

Full Length Article

Synergistic photocatalysis of VO₂-A/g-C₃N₄ composites for efficient degradation of anionic and cationic dyes: Towards a sustainable environmental solution

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ABSTRACT

Due to the outflow of dye effluent from numerous industrial operations, dye pollution is a severe environmental issue. Because of its efficiency and environmental friendliness, photocatalytic degradation is a technology promising for treating dye pollutants. This study used a simple hydrothermal process to synthesise VO₂-A/g-C₃N₄ nanocomposite and its photocatalytic activity for the breakdown of anionic dyes (Xylenol Orange (XO), Rose Bengal (RB)) and cationic dyes (Crystal Violet (CV), Auramine O (AO)) and Mix dyes (1:1 mixture of anionic and cationic dyes) were assessed. XRD, XPS, SEM, FTIR, Photoluminescence, TEM, UV-DRS and BET analysis were used to characterize the nanocomposite. SEM and TEM analyses revealed a distinct morphology of the VAG-4 nanocomposite, with small, irregular VO₂-A nanoparticles dispersed and wrapped around the g-C₃N₄ surface. UV-DRS analysis, using the Tauc relation, indicated that VO₂-A incorporation shifted the absorption edge to longer wavelengths, with VAG-4 showing a peak at 487 nm (1.91 eV). BET analysis of VAG-4 shows a specific surface area of 47.1 m²/g, a pore volume of 0.2125 cm³/g, and an average pore size of 27.9 nm, supporting its potential for effective photocatalytic applications. We assessed the photocatalytic activity of VO₂-A/g-C₃N₄ nanocomposite for the degradation of the anionic dyes (RB, XO), cationic dyes (AO, CV) and Mix dyes. The results demonstrated that the VAG-4 nanocomposite with degradation percentages of RB (83.5 %), XO (75.5 %), AO (73.4 %), and CV (78.2 %) exhibited more enhanced photocatalytic activity than the individual precursors. The nanocomposite's outstanding photocatalytic activity suggests that it has the potential for practical applications in environmental cleanup.

1. Introduction

A significant environmental problem is wastewater discharge from numerous industrial operations involving coloured dyes [1]. In addition to being dirty, wastewater that contains coloured dyes also poses a significant risk to aquatic life and public health [2,3]. Traditional wastewater treatment techniques can produce dangerous byproducts while failing to remove these pollutants [4]. Therefore, new and effective techniques are urgently required to remediate dye contaminants in wastewater [5]. Because of its environmental friendliness and efficiency, photocatalysis has emerged as a viable method for the remediation of dye pollutants [6]. Materials known as photocatalysts can be activated

by light and facilitate chemical reactions, such as oxidizing dye pollution when exposed to light [7]. TiO₂ is one of the most extensively investigated photocatalysts due to its solid photocatalytic activity, stability, and abundance [8]. However, TiO₂ has certain limitations, including the necessity for ultraviolet (UV) light and its inadequate absorption of visible light [9]. To address these challenges, researchers have been exploring a variety of alternative materials, such as metal oxides, metal sulfides, and carbon-based compounds [10–12].

Besides these materials, graphitic carbon nitride (g-C₃N₄) has attracted significance because of its notable features, which include good thermal stability, greater surface area and complete visible light absorption [13]. Carbon and nitrogen atoms form the honeycomb-like

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Scheme 1. Synthesis route of $\text{VO}_2\text{-A/g-C}_3\text{N}_4$ nanocomposites

structure of the two-dimensional, layered substance known as $\text{g-C}_3\text{N}_4$ [14]. Since $\text{g-C}_3\text{N}_4$ has a bandgap of about 2.7 eV, it may effectively absorb visible light [15]. However, $\text{g-C}_3\text{N}_4$ also has several disadvantages that reduce its photocatalytic effectiveness, such as limited electron mobility and increased rate of electron-hole pair recombination [16]. By doping $\text{g-C}_3\text{N}_4$ with other substances to create nanocomposites, scientists have created new and superior photocatalysts to overcome these restrictions [17].

Vanadium oxides (VO_x), transition metal oxides with unique physical and chemical properties, are among the most extensively researched materials due to their distinctive metal-insulator transition (MIT) [18]. The polymorphic structures of Vanadium Dioxide (VO_2) include A, B, C, D, M1, M2, M3, P, R, and T, all of which have relatively distinctive features [19]. Due to its distinctive electrical and structural characteristics, including its low bandgap, $\text{VO}_2\text{-A}$ is regarded as the most promising material out of the bunch [20].

Due to a shift in its electronic structure, the monoclinic crystal structure of $\text{VO}_2\text{-A}$ leads to a sharp increase in conductivity and photocatalytic activity [20]. Its small band gap of roughly 2.5 eV makes it a suitable material for photocatalysis and perfect for absorbing visible light. To optimise the photocatalytic performance of $\text{VO}_2\text{-A}$, scientists have been experimenting with various techniques, including doping with other substances. Doping $\text{VO}_2\text{-A}$ with $\text{g-C}_3\text{N}_4$ results in a nanocomposite with increased photocatalytic activity due to its complementary characteristics. $\text{VO}_2\text{-A}$, in addition to having a large surface area and promoting charge separation, can also act as a co-catalyst by allowing photons and electrons to pass from it through the target molecule via $\text{g-C}_3\text{N}_4$. This doping approach may significantly boost $\text{VO}_2\text{-A}$'s photocatalytic application for various applications, including degrading dye pollutants in wastewater [20].

The findings of our study introduce a novel and efficient approach for the hydrothermal synthesis of $\text{VO}_2\text{-A/g-C}_3\text{N}_4$, which is employed to degrade organic dyes. The study aims to degrade cationic, anionic and mix dyes, including rose Bengal, Xylenol Orange, Auramine O, Crystal Violet and Mix dyes (Anionic and cationic dyes are mixed in a 1:1 ratio) using $\text{VO}_2\text{-A/g-C}_3\text{N}_4$ nanocomposites under visible light. The key novelty of this study lies in the facile and cost-effective synthesis method of $\text{VO}_2\text{-A/g-C}_3\text{N}_4$ nanocomposite, which exhibits excellent photocatalytic activity and excellent reusability, providing a sustainable solution for dye degradation. Compared to previous research which focuses on selective organic oxidation [20], our study focuses on a unique photocatalyst, $\text{VO}_2\text{-A/g-C}_3\text{N}_4$, which shows higher efficiency in dye degradation. The results demonstrate the potential of $\text{VO}_2\text{-A/g-C}_3\text{N}_4$ for

practical applications in wastewater treatment to remove organic dyes.

2. Experiment

2.1. Synthesis

In the hydrothermal synthesis process of graphitic carbon nitride, a crucible containing 10 g of the urea was heated at 550°C in a furnace with 5°C ramp rate over a duration of 3 h. The obtained product was subsequently finely grounded into a powder using an agate mortar and pestle (Scheme 1. a).

$\text{VO}_2\text{-A}$ can be synthesized from powdered V_2O_5 chemical powder through a simple and efficient hydrothermal method that involves oxalic acid as a reducing agent (Scheme 1. b). During this process, 2 gm of V_2O_5 and 5 gm of oxalic acid are mixed with 200 ml of deionized water. The solution is aggressively stirred until the V_2O_5 powder is entirely dissolved. Then, the solution was transferred into a Teflon-lined autoclave and heated for a duration of 12 hours at a temperature of 200°C . Following this, the solution was cooled and collected by centrifugation. To remove impurities, the collected product is repeatedly washed with ethanol and deionized water.

Ultrasonication was used to form the $\text{VO}_2\text{-A/g-C}_3\text{N}_4$ nanocomposites (Scheme 1. c). This process involved mixing the two precursors in a fixed molar ratio of 1:x (where $x = 2, 4$, or 6). The amount of $\text{VO}_2\text{-A}$ was varied while $\text{g-C}_3\text{N}_4$ was kept constant. The mixture was sonicated for 60 min, centrifuged, and washed with ethanol and deionized water. The synthesized nanocomposites were dried at 60°C for 24 h and collected. The samples were abbreviated as VAG-2, VAG-4, and VAG-6.

2.2. Characterization

The structural, morphological, and optical properties of the $\text{VO}_2\text{-A/g-C}_3\text{N}_4$ nanocomposite were characterized using various analytical techniques. X-ray diffraction (XRD) analysis was performed using a Bruker D8 diffractometer. Fourier transform infrared (FTIR) spectroscopy was performed using the KBr pellet technique on a Perkin Elmer Spectrometer instrument in the range of $4000\text{--}400\text{ cm}^{-1}$. Morphological characteristics of the samples were studied using Scanning electron microscopy (SEM) with a JSM 7900-F instrument and Transmission electron microscopy (TEM) with a TEM Talos F200X instrument. BET Analysis was done on BELSORP-maxII analyzing nitrogen gas adsorption-desorption isotherms at a temperature of 77 K. Cyclic voltammetry (CV) tests were done on Autolab PGSTAT204 Potentiostat. X-ray

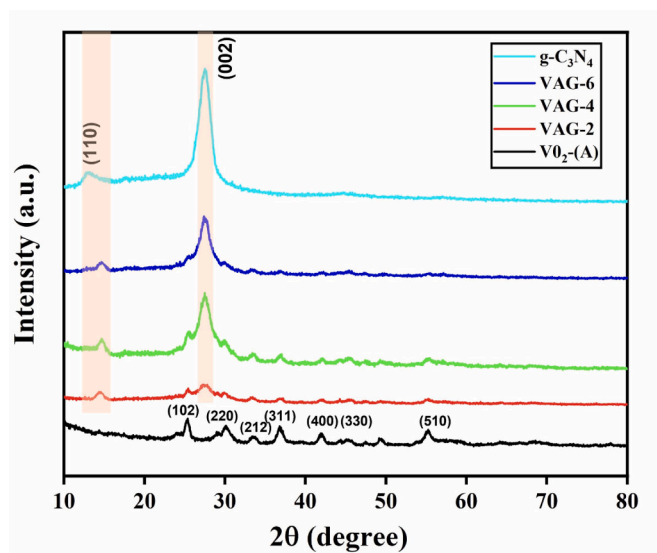


Fig. 1. XRD pattern of VO₂-A / g-C₃N₄ nanocomposites.

photoelectron spectroscopy (XPS) was done on a Thermo Scientific K-Alpha XPS instrument. The UV-Vis Diffuse Reflectance Spectroscopy (UV-DRS) spectrum was obtained using a Shimadzu UV-2600 I spectrophotometer in the 200–800 nm range.

