nitrate, and ammonium metavanadate (Qualigens), were used as provided. The experimental solution was prepared using double-distilled deionized water

2.2. Synthesis of ZnO nanoparticles

The hydrothermal approach was used to synthesize ZnO nanoparticles. In a standard experimental procedure, a solution containing 0.6 M concentration of zinc nitrate was prepared by dissolving it in 100 ml of water. Subsequently, the resultant solution was carefully transferred into a separating funnel. A conical flask was used to administer a solution of oxalic acid at a concentration of 0.4 M. The experimental procedure included the introduction of oxalic acid into a conical flask, followed by the addition of zinc nitrate into a separating funnel. The solution was agitated for a duration of two hours. The resultant solution, which exhibited a white appearance, was subjected to an aging process

lasting 2 h to facilitate gel formation. Subsequently, the solution was dried in a hot air oven at a temperature of 80 °C for a duration of 24 h. The aerogel was subjected to calcination at temperatures of 400 °C, 500 °C, and 600 °C for a duration of 5 h to facilitate the production of ZnO nanoparticles. A solution containing one mole of ammonium metavanadate was prepared by dissolving it in 35 ml of water. The solution was placed in a beaker and kept at a temperature of 80 °C using a magnetic stirrer. A solution containing two moles of silver nitrate was gradually introduced drop by drop into a separating funnel after its dissolution in 35 ml of water. Accordingly, a catalyst was synthesized.

2.3. Synthesis of ZnO infused Ag_3VO_4 nanocomposites

In a typical synthesis, 100 mL of 0.4 M zinc nitrate hexahydrate(A) and 100 mL of 0.6 M oxalic acid (B) were heated separately in deionized water, 100 mL of solution A was quickly added to solution B, 54 mg of Ag_3VO_4 was previously synthesized, and the combined suspension was agitated for 3 h. Filtered and repeatedly rinsed with DI water, the precipitated zinc oxalate dehydrates produced with Ag_3VO_4 is then used. In a silica crucible, the Ag_3VO_4 -zinc-zincate dehydrate-coupled system is heated in a muffle furnace at a rate of 20 °C per minute for 6 h. After 12 h, after the furnace has cooled to room temperature, the $\text{Ag}_3\text{VO}_4/\text{ZnO}$ catalyst is collected and put to use. 2 wt percent of coated Ag_3VO_4 is included in this catalyst.

2.4. Characterization of $\text{Ag}_3\text{VO}_4/\text{ZnO}$ nanocomposites

Morphological and elemental assessments of $\text{Ag}_3\text{VO}_4/\text{ZnO}$ nanoparticles were analyzed using a field emission scanning electron microscope (FEI Quanta FEG200- FESEM) and Bruker's Energy Dispersive Spectroscopy (EDS). Using a Benchtop X-Ray Diffractometer with Cu-K at 0.15,405 Å in the Braggs angle range 2θ (10–80°). To determine the surface chemistry of the sample, XPS (X-ray photoelectron spectroscopy) was carried out using a PHI5000 versa probe III. To learn more about their composition and how it affects their performance, scientists turned to FTIR spectroscopy (ATR diamond accessory of IR tracer 100 AH/ Japan). Using a UV-visible spectrophotometer, the optical properties of the sample synthesis were examined at (UV 2100, Shimadzu).

2.5. Photocatalytic degradation

Acid Green-16(AG-16) and Acid Red-72(AR-72) were used to examine the photocatalytic activity of ZnO, Ag_3VO_4 , and $\text{Ag}_3\text{VO}_4/\text{ZnO}$ nanocomposites. The following steps were taken to test the freshly synthesized materials for their photocatalytic potential: The adsorption-desorption equilibrium between the dye molecules and the photocatalyst surface was determined by combining 20 mg of ZnO, Ag_3VO_4 , and $\text{Ag}_3\text{VO}_4/\text{ZnO}$ nanocomposites with 100 ml of 20 mg/L AG-16, and AR-72 in the dark using a magnet for 30 min. This was done to guarantee that the dye molecules were equally dispersed across the photocatalyst surface. The mixture was exposed to visible light from a 400-Watt Xenon lamp for the permitted 60 min to facilitate photocatalytic breakdown. In order to analyze the photocatalytic degradation process at 640 nm and 515 nm, we tracked the change in absorbance values of AG-16, and AR-72 every 10 min throughout the irradiation operation. The key active chemicals responsible for color deterioration were also investigated in a trapping experiment. The dye solution contained a variety of scavengers, each at a concentration of 5M Isopropyl alcohol (IPA), benzoquinone (BQ), and ethylenediaminetetraacetic acid disodium (EDTA-2Na) were some of the scavengers used. These compounds were included as hole, hydroxyl, and superoxide anion scavengers. Additionally, the method assessed the degree to which the color had changed. Total organic carbon (TOC) was analysed with a Shimadzu TOC-VCPH (Kyoto, Japan) analyser.

$$\text{Degradation efficiency (\%)} = \frac{\text{Initial absorbance} - \text{Final absorbance}}{\text{Final absorbance}} \times 100$$

3. Results and discussion

3.1. Morphological studies

The surface morphology of the ZnO/Ag₃VO₄ photocatalyst was shown in Fig. 1 using pictures captured by a scanning electron microscope. Ag₃VO₄/ZnO was scanned using SEM, and the result was a smooth, uniformly large number of aggregated nanoparticles with an abnormal size of less than 27 nm (various software packages) between nanoparticles [14]. SEM was used in order to further investigate the surface morphology of the catalyst. Images of a sample consisting of 5 wt percent Ag₃VO₄/ZnO at four different magnifications are shown in the figures. At any magnification, the surface of the ZnO nanomaterial, which is represented by the black area, contains cylindrical Ag₃VO₄ nanoparticles, which are represented by the white region. It is possible to confirm the existence of elements such as zinc, silver, vanadium, and oxygen by conducting an EDX study on a sample that was obtained from a specific location. The atomic weight percentages and elemental atomic percentages are shown in Fig. 1E. In addition, an elemental mapping method was used in order to demonstrate the presence of these constituents. The colorful areas are those that have high quantities of the metals zinc, silver, vanadium, and oxygen (Fig. 2).