2.3. Photocatalytic activity

VO₂-A/g-C₃N₄ nanocomposite's photocatalytic activity was assessed using five different dyes: Rose Bengal and Xylenol Orange as anionic dyes, Auramine O and Crystal Violet as cationic dyes and Mix dyes (mixture of anionic and cationic dyes in 1:1). To determine the degradation efficiency, 10 mg of nanocomposites were added to a 100 mL aqueous solution containing the dye at an initial 10 mg/L concentration. The mixture was stirred at a constant rate of 600 rpm and irradiated with a 400 W Xe lamp for 120 min. The degradation efficiency was calculated using the following equation:

$$\text{Degradation efficiency}(\%) = [(C_0 - C_t)/C_0] \times 100 \quad (1)$$

C_0 represents the initial concentration of dye, while C_t represents the final concentrations. To monitor the degradation process, the absorption spectra of the dyes were recorded at a regular interval using a UV-Vis spectrophotometer. The experimental equipment was carefully built to achieve homogeneous irradiation throughout the solution. The reaction

conditions were fine-tuned for each dye's highest degradation efficiency.

3. Results and Discussion

3.1. XRD

The study uses the X-ray diffraction (XRD) technique to identify the crystal structure of nanoparticles, specifically the VO₂-A composite (Fig. 1). The g-C₃N₄ XRD pattern was also examined. It revealed distinctive peaks at 13.2° and 27.4°, corresponding to the (100) and (002) planes, respectively. The XRD examination of the VO₂-A composite revealed peaks at 25°, 30°, 35°, 37°, 42°, 45°, and 56°, corresponding to the (102), (220), (212), (311), (400), (330), and (510) planes. The diffraction peaks revealed important information about the material's crystalline phase and crystal structure [21]. The distinctive peaks of both precursors, g-C₃N₄ and VO₂-A, in the XRD examination of VO₂-A/g-C₃N₄ nanocomposites indicated the successful synthesis. According to the findings, VO₂-A/ g-C₃N₄ nanocomposites have a crystalline structure appropriate for various catalytic applications.

3.2. FTIR

FTIR was used to examine the chemical bonds and functional groups in the VO₂-A/g-C₃N₄ nanocomposites that were made (Fig. 2). The FTIR spectra of g-C₃N₄ showed characteristic peaks and bends at 1640, 1560, 1400, 1310, and 1230 cm⁻¹, which corresponded to the stretching vibrations of C=C, C=N, C=C/N-H bending, C-N stretching, and N-H bending, respectively [22]. The FTIR spectrum of VO₂-A showed peaks and bends at 480, 530, 678, 832, and 976 cm⁻¹, corresponding to the V=O, V-O, O-V-O bending, and O-V-O stretching modes [19]. VO₂-A/g-C₃N₄ nanocomposite's FTIR spectrum show that all the peaks were the same as those of precursors [23]. This demonstrates that nanocomposites were fabricated correctly.

3.3. SEM morphological analysis

Scanning electron microscopy is a sophisticated imaging method that offers information on material surface morphology. add the magnification of 10 kx, SEM analysis of pure g-C₃N₄ revealed a lamellar structure that were heavily agglomerated due to the rapid breakdown of nitrates during heating (Fig. 3a). The SEM analysis of VO₂-A nanoparticle Fig. 3b revealed only a minor degree of agglomeration, indicating the efficiency of co-precipitation approach for creation of well dispersed nanoparticles. The VAG-4 nanocomposite (Fig. 3c) showed a distinctive structure with small, irregularly shaped VO₂-A nanoparticles dispersed

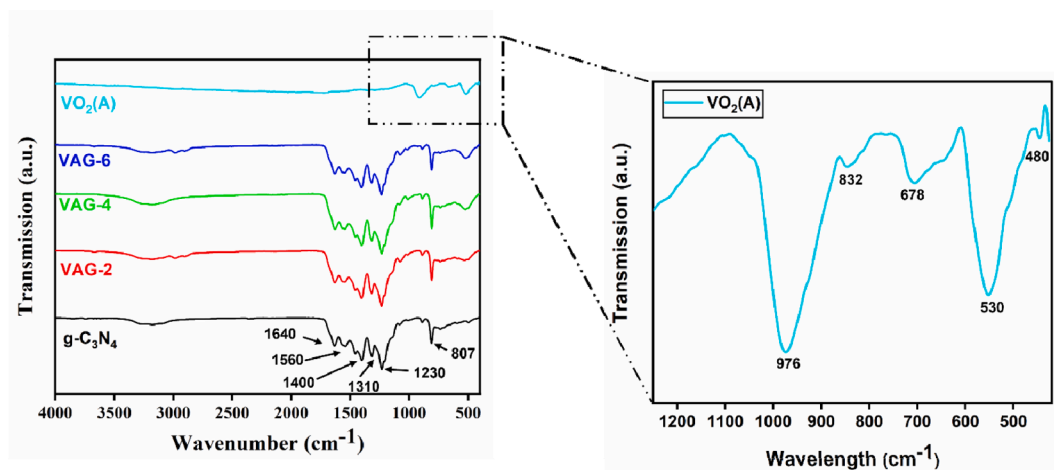


Fig. 2. FTIR spectra of VO₂-A, g-C₃N₄, and VO₂-A / g-C₃N₄ nanocomposites.

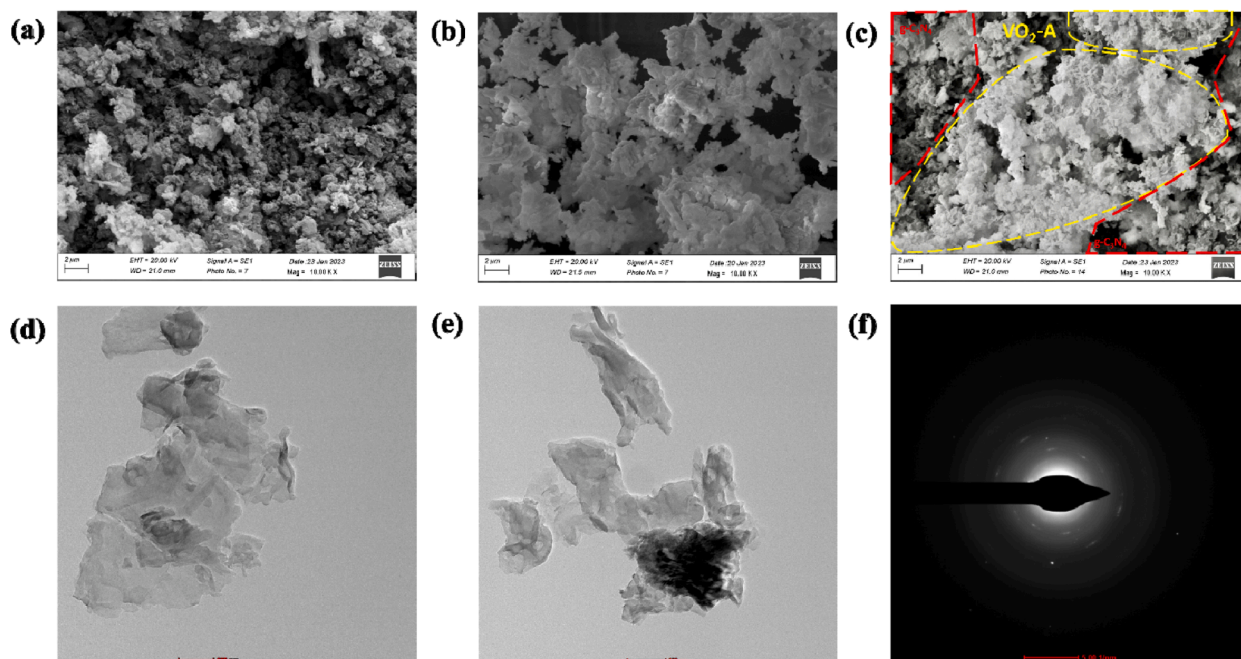


Fig. 3. SEM images of (a) $g\text{-C}_3\text{N}_4$, (b) $\text{VO}_2\text{-A}$, (c) VAG-4 nanocomposite and TEM images of (d) $g\text{-C}_3\text{N}_4$, (e) VAG-4 nanocomposite, (f) SAED pattern of VAG-4 nanocomposite.

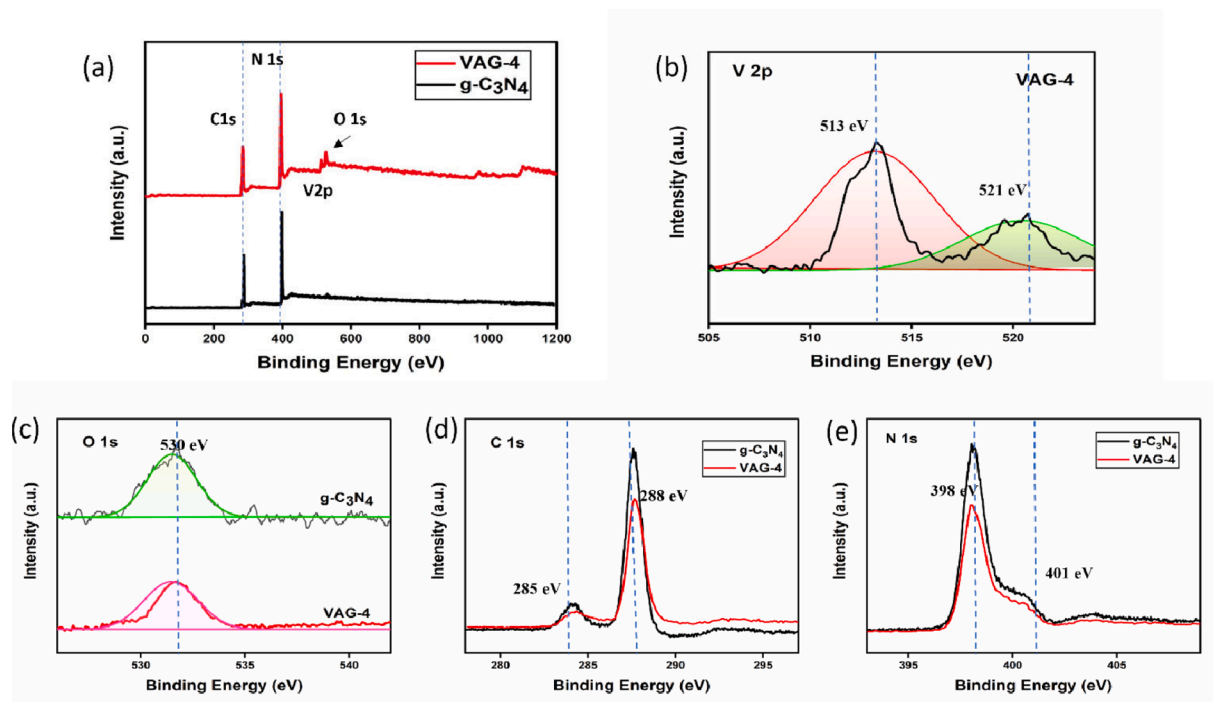


Fig. 4. (a) Wide XPS spectra of $g\text{-C}_3\text{N}_4$ and VAG-4 nanocomposite; XPS spectra of (b) V2p; (c) O1s (d) C1s and (e) N1s.

on the surface of $g\text{-C}_3\text{N}_4$ Nanoparticles. This might be attributed two proper precursors mixing during synthesis.