3.2. X-ray diffraction pattern

The X-ray diffraction pattern of the ZnO nanoparticles synthesized by the sol-gel technique is shown in Fig. 3. The material that was generated exhibited particles inside the nanoscale range, as shown by the observable widening of the XRD peaks. Through the examination of X-ray diffraction (XRD) patterns, we successfully determined the peak intensity, location, and width, together with the Full-Width at Half-Maximum (FWHM) data. The hexagonal wurtzite phase of ZnO, characterized by lattice constants $a = b = 0.324$ nm and $c = 0.521$ nm

(JPCDS card number: 36-1451) [15], it has been meticulously documented in terms of its diffraction peaks at 31.84°, 34.52°, 36.33°, 47.63°, 56.71°, 62.96°, 68.13°, and 69° [15]. These peaks provide evidence for the presence of the hexagonal wurtzite crystal structure in ZnO and can be attributed to crystal planes (100), (002), (101), (102), (103), and (004) [16]. The (002) plane exhibited the most prominent diffraction peak, suggesting that ZnO nanorods (NRs) displayed a preference for development along the c-axis, which may be attributed to their comparatively greater surface energy [17]. Furthermore, the presence of the characteristic X-ray diffraction (XRD) peak of ZnO in the synthesized nanoparticles serves as evidence for the absence of any impurities. The diameter of the ZnO nanoparticles was calculated using the Debye-Scherrer formula [18].

$$D = \frac{0.9 \lambda}{\beta \cos \theta} \times 100$$

Where, 0.89 is Scherrer's constant, λ is the wavelength of X-rays, θ is the Bragg diffraction angle, and β is the full width at half-maximum (FWHM) of the diffraction peak corresponding to plane (101). The use of Scherrer's formula in relation to the full width at half maximum (FWHM) of the more prominent peak associated with the 101 planes, positioned at an angle of 36.33°, resulted in the determination of the average particle size of the examined sample as 16.21 nm. The evaluation of crystallite sizes was performed for the ZnO samples by using the most prominent peak of (101). The X-ray diffraction (XRD) patterns of Ag₃VO₄/ZnO and ZnO materials exhibited no discernible difference, indicating that the diffraction pattern of Ag₃VO₄/ZnO was identical to that of ZnO. Hence, it is evident that the Ag₃VO₄/ZnO composite exhibits the Wurtzite crystal structure of ZnO. Furthermore, it was noticed that there were no newly detected peaks for Ag₃VO₄ in the Ag₃VO₄/ZnO catalyst. However, it was noted that Ag₃VO₄ exhibited more pronounced peaks at certain wavelengths, including 24.88°, 25.62°, 39.82°, 40.44°, 45.44°, 46.56°, 49.45°, 53.35°, 55.48°, 59.13°, and 60.28° (Fig. 1b). The observed absence of the Ag₃VO₄ peak in Ag₃VO₄/ZnO could potentially be attributed to the relatively low concentration of Ag₃VO₄ on the ZnO substrates.

3.3. FTIR spectra

ZnO, Ag₃VO₄, and Ag₃VO₄/ZnO are the products that were generated, and their FT-IR spectra are shown in Fig. 4. The OH stretching vibrations that were present in each and every sample were in the range of 3400 to 3450 cm⁻¹. A significant vibration band with a frequency range of 400 to 500 cm⁻¹ was found to be the most effective way to illustrate the stretching mode of the Zn-O bond. This band is shown in Fig. 4A. The high absorption peak at 769 cm⁻¹ that is generated by VO₄-3V-O bonding is shown in Fig. 4B. On the other hand, the weak absorption peak that is created by Ag-O bonding is displayed at 497 cm⁻¹. It is determined that these two peaks represent strong absorption peaks and weak absorption peaks, respectively. A further discovery was made about the existence of shallow O-H water bending and stretching bands. It is [14] Additionally observed were the frequencies of 3423 cm⁻¹, 1625 cm⁻¹, and 1392 cm⁻¹, respectively, which were adsorbed on the surface of Ag₃VO₄. The numbers [18,19]. Stretching vibrations of the Zn-O, VO₄, and Ag-O bonds were discovered in the frequency range of 925-470 cm⁻¹, as shown in Fig. 4C. This has been determined by the stretching vibrations. It was determined that the atoms of Ag₃VO₄ were successfully incorporated into the crystal structure of ZnO [20].

3.4. XPS analysis

As can be seen in Fig. 5, the inclusion of Ag₃VO₄ into the ZnO matrix was also confirmed by high-resolution XPS. The existence of Ag₃VO₄ was established by the core-level spectra of Ag 3d in Fig. 3A, which displayed strong peaks of Ag⁺ at 367 and 373 eV for Ag 3d_{5/2} and Ag 3d_{3/2}, respectively. Additionally, the spectra of V 2p shown in Fig. 3b indicated

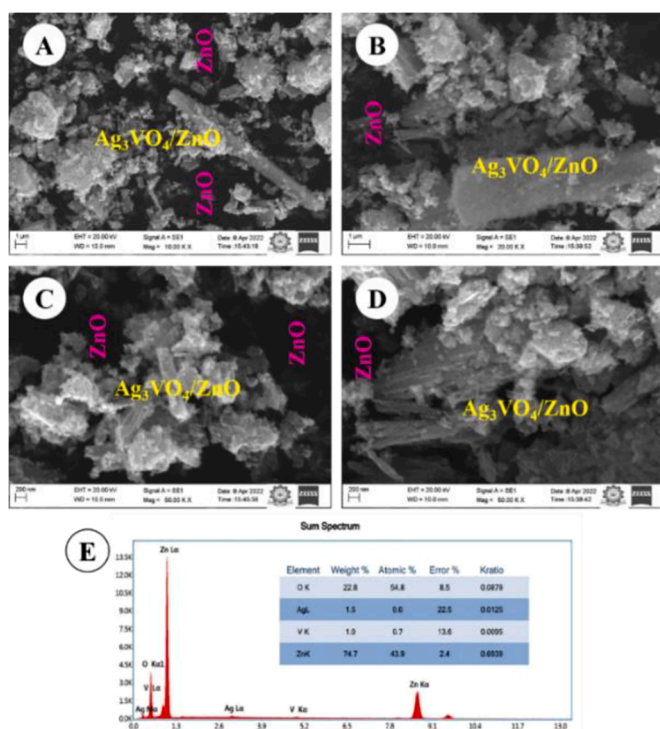


Fig. 1. SEM with EDS analysis of Ag₃VO₄/ZnO nanocomposites.

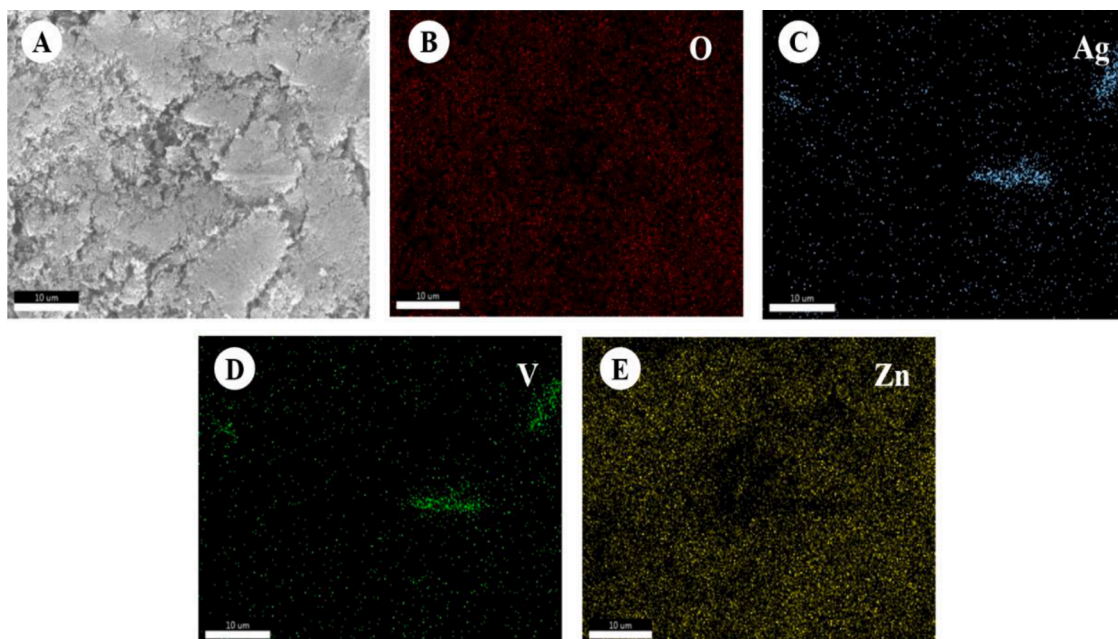


Fig. 2. Elemental color mapping images of $\text{Ag}_3\text{VO}_4/\text{ZnO}$ nanocomposites.

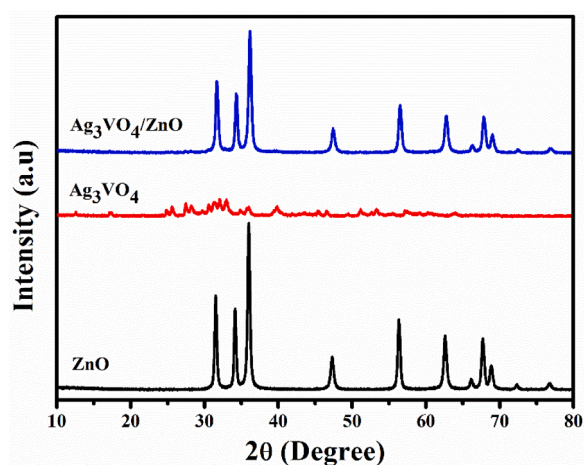


Fig. 3. XRD pattern of ZnO , Ag_3VO_4 , and $\text{Ag}_3\text{VO}_4/\text{ZnO}$ nanocomposites.

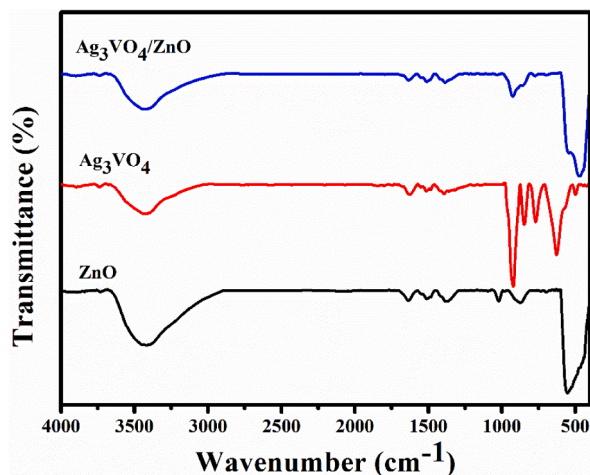


Fig. 4. FTIR spectrum of ZnO , Ag_3VO_4 , and $\text{Ag}_3\text{VO}_4/\text{ZnO}$ nanocomposites.

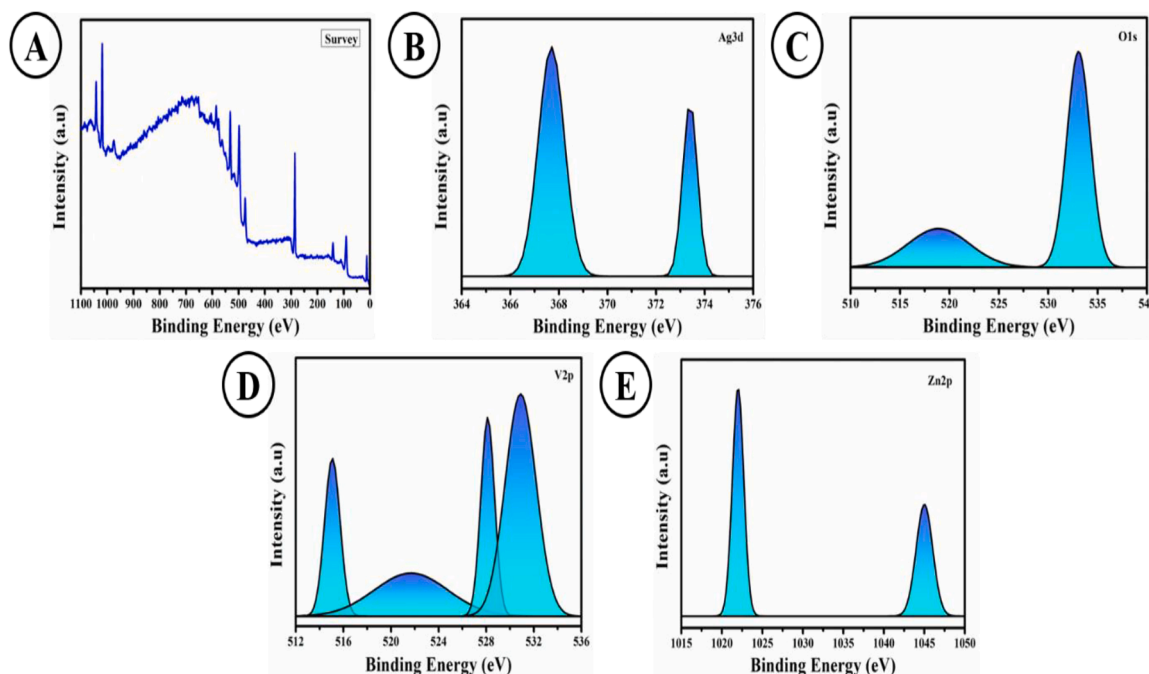
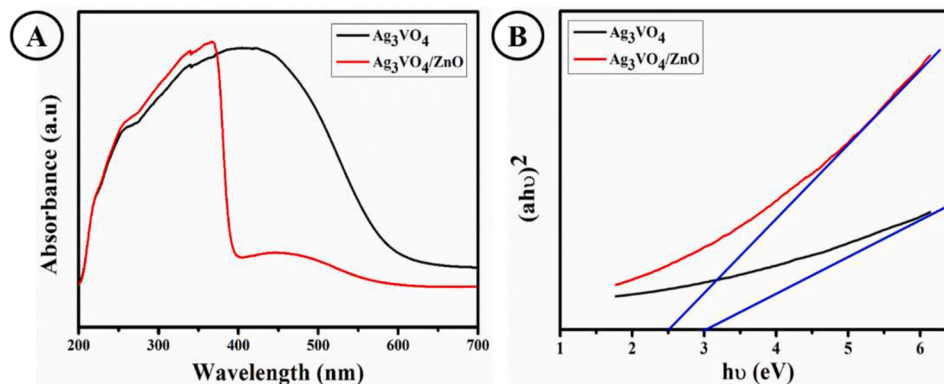
the oxidation number ($+5$) for the primary binding energies seen at 515 and 521 eV. These energies specified the $\text{V } 2p_{3/2}$ and $\text{V } 2p_{1/2}$ orbits that were observed in heterojunctions that were identical to one another [21, 22]. Sharp XPS peaks of Zn^{2+} were found at 1022 and 1045 eV for $\text{Zn } 2p_{3/2}$ and $\text{Zn } 2p_{1/2}$, respectively, and are comparable to the wurtzite ZnO nanoparticles, as shown in Fig. 5E. In Fig. 5C of the $\text{O } 1s$ spectra, the lattice oxygen and the other adsorbed oxygen species were indicated at 518 eV and 533 eV, respectively [23]. As a result, the structural characterization of the triblock copolymer assisted sol-gel produced ZnO that was combined with coprecipitated Ag_3VO_4 was carried out slowly.