3.4. TEM analysis

The morphological properties of a material can be evaluated using transmission electron microscopy. The TEM analysis of pure $g\text{-C}_3\text{N}_4$ in Fig. 3d revealed a layering structure with several stacking layers characteristic of 2D layered material. In Fig. 3e, the VAG-4 nanocomposite

had a rough texture, indicating improved catalytic activity, and small, irregularly shaped $\text{VO}_2\text{-A}$ nanoparticles wrapped around the surface of the $g\text{-C}_3\text{N}_4$ layer, giving it a distinct morphology. The SAED pattern of the VAG-4 composite in Fig. 3f showed a bright ring of spots, indicating the crystalline nature and reduced size of $\text{VO}_2\text{-A}$ nanoparticles, with solitary dots observed due to the $g\text{-C}_3\text{N}_4$ matrix. This shape allows for more active dye absorption and degradation sites, making it an excellent photocatalyst. The TEM images show that $\text{VO}_2\text{-A}$ nanoparticles were successfully dispersed on the surface of $g\text{-C}_3\text{N}_4$, resulting in increased

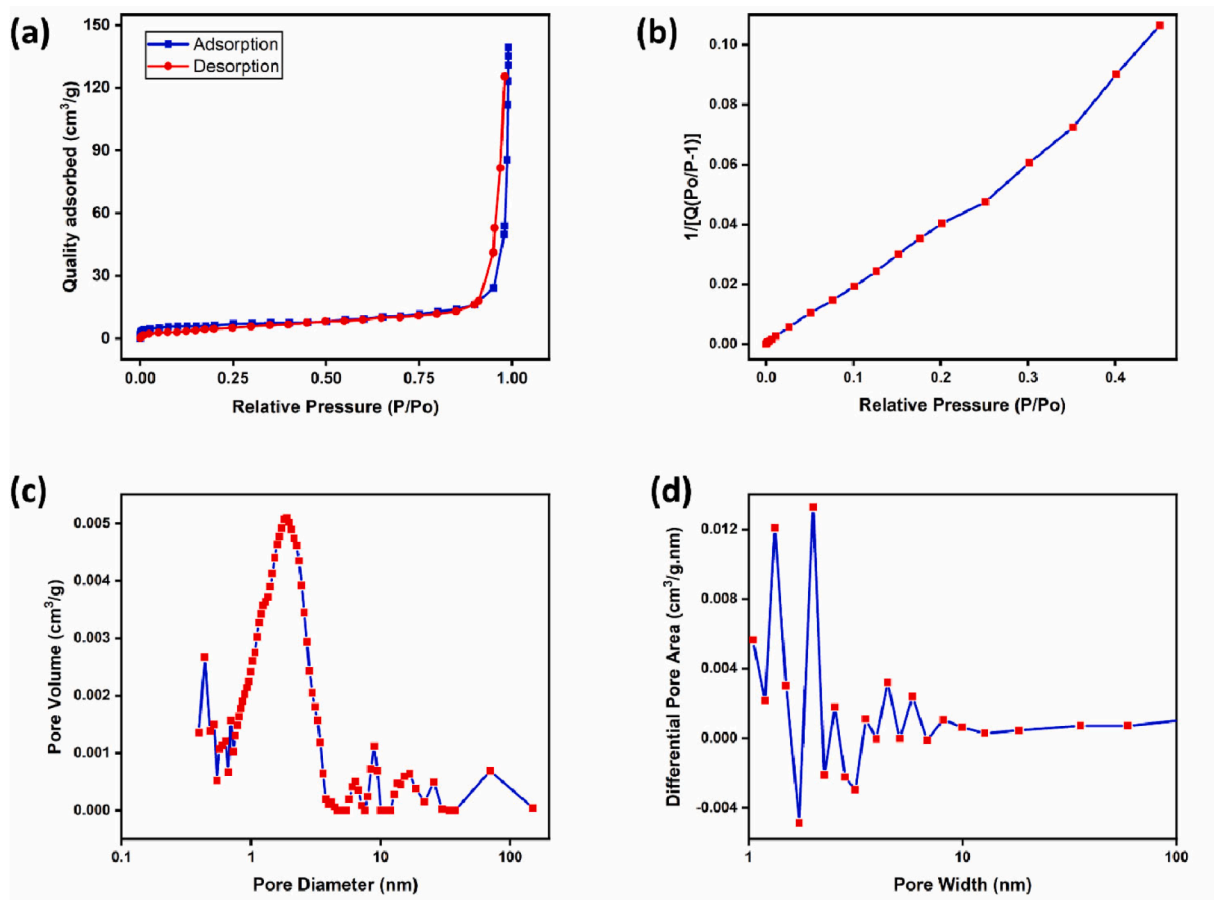


Fig. 5. BET analysis of VAG-4 (a) nitrogen absorption–desorption isotherms; (b) linear fit plot for surface area; (c) pore size distribution plot; (d) bjh adsorption differential pore area plot.

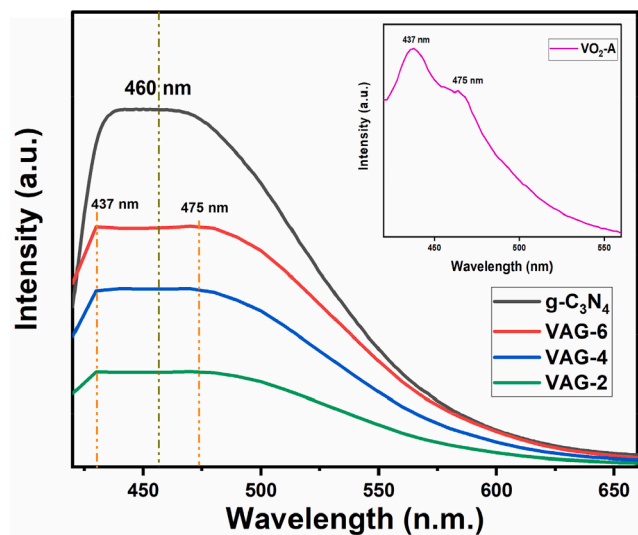


Fig. 6. PL Spectra of prepared nanocomposites.

photocatalytic activity.

3.5. X-ray photoelectron spectroscopy (XPS)

XPS was used to learn more about the chemical makeup of surfaces. XPS is a helpful method for examining the electronic and chemical

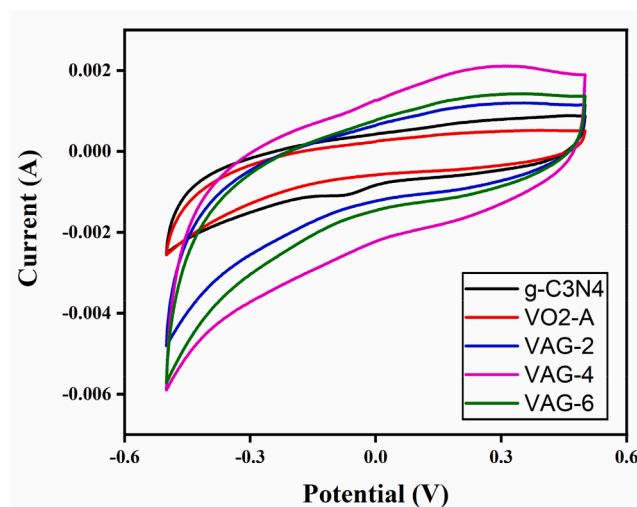


Fig. 7. Cyclic voltammetry of prepared nanocomposites.

characteristics of VO₂-A/g-C₃N₄ nanocomposites. VO₂-A/g-C₃N₄'s XPS spectra often show several peaks that correlate to the various elements in the sample. Investigating the g-C₃N₄ portion of the nanocomposite involves using the C1s part of the spectrum. The C1s spectra of VO₂-A/g-C₃N₄ nanocomposites often peak at about 288 eV, which denotes the presence of C-(N)₃ and C-(C=N) bonds in the g-C₃N₄ (Fig. 4d). This peak demonstrates that g-C₃N₄ is present in the nanocomposite. Indicated by