3.5. UV-Visible spectroscopy

Fig. 6 displays the UV-visible spectra of ZnO as well as the composites of Ag_3VO_4 and ZnO . The absorption spectrum of pure ZnO showed a distinct absorption edge at around 419 nm, but bulk Ag_3VO_4 had a broader absorption range in the visible region, with an absorption edge located roughly 546 nm away. The spectrum absorption edges of $\text{Ag}_3\text{VO}_4/\text{ZnO}$ composites are shown in Fig. 6, with corresponding values of 366 nm and 419 nm. A semiconductor with a narrow energy band gap, such as Ag_3VO_4 , has the potential to cause a gradual increase in absorption in the visible spectrum. This would cause a shift towards longer wavelengths in the absorption edges. The introduction of Ag_3VO_4 into ZnO resulted in a drop in the energy band gap from 3 eV to 2.5 eV, representing a reduction of 0.5 eV compared to ZnO . The $\text{Ag}_3\text{VO}_4/\text{ZnO}$ composites exhibit a heightened level of visual absorption in comparison to pure ZnO . Indeed, the $\text{Ag}_3\text{VO}_4/\text{ZnO}$ composites exhibit a higher level of visual absorption in comparison to Ag_3VO_4 alone. The higher absorption in the visible region may be attributed to the production of an $\text{Ag}_3\text{VO}_4/\text{ZnO}$ heterojunction. Furthermore, the absorbance increase observed may be attributed to the potential contribution of surface plasmon resonance (SPR) caused by Ag species derived from Ag_3VO_4 [24,25].

3.6. Photodegradation studies

The photocatalytic performance of ZnO , Ag_3VO_4 , and $\text{Ag}_3\text{VO}_4/\text{ZnO}$ nanocomposites was analyzed under 500 W of Xenon lamp illumination using Acid Green-16 (AG-16) and Acid Red-72 (AR-72) as test chemicals. The degradation efficiency (AG-16 and AR-72) of the target dye on the

Fig. 5. XPS spectra of $\text{Ag}_3\text{VO}_4/\text{ZnO}$ nanocomposites.Fig. 6. UV-visible spectrum of Ag_3VO_4 and $\text{Ag}_3\text{VO}_4/\text{ZnO}$ nanocomposites.

newly manufactured photocatalysts changes with reaction time, as shown in Figures-7 and 8. These photocatalysts are currently in the production phase. Nanocomposite (ZnO , Ag_3VO_4 , and $\text{Ag}_3\text{VO}_4/\text{ZnO}$) nanoparticles showed 41.31 %, 52.3 %, and 61.74 % degradation when exposed to a visible source for 20 min, while pure ZnO nanoparticles showed 41.19 %, 52.46 % degradation, and 61.26 % degradation. The color faded with time, as measured by a lessening of the absorption peak strength of the AG-16 and AR-72 dyes at various times. Since the absorption peak's strength decreased with time, it's possible that photo-degradation of the dye is to blame for the color shift [26]. The experimental findings suggest that AG-16 and AR-72 are degraded more quickly by photocatalytic degradation in Ag_3VO_4 and $\text{Ag}_3\text{VO}_4/\text{ZnO}$ nanocomposites than in ZnO after 60 min of exposure to visible light. The assumption that Ag_3VO_4 and $\text{Ag}_3\text{VO}_4/\text{ZnO}$ nanocomposites are more stable than ZnO led to this finding.

This is shown by the fact that the absorption peak has almost disappeared entirely. In addition to this, it was found that the photo-degradation efficiency of AG-16 and AR-72 dyes was improved when ZnO was used as the catalyst. when being illuminated for 60 min, Ag_3VO_4 displayed (82.86 %) for AG-16 and (82.74 %) for AR-72, while the composite exhibited $\text{Ag}_3\text{VO}_4/\text{ZnO}$ (89.56 %) for AG-16 and (87.91

%) for AR-72. These results were obtained when the Ag_3VO_4 was exposed to light. When measured against the rate of AG-16 decomposition, the rate of AG-16 degradation was significantly quicker. The study indicates that the photocatalytic activity of the $\text{Ag}_3\text{VO}_4/\text{ZnO}$ nanocomposite under UV-visible irradiation is much higher than that of ZnO and Ag_3VO_4 respectively. The comparison of the three different sets of data reveals this to be true. This was a result of the very simple design of AG-16 and AR-72. In addition to this, when employed by itself, AG-16 and AR-72 has the potential to function as a photocatalyst sensitizer. This behavior may have something to do with the presence of Ag_3VO_4 on ZnO nanosheets, which promotes the separation of electrons and holes, as can be seen in Fig. 7 and Fig. 8(A). The statistics illustrate the probability of this occurring [27,28].

In order to study the degradation of AG-16 and AR-72, the $\ln(C_0/C_t)$ versus time graphs were plotted for ZnO , Ag_3VO_4 and $\text{Ag}_3\text{VO}_4/\text{ZnO}$ nanocomposites. The observed rate constants for AG-16 degradation were $k_1=0.0248 \text{ min}^{-1}$, $k_2=0.0263 \text{ min}^{-1}$, and $k_3=0.0251 \text{ min}^{-1}$, while for AR-72 degradation, the rate constants were $k_1=0.0245 \text{ min}^{-1}$, $k_2=0.0262 \text{ min}^{-1}$, and $k_3=0.0260 \text{ min}^{-1}$, respectively [29]. These results indicate that the nanomaterials follow pseudo-first-order kinetics, as determined by the Langmuir-Hinshelwood model.

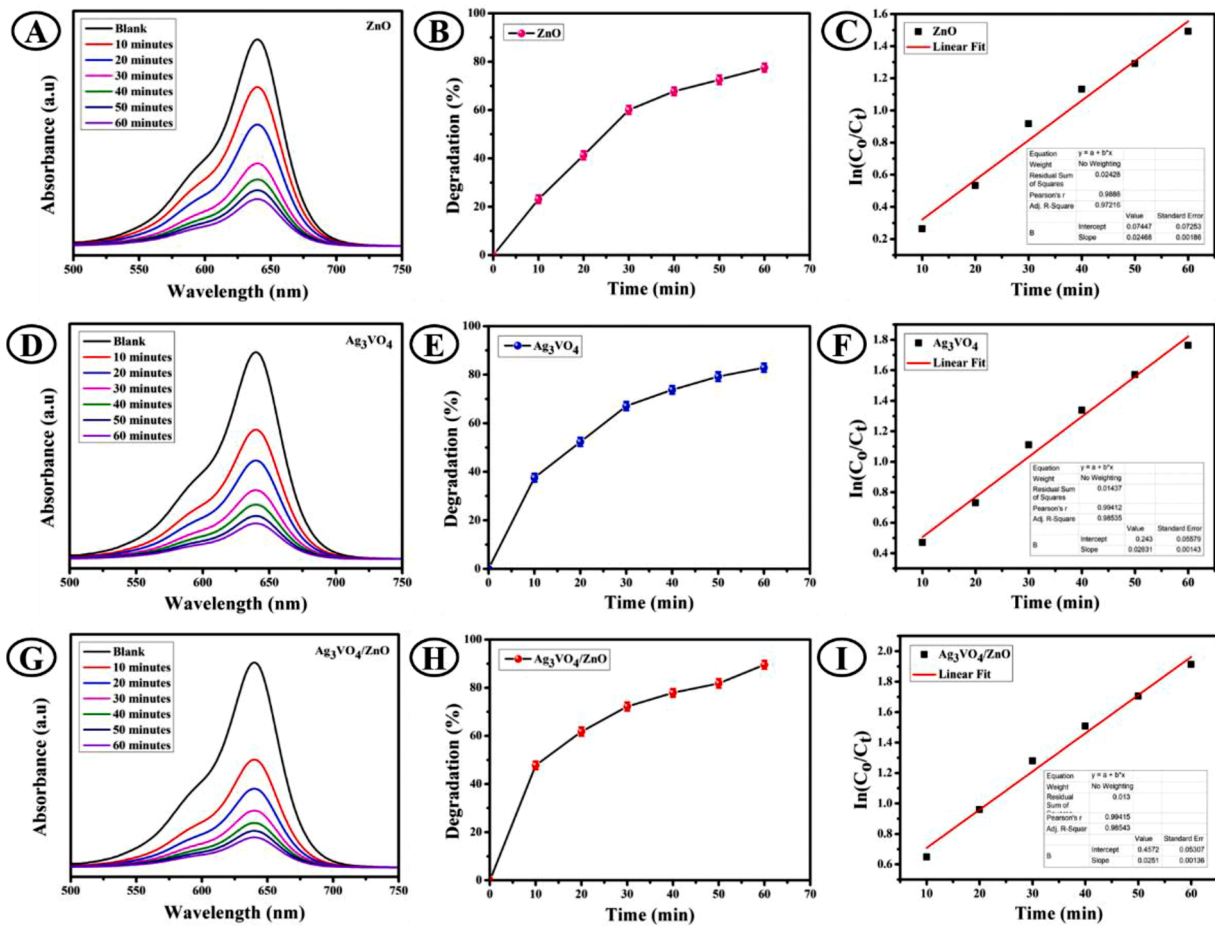


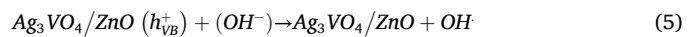
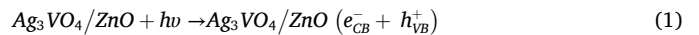
Fig. 7. Photodegradation studies of ZnO, Ag₃VO₄, and Ag₃VO₄/ZnO nanocomposites using Acid Green-16 (AG-16). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

$$\ln \frac{C_0}{C_t} = kt$$

The symbol 'k' stands for the pseudo-first-order rate constant for the photodegradation of AG-16 caused by AR-72 (min^{-1}). Regression values (R^2) for AG-16 on Ag₃VO₄/ZnO (0.9854) were much closer to one than for Ag₃VO₄ (0.9941), and AR-72 on Ag₃VO₄/ZnO (0.9909) were much closer to one than for Ag₃VO₄ (0.9861) which showed that first-order kinetics fit the nano-composite system better than Ag₃VO₄/ZnO nanoparticles [30].

The Ag₃VO₄/ZnO composite was shown to improve the photocatalytic degradation of AG-16 and AR-72 by the production of electron-hole pairs between the valence and conduction bands of Ag₃VO₄/ZnO. This process was triggered by the absorption of UV light by Ag₃VO₄/ZnO, as seen in Fig. 8. The photogeneration of electron-hole pairs between the valence (VB) and conduction (CB) bands of Ag₃VO₄/ZnO was shown. The temporal uptake of AG-16 and AR-72 by Ag₃VO₄/ZnO is shown below, measured in seconds. Moreover, the electrostatic interactions were responsible for the adsorption capacity of zinc oxide in the combined process of adsorption and photodegradation of AG-16 and AR-72 [31,32]. Reactant entrapment or reactant absorption is an additional property of aided photocatalysts that has been shown to enhance the transportation of reactants to active sites. This was shown by the observation that the photocatalysts that were supported had a significant inclination to either capture or absorb reactants [33]. The observed increase in photocatalytic activity in this study may have been attributed to a synergistic effect resulting from many causes. Several variables contributing to the performance of the Ag₃VO₄/ZnO nanocomposite include its high surface area, well-defined structure, efficient charge

carrier separation, outstanding electrical characteristics, and exceptional optical properties [34]. The following elucidation pertains to the proposed photocatalytic mechanism for nanocomposites:



The nanocomposite's behavior is superior to that of Ag₃VO₄/ZnO nanocomposites due to the graphene layers' capacity to decelerate the rearrangement process, as suggested by the theorized mechanisms. Moreover, the photocatalytic efficiency of an Ag₃VO₄/ZnO nanocomposite has the capacity to be enhanced due to its exceptional structure, high rate of charge carrier separation, expansive surface area, and outstanding optical and electrical properties of graphene layers. All of these contributing variables may account for the superiority of the graphene layers [35].