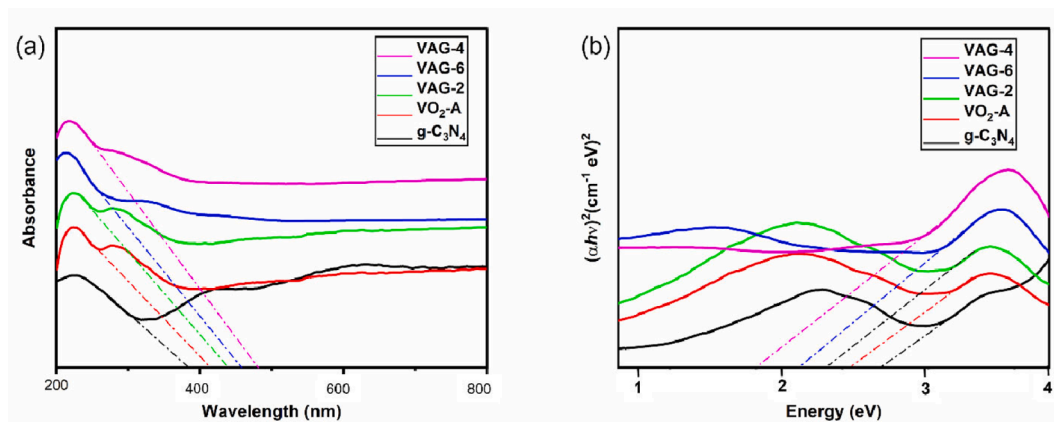
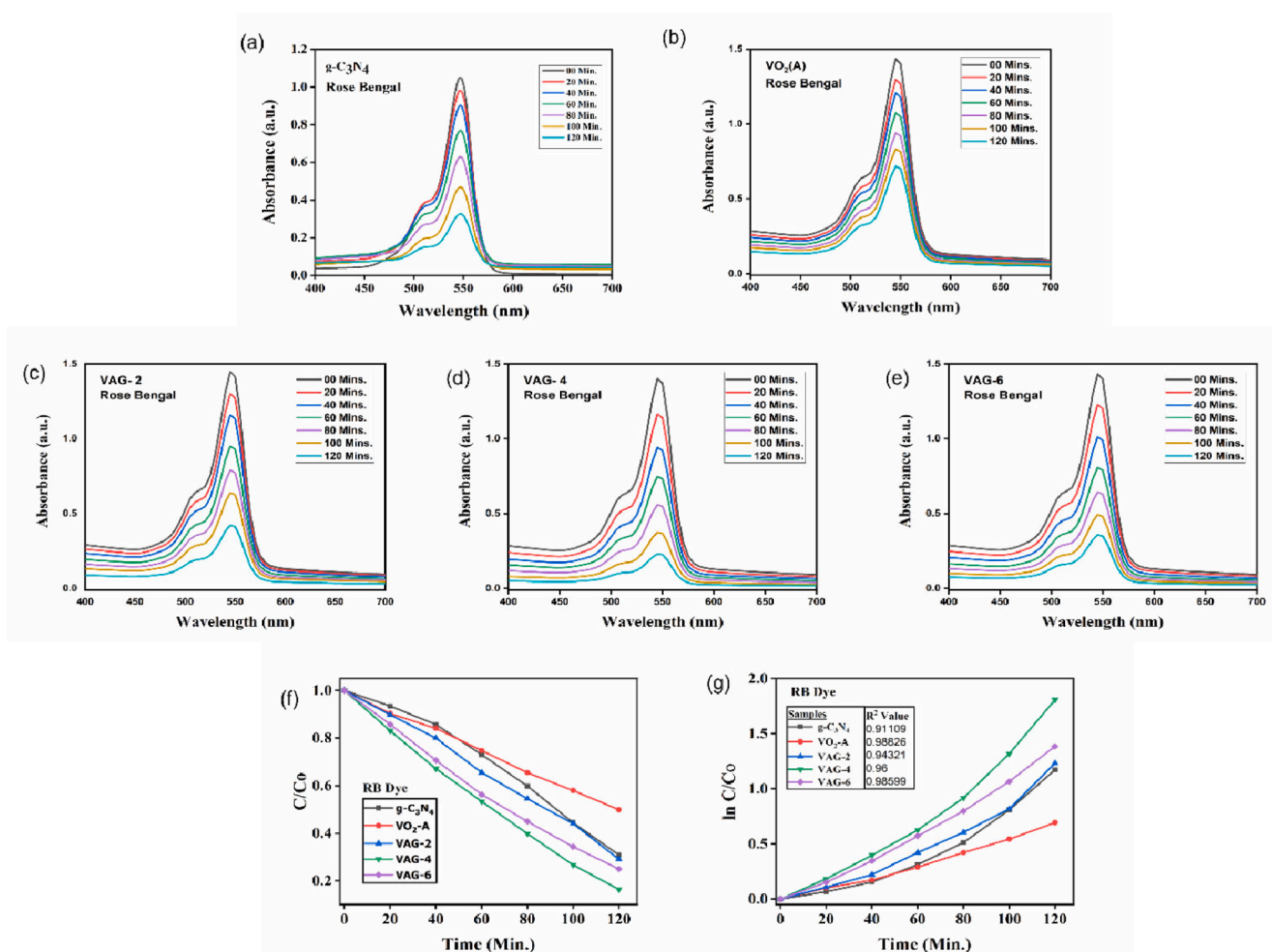


Fig. 8. (a) UV-Vis DRS, (b) Tauc plot of nanocomposites.

Fig. 9. (a-e) RB dye's absorbance spectra, (f) Photocatalytic activity comparison (g) RB dye's $\ln(C_0/C_t)$ plot.

two peaks in the N1s spectra of g-C₃N₄ and VO₂-A/g-C₃N₄, respectively, at 398 and 401 eV, are sp²-hybridized N atoms in the tri-s-triazine ring and tertiary N atoms in the heptazine ring (Fig. 4e).

Additionally, the O 1s region of the spectrum can reveal important details about the sample. In VO₂-A/g-C₃N₄ nanocomposites, the O 1s spectrum typically displays primary peaks at around 530 eV, corresponding to the oxygen atoms bonded to carbon or nitrogen atoms in the lattice structure of the material (Fig. 4c). The V 2p region of the spectrum is particularly informative, as it provides critical insights into the

oxidation state of the vanadium present in the sample. In VO₂-A/g-C₃N₄ nanocomposites, the V2p spectrum generally shows two prominent peaks at approximately 513 and 521 eV, representing the V2p 3/2 and V2p 1/2 levels, respectively (Fig. 4b). The intensity ratio of these two peaks can indicate the relative amounts of V5+ and V4+ in the sample.

3.6. BET analysis

The surface area and pore size distribution of VO₂-A/g-C₃N₄

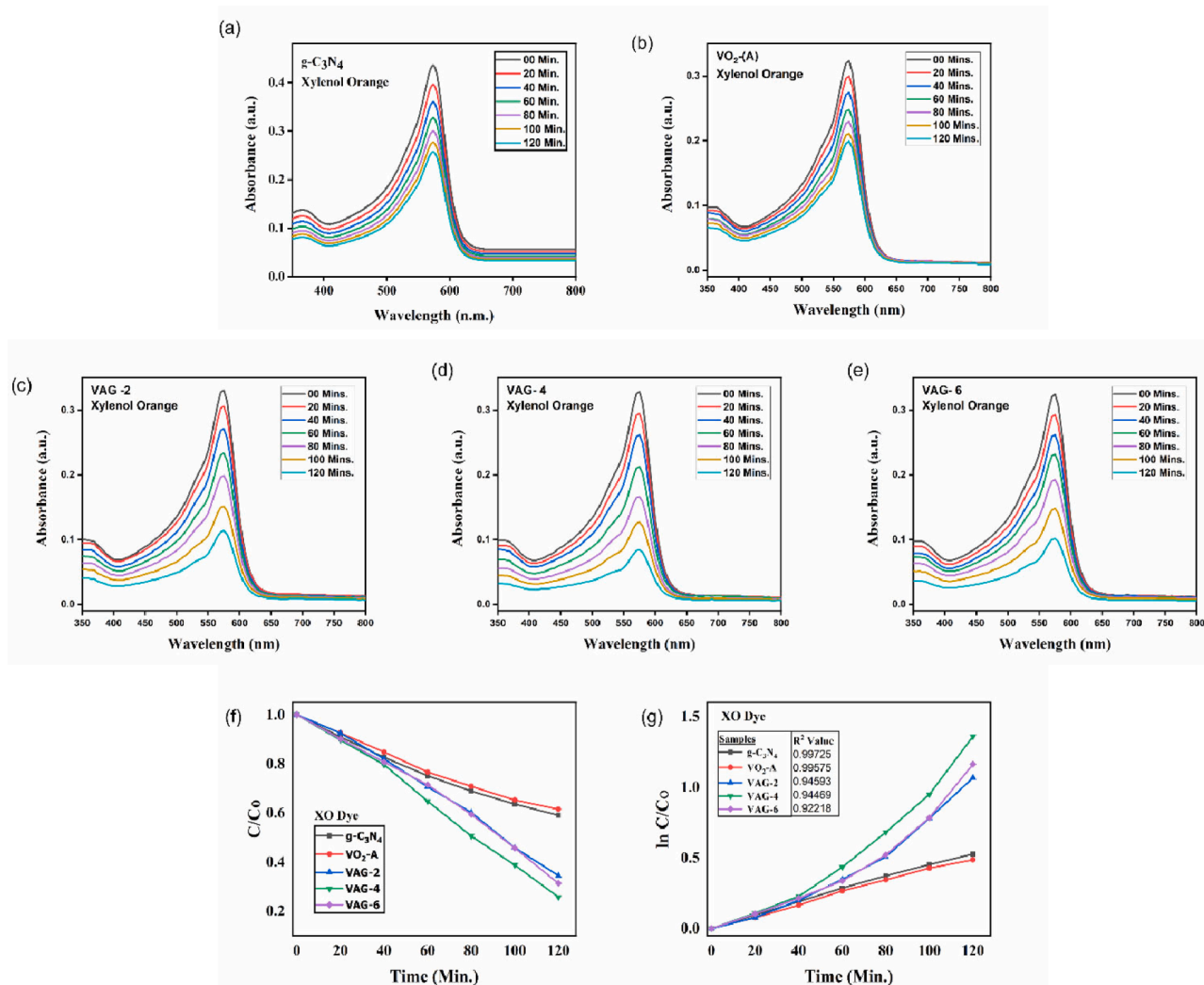


Fig. 10. (a-e) XO dye's absorbance spectra, (f) Photocatalytic activity comparison (g) XO dye's $\ln(C_0/C_t)$ plot.

nanocomposite (VAG-4) was assessed through nitrogen gas adsorption-desorption isotherms at 77 K. Fig. 5a illustrates a type IV adsorption-desorption isotherm. Fig. 5b presents a multi-point BET nitrogen adsorption plot, indicating a specific surface area of 47.1 m²/g. Fig. 5c presents the pore volume distribution, indicating a measured value of 0.2125 cm³/g. Fig. 5d illustrates a BJH plot that reveals the pore size distribution, with an average pore size of 27.9 nm for VAG-4. This BET analysis reveals that VAG-4's high surface area and optimal pore size improve photocatalytic performance by providing abundant active sites, leading to more efficient degradation of organic dyes.

3.7. Photoluminescence

Photoluminescence (PL) is the emission of light by a material after absorbing light of a different wavelength. In the case of $g\text{-C}_3\text{N}_4$, the main peak in the PL spectrum is around 460 nm (Fig. 6). This peak corresponds to the radiative recombination of electron-hole pairs that are created when $g\text{-C}_3\text{N}_4$ absorbs light in the visible region of the spectrum. The PL spectrum of $\text{VO}_2\text{-A}$ nanocomposites typically shows two main peaks: approximately 437 nm and 475 nm. The peak at 437 nm is associated with the radiative recombination of electron-hole pairs that are created in the $\text{VO}_2\text{-A}$ component of the nanocomposites. In comparison, the peak at 475 nm is thought to be caused by a transition between defect states in the $\text{VO}_2\text{-A}$ lattice. The decrease in PL intensity of $\text{VO}_2\text{-A}/g\text{-C}_3\text{N}_4$ nanocomposites in VAG-6, VAG-4, and VAG-2 can be

attributed to the nanocomposites' increasing surface area-to-volume ratio. Also, the decreased photoluminescence intensity indicates the slower recombination rate of electrons and holes, which thus increases the photocatalytic activity.