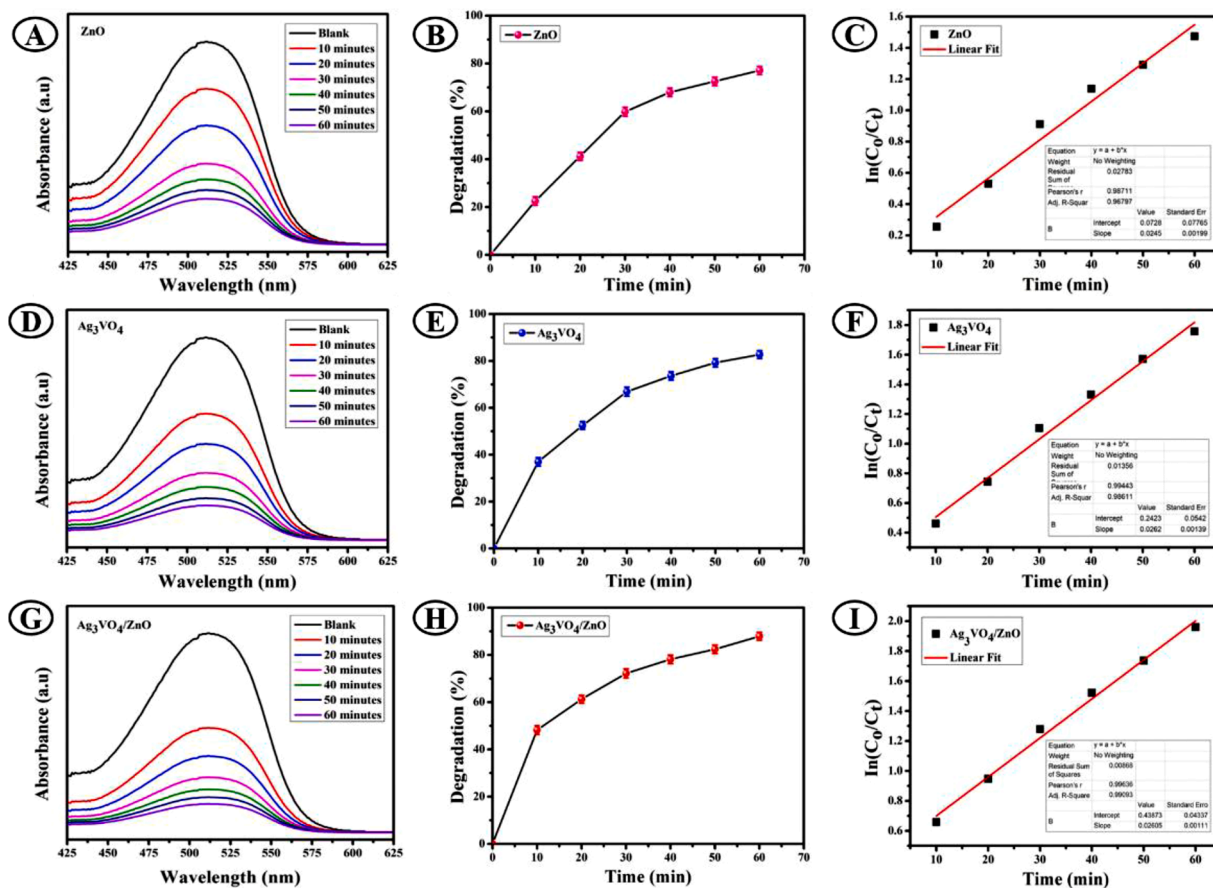


Fig. 8. Photodegradation studies of ZnO, Ag₃VO₄, and Ag₃VO₄/ZnO nanocomposites using Acid Red-72(AR-72). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3.6.1. Radical entanglement

The researcher conducted experiments using photocatalysts and light sources, along with several radical scavengers including EDTA-2 Na as a hole-quencher (h^+), to investigate the involvement of reactive oxidizing species in the degradation of AG-16 and AR-72 dyes. IPA effectively suppressed the hydroxyl radical ($\bullet OH$), but BQ effectively neutralized the superoxide radical anion ($\bullet O_2^-$). The quenchers infiltrated the photocatalyst system during its degradation. According to Fig. 10, the addition of BQ to the reaction vessel resulted in a degradation rate of 24.12 % for AG-16 and 25.62 % for AR-72. This exemplifies the significance of BQ in the decomposition of dye and highlights the involvement

of ($\bullet O_2^-$) in this mechanism. Unlike ($\bullet OH$) and (h^+), the presence of EDTA-2 Na and IPA did not affect the degradation of the dye, suggesting that these ions had little effect on the photocatalytic activity [36] (Fig. 9).

An experiment was conducted to assess the efficacy of removing AG-16 and AR-72 dyes. This was done by mixing 50 mL of a dye solution with 1 mL of isopropyl alcohol (IPA) in order to investigate the activation and impact of hydroxyl radicals ($\bullet OH$). Fig. 10 demonstrates a significant inhibition of photocatalytic studies with the introduction of alcohol (b)The Ag₃VO₄/ZnO catalysts produced maximum $\bullet OH$ radical outputs of 65.34 % for AG-16 and 62.76 % for AR-72 after UV

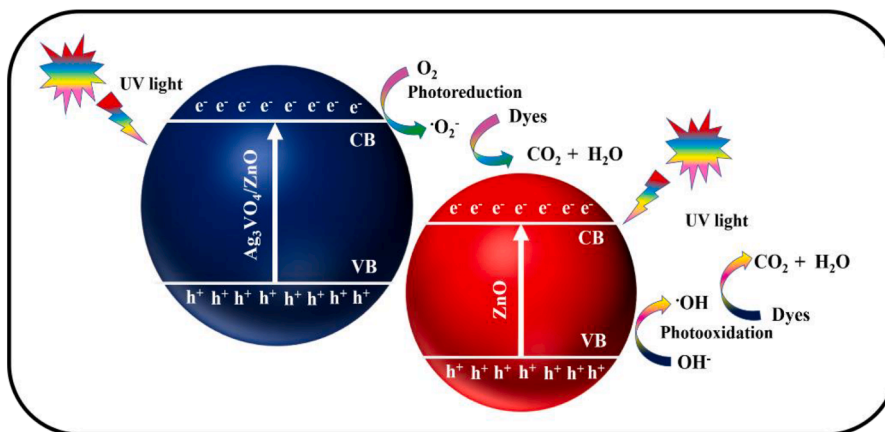


Fig. 9. Schematic mechanism of photocatalytic activity by ZnO and Ag₃VO₄/ZnO nanocomposite.

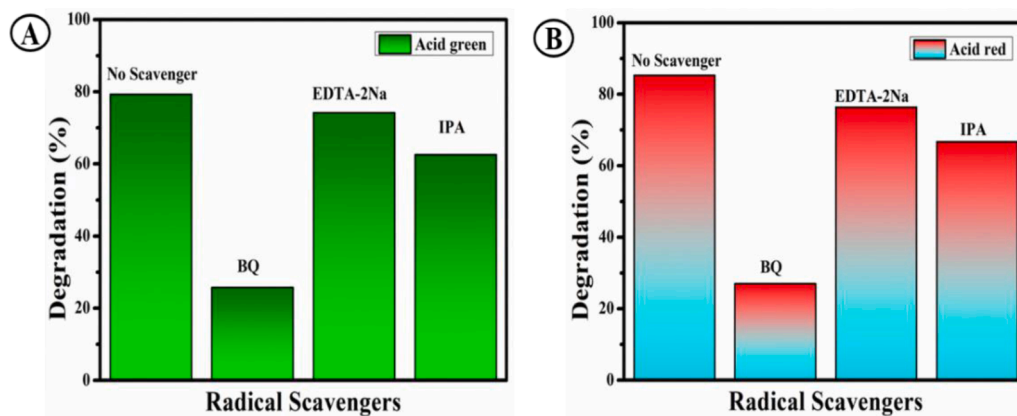


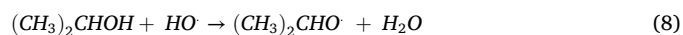
Fig. 10. Scavenger's studies on photocatalytic degradation of A). Acid Green-16(AG-16), and B). Acid Red-72(AR-72) over $\text{Ag}_3\text{VO}_4/\text{ZnO}$ nanocomposite. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

irradiation. This study provides a comprehensive analysis of the very efficient scavenging of radicals by IPA, which occurs at an exceptionally fast rate. This process involves the consumption of $\bullet\text{OH}$ radicals, as shown by Equation-8. The decolorization method of AG-16 and AR-72 dyes utilizes $\bullet\text{OH}$ (Equation-9). However, the overall number of radicals produced in the medium and directly involved in contaminant oxidation can vary significantly due to various recombination processes between hydroxyl radicals ($\bullet\text{OH}$) and other radicals (Equation-10–12) [37].