3.8. Cyclic voltammetry (CV)

Cyclic voltammetry (CV) is a commonly employed electrochemical technique for evaluating both the qualitative and quantitative characteristics of synthesized electrode materials. This study involved conducting cyclic voltammetry on modified electrodes in 1 M H_2SO_4 across a potential range of 0.5 to -0.5 V at a scan rate of 50 mV/s to evaluate the electroactive surface area and reaction kinetics (Fig. 7). In comparison to pure $\text{VO}_2\text{-A}$ and GCN, the VAG nanocomposite series exhibited an increased surface area, indicating a notable interaction between $\text{VO}_2\text{-A}$ and GCN nanoparticles. VAG-4 demonstrated a significant rise in peak current while showing only a slight shift in peak potential, suggesting improved electrocatalytic performance. The enhancement observed can be linked to the reduction in particle sizes and the increase in surface area, which together create more reactive sites, thereby facilitating a more effective photodegradation process for organic dyes.

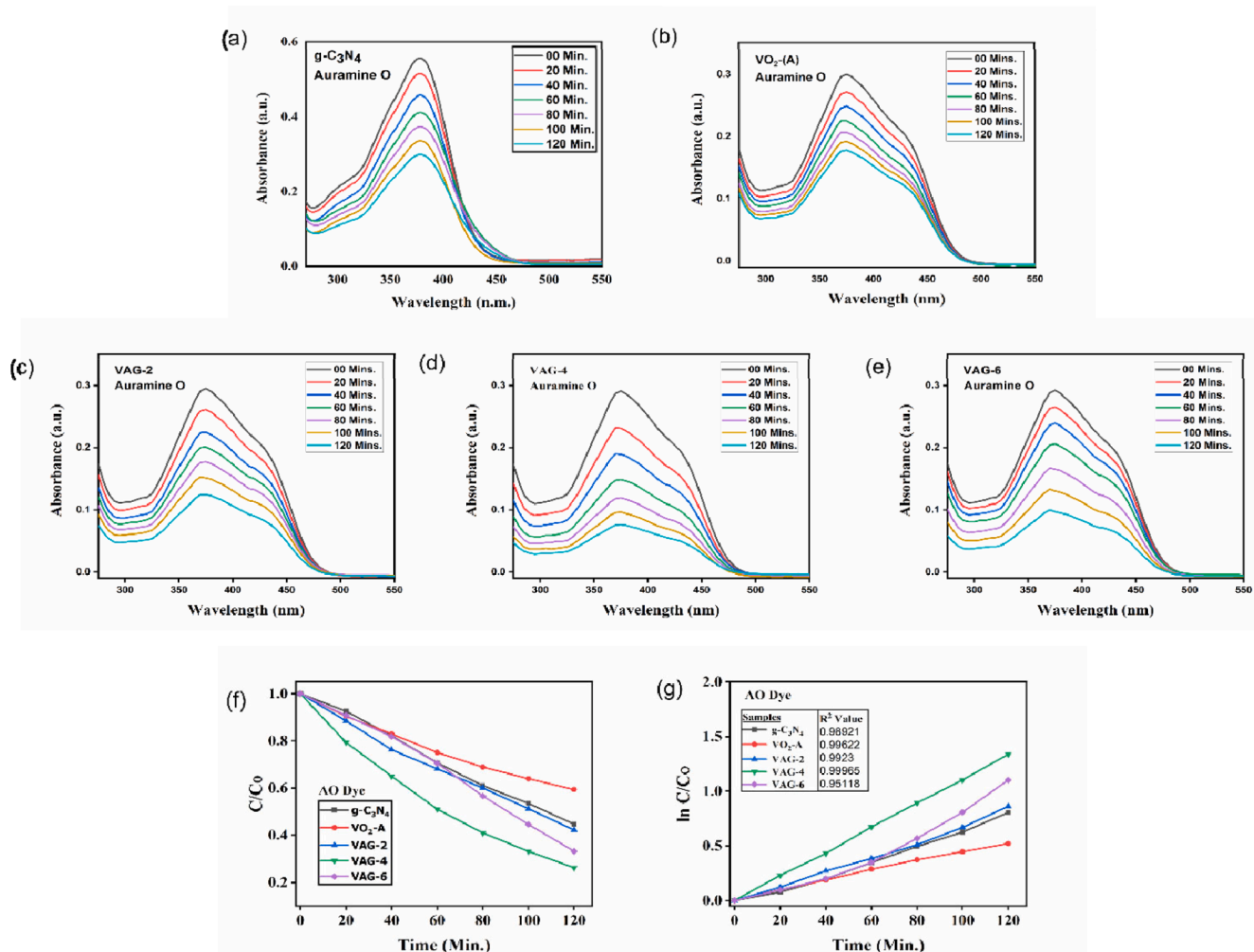


Fig. 11. (a-e) AO dye's absorbance spectra, (f) Photocatalytic activity comparison (g) AO dye's $\ln(C_0/C_t)$ plot.

3.9. UV-DRS

VO₂-A/g-C₃N₄ nanocomposite's optical properties were investigated using UV-Vis DRS spectra (Fig. 8a,b). The energy bandgap, an essential parameter for assessing electrical properties, was determined using the Tauc Relation equation

$$\alpha h\nu = A(h\nu - E_g)^n \quad (2)$$

where the absorption coefficient is denoted by α , $h\nu$ represents photon energy, E_g is the optical bandgap, and A is a constant. Based on the analysis, a value of $n = 2$ best fit the absorption data, indicating a direct permitted bandgap. The absorption edge of pure g-C₃N₄ was observed at a wavelength of 382 nm, corresponding to an energy of 2.7 eV. VO₂-A, on the other hand, showed an absorption peak at 412 nm, indicating a lower energy level of 2.56 eV compared to GCN. Incorporation of VO₂-A into g-C₃N₄ shifted the absorption edge to longer wavelengths in the nanocomposites. VAG-2 showed a peak absorption at 438 nm (2.45 eV), while VAG-4 exhibited a peak at 487 nm (1.91 eV). Despite a higher VO₂-A concentration, VAG-6 displayed a higher energy level than VAG-4, which peaked at 481 nm (2.03 eV). This trend reflects the complex interplay of factors including VO₂-A interaction and integration within the g-C₃N₄ matrix, nanoparticle agglomeration, and potential electronic structure modifications, collectively influencing band structure and optical properties, resulting in increased bandgap energy [24].

3.10. Photocatalytic activity

VO₂-A/g-C₃N₄ nanocomposite's photocatalytic efficiency for visible light irradiation was assessed by examining their photocatalytic activity for 120 min and measuring the degradation of anionic and cationic dyes. The results indicate that the order of photocatalytic degradation of Rose Bengal dye follows the sequence: VAG-4 (83.5 %) > VAG-6 (75 %) > VAG-2 (71.4 %) > g-C₃N₄ (69.2 %) > VO₂-A (50.2 %). VAG-4 exhibited the highest degradation efficiency with a rate of 83.5 %, which is higher than that of VO₂-A and GCN. These findings suggest that VAG-4 is a highly efficient photocatalyst for degrading Rose Bengal dye (Fig. 9a-e). The outstanding performance of VAG-4 may be related to its distinct surface area, crystal structure, and optical characteristics, which improve the charge transfer and separation processes and encourage the production of reactive oxygen species.

The efficiency of various photocatalysts in the degradation of XO dye was evaluated, and the results are presented in Fig. 10(a-e). The order of degradation efficiency of the photocatalysts was found to be VAG-4 (75.7 %) > VAG-6 (68.7 %) > VAG-2 (66.6 %) > g-C₃N₄ (41.6 %) > VO₂-A (38 %). Based on the findings, VAG-4 is the photocatalyst with the highest potential for degrading XO dye out of all the tested photocatalysts. It is possible that the excellent features of VAG-4, such as its surface area, pore size, and crystal structure, are responsible for its exceptionally rapid rate of deterioration.

The progression of degradation of Auramine O dye was evaluated as follows: VAG-4 (73.4 %) > VAG-6 (66 %) > VAG-2 (60 %) > g-C₃N₄ (46.4 %) > VO₂-A (40 %). VAG-4 nanocomposite had the highest

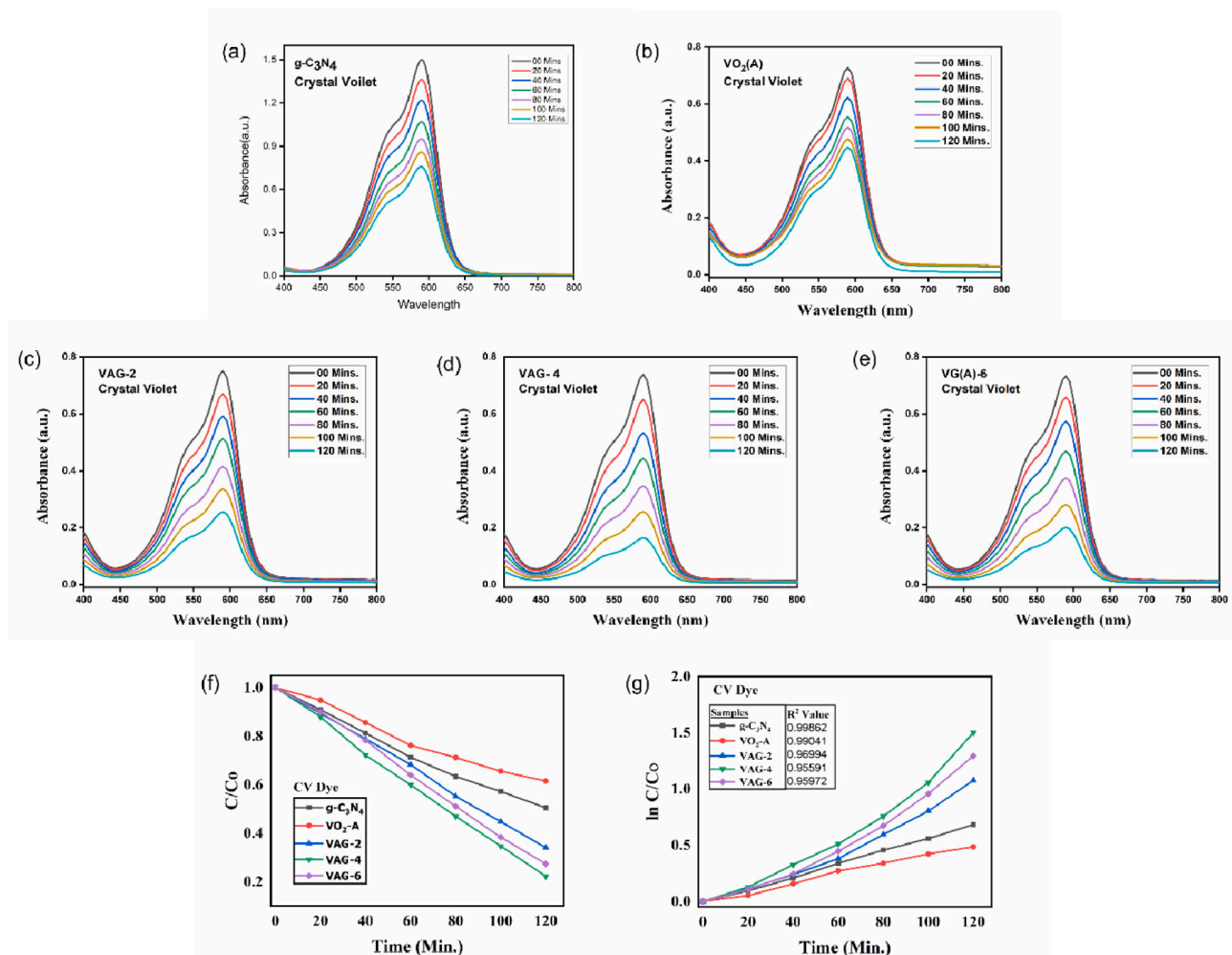


Fig. 12. (a-e) CV dye's absorbance spectra, (f) Photocatalytic activity comparison (g) CV dye's $\ln(C_0/C_t)$ plot.

degrading efficiency (Fig. 11a–e). The VAG-4 composite demonstrated 1.83 times and 1.58 times greater degrading efficiencies than $\text{VO}_2\text{-A}$ and $\text{g-C}_3\text{N}_4$ respectively. VAG-4's superior performance is due to its unique surface area, crystal structure, and optical properties, which enhance charge transfer and separation and promote reactive oxygen species generation.

The degradation efficiency of CV dye utilizing various precursors and composites was examined to find the optimal photocatalyst. The effectiveness of degradation went in the following order: VAG-4 (78.3 %) > VAG-6 (72.7 %) > VAG-2 (66.2 %) > $\text{g-C}_3\text{N}_4$ (48.6 %) > $\text{VO}_2\text{-A}$ (38.7 %). These findings suggest that VAG-4 has the maximum degradation efficiency, making it the most effective photocatalyst for the degradation of CV dye (Fig. 12a–e).

The progression of degradation of Mix dye was evaluated as follows: VAG-4 (77 %) > VAG-6 (73 %) > VAG-2 (66.5 %) > $\text{g-C}_3\text{N}_4$ (53.3 %) > $\text{VO}_2\text{-A}$ (40.6 %). VAG-4 nanocomposite had the highest degrading efficiency (Fig. 13a–e). The VAG-4 composite demonstrated 1.89 times and 1.44 times greater degrading efficiencies than $\text{VO}_2\text{-A}$ and $\text{g-C}_3\text{N}_4$, respectively.

Because VAG-4 had a larger surface area and more reaction-active sites than any other nanocomposites, it demonstrated greater photocatalytic efficiency. A higher deterioration rate resulted from the larger surface area's improved light absorption and utilization. Contrarily, VAG-6 displayed less degradation than VAG-4 while having a greater molar mass of the $\text{VO}_2\text{-A}$ precursor. This might be because VAG-6 had fewer active locations for the reaction due to its smaller surface area. Additionally, the larger particle size of VAG-6 could have contributed to

a decrease in light absorption and utilization efficiency. Thus, while molar mass is essential in determining photocatalytic efficiency, it is not the only factor. Surface area and particle size also play crucial roles [25]. Table 1 shows the degradation efficiency of prepared nanocomposites, and Table 2 compares the degradation efficiency of prepared nanocomposites with those of previously published works.

3.11. Kinetics and Statistics

The photocatalytic degradation of dyes can be modeled by Langmuir-Hinshelwood's pseudo-first-order kinetic equation, represented as

$$\ln(C_0/C_t) = K_{app}t \quad (3)$$

where the rate constant (K_{app}) is determined by dye's initial concentration (C_0) and its concentration at a specific time (C_t). Table 3 shows the prepared nanocomposites' apparent rate constant (K min^{-1}). The R^2 values obtained from the first-order kinetic model presented in Table 4 indicate the effectiveness of $\text{V}_2\text{O}_5/\text{g-C}_3\text{N}_4$ nanocomposites as photocatalysts for dye degradation.

The apparent rate constant (ARC) values for all dye degradations are shown in Table 3. These values demonstrated that VAG-4 consistently exhibited the highest rates across all dyes tested. For RB dye degradation, VAG-4 had an ARC of $0.01466 \text{ K min}^{-1}$. For XO dye, the ARC was $0.0111 \text{ K min}^{-1}$. For AO dye, VAG-4's ARC was $0.0111 \text{ K min}^{-1}$. For CV dye, the ARC was $0.01213 \text{ K min}^{-1}$. Lastly, for mixed dye degradation, VAG-4 had an ARC of $0.01178 \text{ K min}^{-1}$. These superior ARC

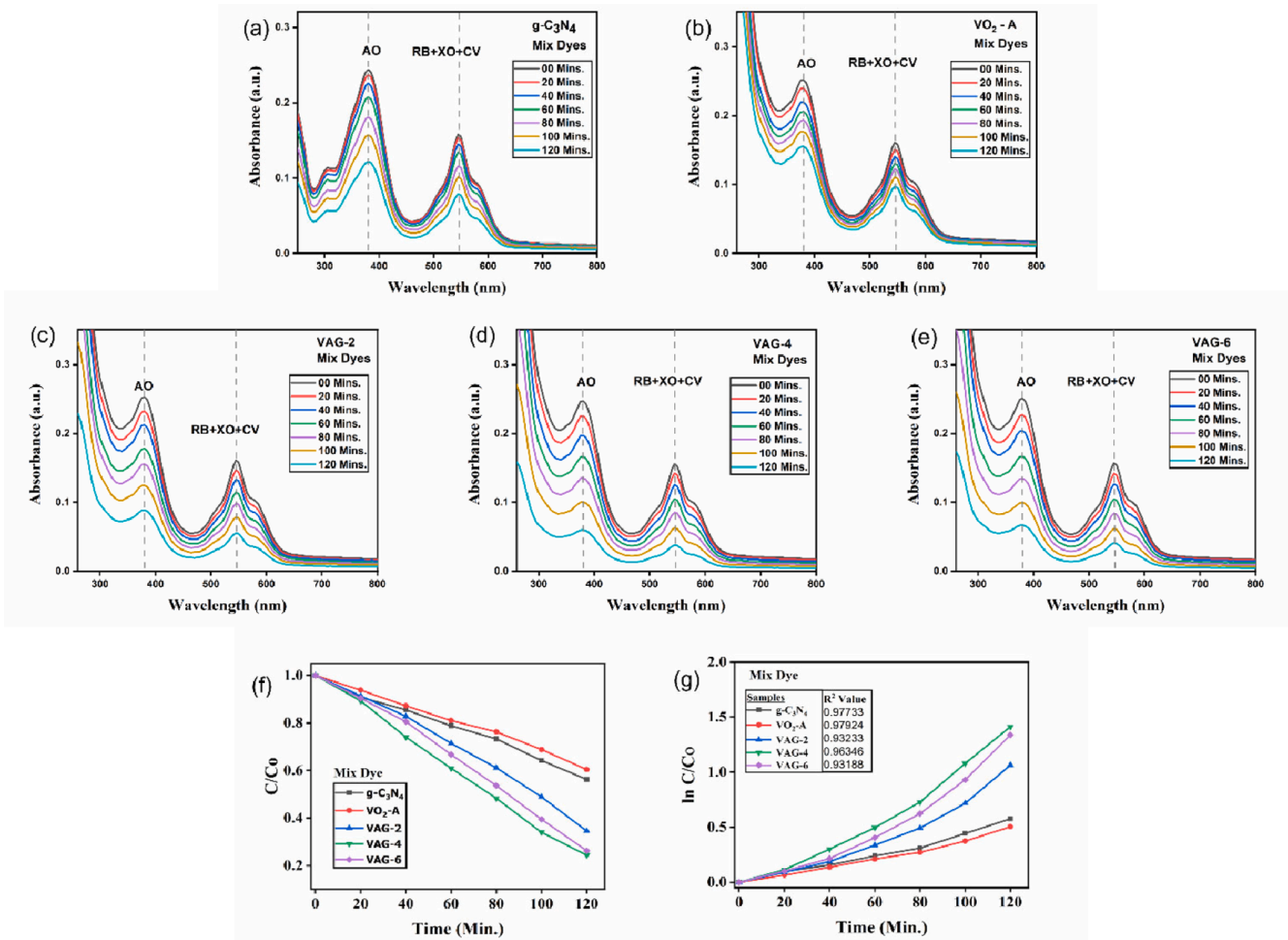


Fig. 13. (a-e) Mix dye's absorbance spectra, (f) Photocatalytic activity comparison (g) Mix dye's $\ln(C_0/C_t)$ plot.

Table 1
Degradation efficiency of synthesised nanocomposites.

S. No.	Sample	Rose Bengal Dye	Xylenol Orange Dye	Auramine O Dye	Crystal Violet Dye	Mix Dyes
1	g-C ₃ N ₄	69.2	41.6	46.4	48.6	53.3
2	VO ₂ -A	50.2	38	40	38.7	40.6
3	VAG-2	71.4	66.6	60	66.2	66.5
4	VAG-4	83.5	75.7	73.4	78.3	77
5	VAG-6	75	68.7	66	72.7	73

Table 3
Apparent rate constant ($K \text{ min}^{-1}$) for prepared nanocomposites.