Scavengers, including EDTA, were used to examine the formation and significance of photo-generated holes (h^+) in photocatalytic study. With regards to Fig. 10. The efficiency of photocatalytic decolorization decreased from 100 % to 85.69 % for AG-16, and from 91.81 % to 85.69 % for AR-72, following the introduction of 5 mg of EDTA for a duration of 60 min. The following replies may provide insight on the findings: Two possible factors contribute to the significant decrease in bleaching effectiveness. Eqs. (13) and (14) illustrate that the holes (h^+) first undergo reactions with H_2O and OH^- , resulting in the production of a significant amount of hydroxyl radicals. Furthermore, the catalyst in an excited state has the ability to generate vacancies, which may then be used to directly oxidize the dye molecules according to Equation-15. Due to the consumption of holes by the first and second processes, the rate of rearrangements between electrons and holes is decreased. As a result, the half-lives of electrons are prolonged and reactive oxygen species (ROS) are generated at greater rates from electrons [38]. The effects of this phenomenon will be examined in the context of $\bullet\text{O}_2$ -scavengers. The progressive incorporation of radicals onto the $\text{Ag}_3\text{VO}_4/\text{ZnO}$ catalyst may be shown in Fig. 10.

The addition of 5 mg of benzoquinone to a 50 mL aqueous solution of dye significantly reduced the degradation rates of AG-16 and AR-72 dyes. Within a span of 60 min, the elimination rates of dyes (AG-16 and AR-72) utilizing an $\text{Ag}_3\text{VO}_4/\text{ZnO}$ catalyst reached zero while $\bullet\text{O}_2$ -scavenging was taking place. In contrast, the removal efficiency of AG-16 employing a ZnO photocatalyst declined from 100 % to 20 % over the same duration. The superoxide radical is commonly acknowledged to have a pivotal function in the degradation of some pigments found in pollution. The process of electron/hole recombination may be decelerated by using the electrons generated by light, as shown in Equation-16. The following mechanisms, which result in the removal of $\bullet\text{O}_2$ - radicals and hydroxyl radicals from this source, provide a comprehensive explanation for the observed results. Initially, the superoxide radical anion may rapidly oxidize the contaminating molecule (Equation-17) or undergo a reaction with H^+ to form the hydroperoxyl radical $\bullet\text{OOH}$ (Equation-18). The color molecules undergo oxidation in this process (Equation-19). Furthermore, the superoxide anion has the ability to generate H_2O_2 and decompose it into hydroxyl radicals either directly (Equation-20) or indirectly (Equation-21) as described by (Equation-22)

and (Equation-23).



3.7. ZnO, Ag_3VO_4 , and $\text{Ag}_3\text{VO}_4/\text{ZnO}$ nanocomposites reusability and stability over degradation by photocatalysis of Acid Green-16(AG-16) and Acid Red-72(AR-72)

The study investigated the photocatalytic durability and recyclability of ZnO, Ag_3VO_4 , and $\text{Ag}_3\text{VO}_4/\text{ZnO}$ nanocomposites after three cycles of photocatalytic activity. The findings of three distinct cycles using ZnO, Ag_3VO_4 , and $\text{Ag}_3\text{VO}_4/\text{ZnO}$ nanocomposites are shown in Fig. 11. The data is presented as the ratio of removal efficiency (in percent) to reaction time (in minutes). Following each cycle, the catalyst may be retrieved for further use by the process of centrifugation, which involves separating the newly obtained colors from the catalyst and then precipitating them. The investigation revealed that nanocomposites consisting of ZnO, Ag_3VO_4 , and $\text{Ag}_3\text{VO}_4/\text{ZnO}$ exhibited excellent

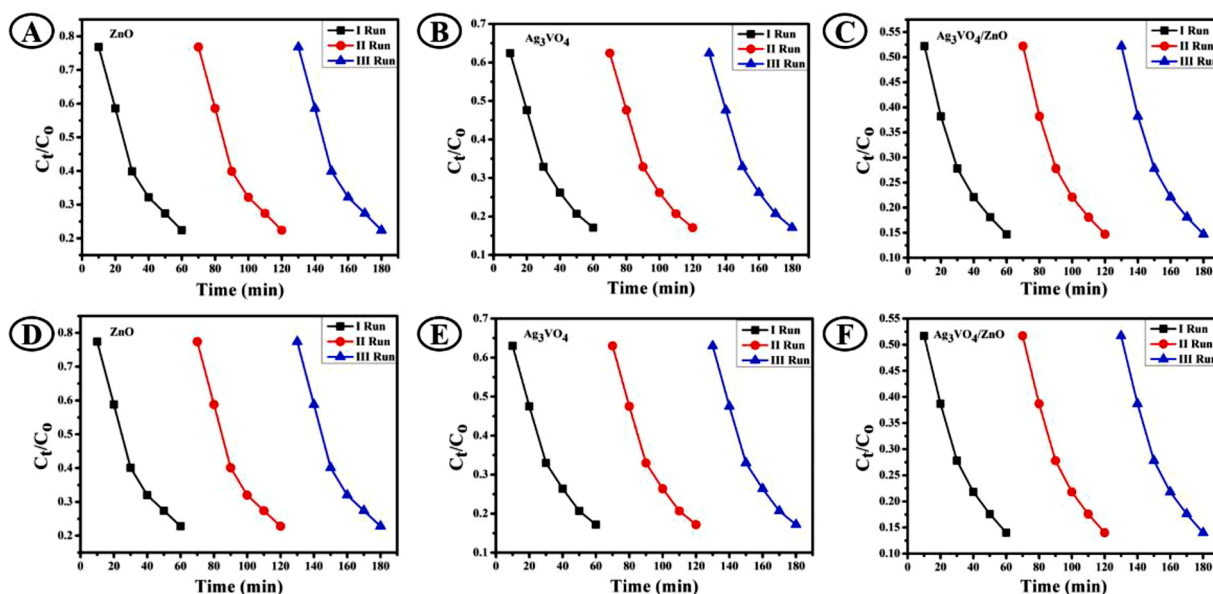


Fig. 11. Evaluation of the reusability of ZnO, Ag_3VO_4 , and $\text{Ag}_3\text{VO}_4/\text{ZnO}$ nanocomposites for photocatalytic degradation of A). Acid Green-16(AG-16), and B). Acid Red-72(AR-72). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

performance and were capable of several recyclings under visible light exposure. Fig. 11 demonstrates that the catalyst's efficiency might diminish by up to 10 % after being utilized three times. Following three cycles, there was no apparent reduction in the photocatalytic activity. The degradation rates of Acid Green-16(AG-16) and Acid Red-72(AR-72) dyes in ZnO, Ag_3VO_4 , and $\text{Ag}_3\text{VO}_4/\text{ZnO}$ nanocomposite were 84.96 %, 91.81 %, and 84.76 % respectively in the first run, 83.45 %, 89.62 %, and 82.61 % respectively in the second run, and 81.78 %, 87.66 %, and 80.92 % respectively in the third run. Furthermore, subsequent to the first test, it was discovered that an extended period of incubation was necessary to ensure the successful degradation of the dye [39,40]. The decrease in photocatalytic degradation studies seen after three cycles of reusability is likely due to overcrowding and/or a gradual decline in photocatalytic analysis efficiency [41-44]. These results further bolster the hypothesis that the technology might be used for wastewater treatment in environments that closely correspond to real-world environments [45-48].