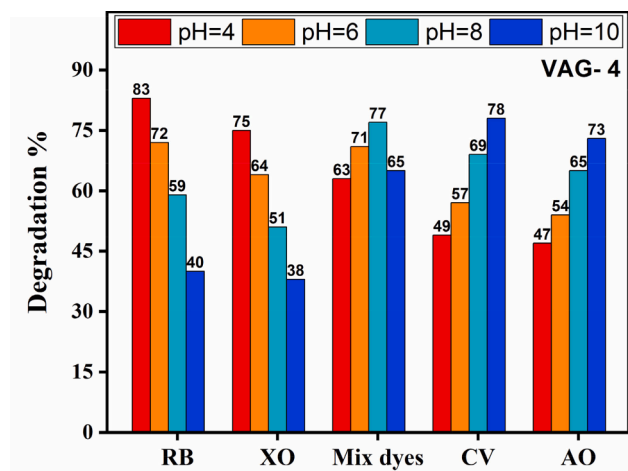
S. No.	Sample	Rose Bengal Dye	Xylenol Orange Dye	Auramine O Dye	Crystal Violet Dye	Mix Dyes
1	g-C ₃ N ₄	0.00959	0.00443	0.0068	0.00575	0.00459
2	VO ₂ -A	0.00575	0.00418	0.00436	0.00425	0.00405
3	VAG-2	0.00983	0.00878	0.007	0.00887	0.00848
4	VAG-4	0.01466	0.0111	0.01111	0.01213	0.01178
5	VAG-6	0.0115	0.00921	0.0091	0.01074	0.01085

Table 2
Comparative analysis of dye degradation results from previously reported studies.

Dye	Catalyst Used	Illumination Source	Degradation Efficiency (%)	Time (Min)	Reference
Auramine O	CeO ₂	Halogen lamp (50 W)	35	90	[26]
	SiO ₂ / g-C ₃ N ₄	Xe Lamp (400 W)	70	120	[27]
	VO ₂ -A/g-C ₃ N ₄	Xe Lamp (400 W)	73.4	120	This Work
Xylenol orange	g-C ₃ N ₄	Tungsten Lamb (200 W)	15	120	[6]
	TiO ₂	UV lamp (7 W)	70	175	[28]
	VO ₂ -A/g-C ₃ N ₄	Xe Lamp (400 W)	75.7	120	This Work
Rose Bengal	Ag/CeO ₂	Sunlight	96 %	180	[29]
	CeO ₂ /GCN	400 W Xe Lamp	79.2 %	90	[7]
	VO ₂ -A/g-C ₃ N ₄	Xe Lamp (400 W)	83.5	120	This Work
Crystal violet	g-C ₃ N ₄	200 W XE lamp	51	120	[6]
	VO ₂ -A/g-C ₃ N ₄	Xe Lamp (400 W)	78.3	120	This Work

Table 4R²Value for prepared nanocomposites.

S. No.	Sample	Rose Bengal Dye	Xylenol Orange Dye	Auramine O Dye	Crystal Violet Dye	Mix Dyes
1	g-C ₃ N ₄	0.91109	0.99725	0.98921	0.99862	0.97733
2	VO ₂ -A	0.98826	0.99575	0.99622	0.99041	0.97924
3	VAG-2	0.94321	0.94593	0.9923	0.96994	0.93233
4	VAG-4	0.96	0.94469	0.99965	0.95591	0.96346
5	VAG-6	0.98599	0.92218	0.95118	0.95972	0.93188

**Fig. 14.** Effect of pH on Anionic, Cationic and Mix dyes.

values of VAG-4 compared to other nanocomposites indicate a higher rate of photocatalytic degradation. This enhanced performance can be attributed to the synergistic interaction between VO₂-A and g-C₃N₄, which results in a more extensive surface area and more effective charge transfer.

The R² value is an essential statistical parameter determining the model's fitness to the experimental data (Figs. 9–13g). The R² values for the VAG-4 nanocomposite were calculated for all five dyes (as shown in Table 4), i.e., Rose Bengal (0.96), Xylenol Orange (0.94469), Auramine O (0.99965), Crystal Violet (0.95591) and Mix dyes (0.96346). The high R² values obtained for VAG-4 suggest that the model fits well with the experimental data, indicating its high photocatalytic efficiency in the degradation of the four dyes. The higher the R² value, the better the photocatalytic activity of the nanocomposite, which is directly related to its ability to degrade the dyes under UV irradiation. Therefore, the high R² values obtained for VAG-4 indicate its outstanding photocatalytic activity than the other nanocomposites, which is helpful in the development of efficient photocatalysts.

3.12. Effect of pH

The degradation of anionic and cationic dyes was investigated at different pH levels (Fig. 14). The results demonstrated that the VAG-4 nanocomposite exhibited superior degradation performance for anionic dyes, at lower pH 4 with degradation values of 83.5 % and 75.5 % for Rose bengal and Xylenol orange, respectively (Table 5). On the other hand, for cationic dyes like crystal Violet and auramine O, the degradation rates were higher at basic pH value, with the maximum degradation occurring at pH 10. Crystal Violet exhibited a degradation efficiency of 78.2 %, while auramine O showed a degradation efficiency of 73.4 % at pH 10. For Mix dyes, the improved degradation efficiency of 77 % was observed at pH 8. The variation in degradation rates at different pH values can be attributed to the interactions between the dyes and nanocomposites. at lower pH levels, the higher concentration

of H⁺ ions enhance the binding of cationic dyes to the nanocomposite, leading to more efficient degradation.

In contrast, the negatively charged anionic dyes experience weaker interactions due to shielding effect of H⁺ ions, resulting in slower degradation rates. At higher pH levels, OH⁻ ions neutralize the negative charge of anionic dyes, promoting stronger interaction with the nanocomposite and consequently increasing degradation efficiency. However, the positive charge of cationic dyes is shielded by OH⁻ ions, weakening their interactions and leading to slower degradation rates [30]. For mixed dyes, the degradation efficiency varies with pH due to the combined effects on both cationic and anionic dyes. At higher pH levels, the neutralization of anionic dyes by OH⁻ ions and the weakening interactions of cationic dyes due to OH⁻ shielding result in optimal degradation efficiency at slightly alkaline conditions [23]. These findings highlight the significance of pH in influencing the photocatalytic degradation of dyes and provide insights for the design and optimization of photocatalytic systems for wastewater treatment applications.

3.13. Effect of catalyst loading

To investigate the effect of catalyst concentration on the photoactivity of VAG-4 nanocomposite, various concentrations of VAG-4 nanocomposite ranging from 0.01 to 0.07 g/100 mL were utilized at pH 4 for anionic dyes, pH 10 for cationic dyes and pH 08 for Mix dyes. The study revealed that the photocatalytic activity increased with increasing catalyst amount up to 0.05 g, which was attributed to the increased availability of active sites on the catalyst surface. However, when the catalyst amount was increased beyond 0.05 g, the photocatalytic activity decreased due to the enhanced light scattering phenomenon, making it difficult for light to reach the dye molecules., VAG-4 nanocomposite showed the highest degradation efficiency at a concentration of 0.05/100 gmL⁻¹ (Table 6). These results suggest optimizing the catalyst concentration is critical for achieving maximum photocatalytic efficiency.

3.14. Reusability

The recycling efficiency of VAG-4 nanocomposites were studied over 5 cycles by analyzing the degradation percentages of five different dyes (rose Bengal, Xylenol Orange, Auramine O, Crystal Violet and Mix dyes) (Fig. 15a). The result showed that the nanocomposites had consistent degradation efficiency for all 5 cycles, with little decline in degradation percentages for each cycle. Although the degradation rates of different dyes from first cycle to fifth cycle showed a decreasing trend from 83 % to 61 % for Rose Bengal, 75 % to 53 % for Xylenol Orange, 73 % to 50 % for Auramine O, 78 % to 57 % for Crystal Violet and 77 % to 52 % for Mix Dyes but was not very significant showing the stability of the nanocomposites towards photocatalytic activity even after fifth cycle. Notably, even after five cycles, the nanocomposites showed no appreciable reduction in effectiveness, demonstrating their potential for repeated application (Fig. 15b–e).

Furthermore, data indicated that the nanocomposites could scale up the process for all cycles when employing a constant concentration (c/c₀). The VAG-4 nanocomposites demonstrated persistent and constant photocatalytic activity for five cycles, indicating the possibility of their repeated usage in photocatalytic applications.

3.15. Mechanism

Photocatalysis is a method that uses light to activate a catalyst and start a chemical reaction. g-C₃N₄ and VO₂-A both function as photocatalysts. Due to their broadband gaps, g-C₃N₄ and VO₂-A can absorb UV light and undergo excitation from the valence band (VB) to the conduction band (CB) [31]. The photocatalyst produces electron-hole pairs in the CB and VB when it absorbs light energy. Then, these electron-hole pairs move to the photocatalyst's surface, where they can participate in