3.8. Mineralization of dye

The total organic carbon (TOC) was measured in order to investigate the mineralization of Acid Green-16 (AR-16) and Acid Red (AR-72) in order to determine their respective mineralization. The removal of total organic carbon is illustrated in Fig. 12 by displaying how the breakdown

of AG-16 and AR-72 takes place when they are exposed to ultraviolet light. After being subjected to ultraviolet (UV) irradiation for a period of up to two hours, the total organic carbon (TOC) was shown to have seen an instantaneous drop. The mineralization of AG-16 and AR-72 occurred as a result of irradiation with a nanocomposite composed of $\text{Ag}_3\text{VO}_4/\text{ZnO}$ for a period of five hours. The mineralization occurred at approximately 86.65 % and 89.82 % of total organic carbon reduction, respectively. The image shown in Fig. 13 was taken after the photo-synthetic studies were completed. It is clear that this image has not undergone any morphological changes.

4. Conclusion

In conclusion, the synthesized ZnO incorporated Ag_3VO_4 nanocomposites demonstrate promising catalytic activity for the UV-assisted degradation of Acid Green-16(AG-16) and Acid Red-72(AR-72), showcasing their potential as efficient catalysts in wastewater treatment applications. Further research is warranted to explore their broader environmental remediation applications. UV-visible spectroscopy was used in order to investigate the nucleation and development of ZnO, Ag_3VO_4 , and $\text{Ag}_3\text{VO}_4/\text{ZnO}$ nanocomposite. The absorption spectra of the process were consulted in order to ensure that these measurements were accurate. Scanning electron microscopy, often known as SEM, was used in this study so that the form and structure of nanoparticles could

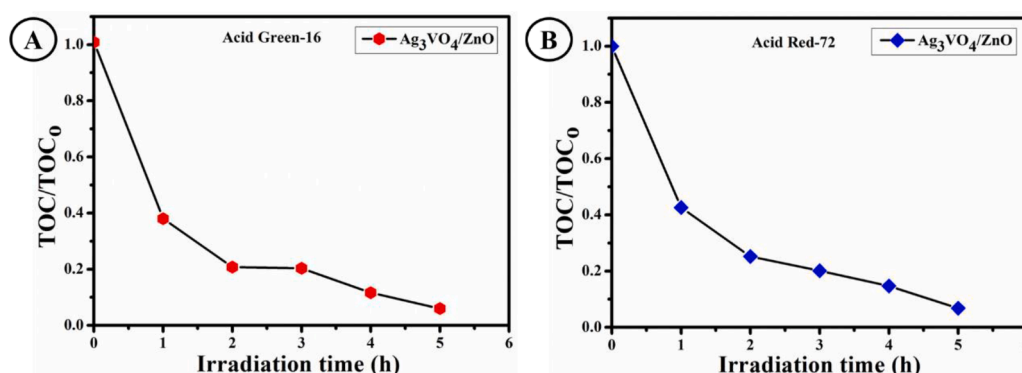


Fig. 12. Total Organic Carbon (TOC) of AG-16 and AR-72 during the photodegradation with $\text{Ag}_3\text{VO}_4/\text{ZnO}$ nanocomposites using UV light.

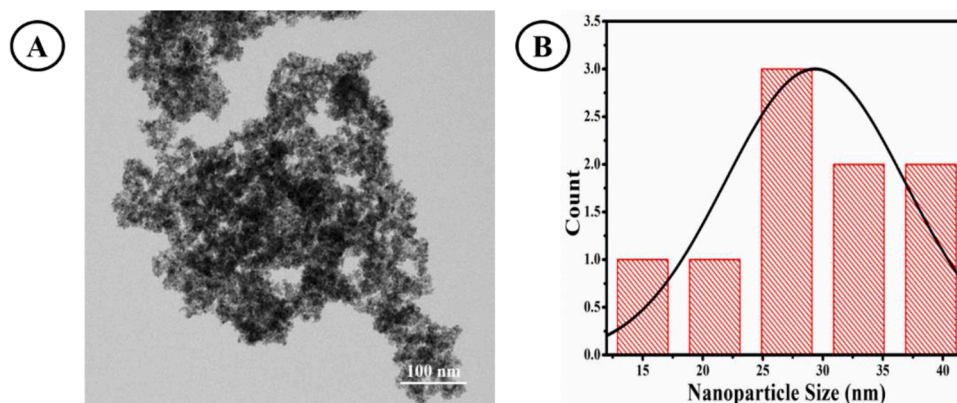


Fig. 13. After photodegradation studies HRTEM image of $\text{Ag}_3\text{VO}_4/\text{ZnO}$ nanocomposites using UV light.

be analyzed. The biosynthesized ZnO , Ag_3VO_4 , and $\text{Ag}_3\text{VO}_4/\text{ZnO}$ nanocomposites all had crystal structures and particle sizes of around 16.37, 14.21, and 15.42 nm, respectively. Particle size and crystallinity were studied with the use of X-ray diffraction (XRD) peaks, which verified the biosynthesized crystal structures. This study revealed a viable method for the breakdown of Acid Green-16(AG-16) and Acid Red-72(AR-72). The research used biosynthesized ZnO , Ag_3VO_4 , and $\text{Ag}_3\text{VO}_4/\text{ZnO}$ nanocomposite. It also discussed the catalytic activity that gets rid of the dyes that are harmful to the environment. The first-order reaction kinetics was then followed by the photocatalytic performance against Acid Green-16(AG-16) and Acid Red-72(AR-72) dyes, both of which had a maximum degradation efficiency of 87.91 % and 89.56 % respectively. The Acid Green-16(AG-16), and Acid Red-72(AR-72) photocatalytic process that was created has the potential to replace the techniques that are currently used to treat Acid Green-16(AG-16), and Acid Red-72(AR-72). This is because the proposed process is superiorly simple, inexpensive, non-toxic, and recyclability, as well as stable, and output. This indicates that the proposed method for using photocatalysis in wastewater treatment may prove to be the approach that is most effective. The investigation into synthesized ZnO incorporated Ag_3VO_4 nanocomposites as a catalyst for UV-assisted degradation of Acid Green-16(AG-16) and Acid Red-72(AR-72) has yielded ground-breaking insights. Our research reveals a novel and highly effective catalyst system that can significantly accelerate the degradation of these challenging organic dyes under UV irradiation. The synergistic interactions between ZnO and Ag_3VO_4 in the nanocomposites have not only enhanced the catalytic activity but also demonstrated remarkable stability, highlighting their unique potential for sustainable and efficient wastewater treatment and pollution control. This novel catalyst system represents a significant advancement in the field of environmental remediation, with promising implications for addressing water pollution challenges.

CRedit authorship contribution statement

S. Sasikruba: Methodology, Formal analysis. **R. Siranjeevi:** Supervision, Investigation, Formal analysis. **I. Muthuvel:** Validation, Investigation, Formal analysis. **G. Thirunarayanan:** Writing – review & editing. **T. Rajachandrasekar:** Supervision, Methodology, Investigation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data that has been used is confidential.

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