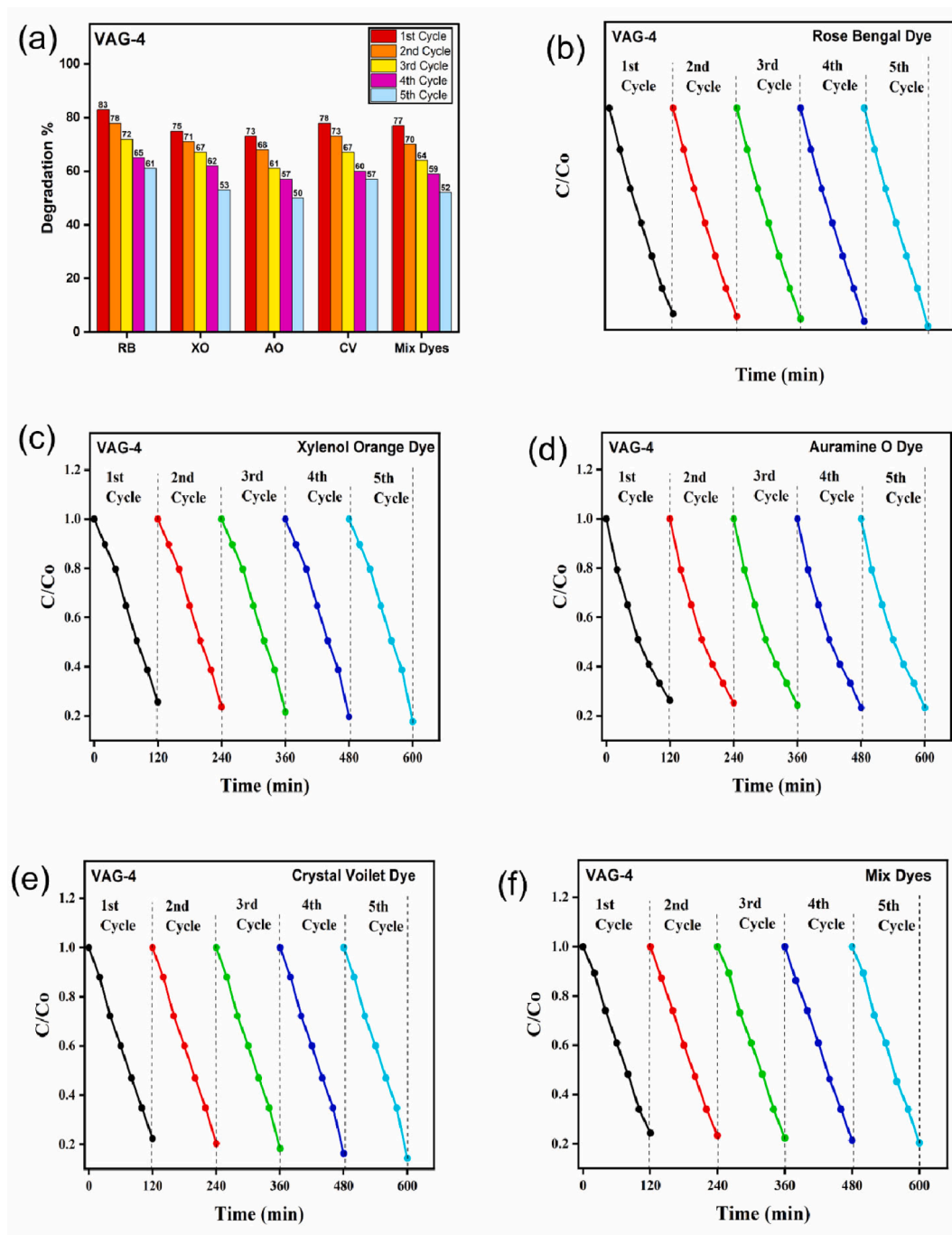
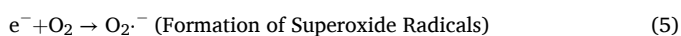
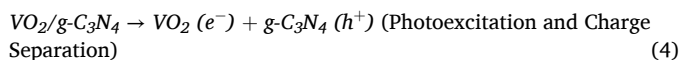


Fig. 15. (a) Investigation of dye photocatalytic degradation of dyes using VAG-4 nanocomposite in recycling experiments, (b-f) comparative analysis of photocatalytic degradation over 5 cycles using VAG-4 nanocomposite.

chemical reactions (Fig. 16). The overall chemical reaction can be represented as follows:



These hydroxyl radicals can degrade pollutants through oxidation and cleavage of chemical bonds. Therefore, the photocatalytic degradation of pollutants is a multistep process involving the generation of

reactive species and their reaction with pollutants to form degradation products. The degradation efficiency of g-C₃N₄ and VO₂-A photocatalysts depends on various factors, such as the band gap energy, surface area, and crystal structure. These photocatalyst's wide band gap energy allows them to absorb light in the UV region, which is more energetic and can generate more electron-hole pairs. Additionally, the surface area of the photocatalyst can also affect the degradation efficiency since it provides more active sites for chemical reactions. Finally, the crystal structure of the photocatalyst can also affect the degradation efficiency since it can affect the mobility and reactivity of the electron-hole pairs [32].

In conclusion, the production of electron-hole pairs, which can interact with adsorbed oxygen to create superoxide radicals, occurs

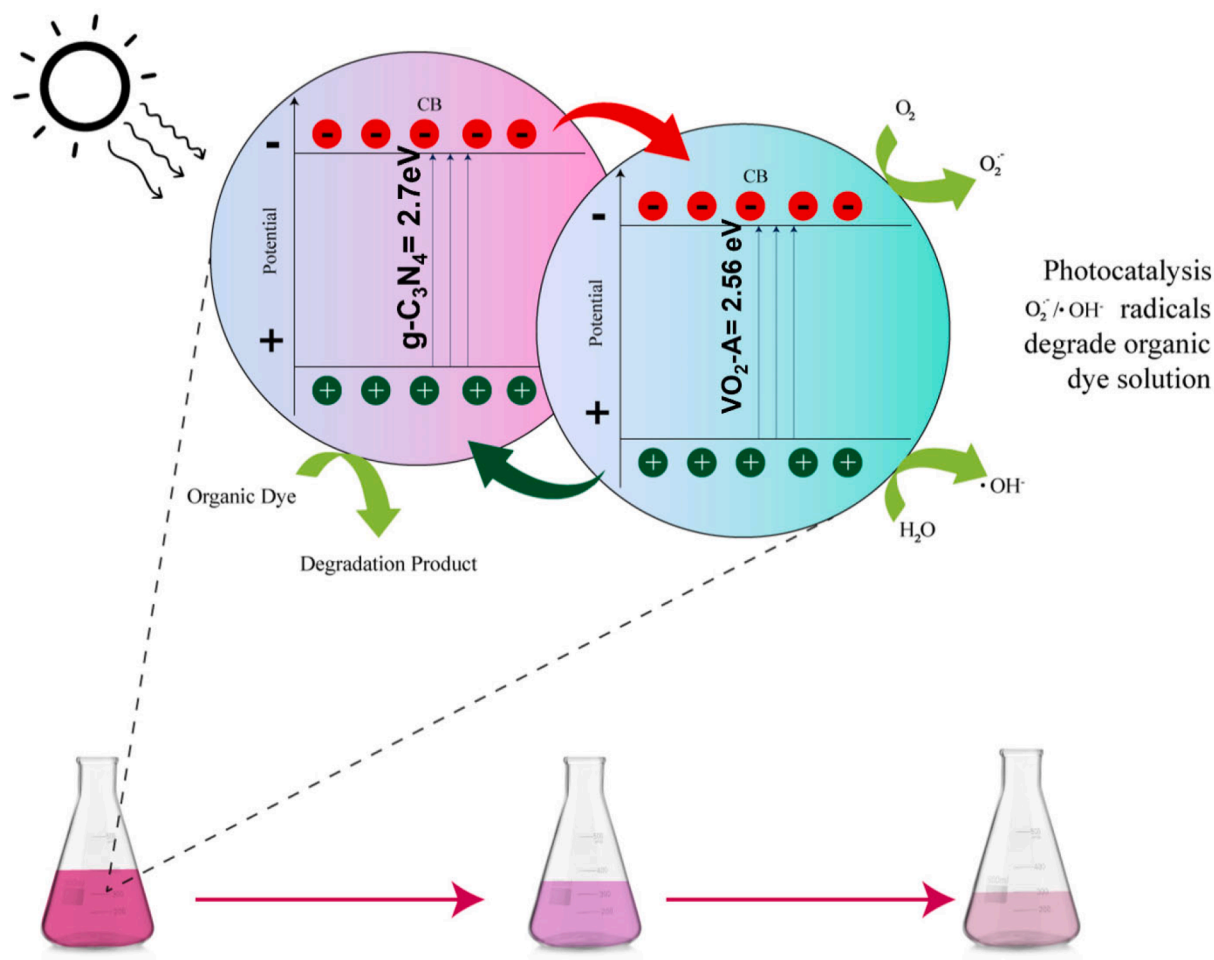


Fig. 16. Mechanism of Photocatalysis.

Table 5

Photocatalytic Degradation efficiency of VAG-4 composite at various pH conditions.

S. NO.	pH Value	Rose Bengal dye	Xylenol Orange dye	Auramine O dye	Crystal Violet dye	Mix dyes
1.	pH = 4	83	75	47	49	63
2.	pH = 6	72	64	54	57	71
3.	pH = 8	59	51	65	69	77
4.	pH = 10	40	38	73	78	65

during the photocatalytic destruction of contaminants utilizing g-C₃N₄ and VO₂-A. After reacting with water, these superoxide radicals can create hydroxyl radicals. These highly reactive species can oxidize and destroy organic contaminants. The efficiency of this process depends on several variables, including the photocatalyst's surface area, crystal

structure, and band gap energy.

4. Conclusion-

In conclusion, a promising method for creating effective photocatalysts for dye degradation is the simple hydrothermal synthesis of VO₂-A/g-C₃N₄ composite. The synthesised nanocomposites showed outstanding photocatalytic degradation for the breakdown of both cationic, anionic and mixed dyes. SEM and TEM analyses revealed a distinct morphology of the VAG-4 nanocomposite, with small, irregular VO₂-A nanoparticles dispersed and wrapped around the g-C₃N₄ surface. UV-DRS analysis, using the Tauc relation, indicated that VO₂-A incorporation shifted the absorption edge to longer wavelengths, with VAG-4 showing a peak at 487 nm (1.91 eV), the XRD analysis validated the successful synthesis of the VO₂-A/g-C₃N₄ composite. The BET results indicate that VAG-4's high surface area, moderate pore volume, and optimal pore size make it well-suited for enhanced photocatalytic degradation of organic dyes. VO₂-A/g-C₃N₄ composite has a lower

Table 6

Degradation efficiency of photocatalysts at different concentrations.

S.No.	Catalyst Concentration (g / 100 mL)	Rose Bengal (pH = 4)	Xylenol Orange (pH = 4)	Auramine O (pH = 10)	Crystal Violet (pH = 10)	Mix Dyes (pH=8)
1.	0.01	83.5	75.7	73.4	78.3	77
2.	0.03	89.1	85.9	82.4	87.3	85.1
3.	0.05	96.8	93.4	90.1	95.7	92.4
4.	0.07	92.8	89.4	87.2	91.7	87.9

bandgap than separate precursors, according to the bandgap analysis, which increases its photocatalytic activity. The anionic and cationic dyes' degradation kinetics also demonstrated that they were most effective at pH 4 and 10, respectively. For all dyes, the VAG-4 nanocomposite showed the highest ARC. The recyclability investigation further showed that the VO₂-A/g-C₃N₄ composite maintained high photocatalytic activity even after five cycles, demonstrating its exceptional stability and reusability. In conclusion, the simple hydrothermal synthesis of VO₂-A/g-C₃N₄ composite is a novel and promising method for producing effective photocatalysts with improved stability, reusability, and photocatalytic activity. The results of this work can offer important insights into the creation of more effective and affordable photocatalysts for use in applications such as environmental cleanup and energy conversion.

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Ethical Approval

There is no need for formal consent for this sort of research.

Consent to participate

Not applicable.

Consent to Publish

Not applicable.

CRediT authorship contribution statement

Sachin Shoran: Writing – original draft, Visualization, Methodology, Conceptualization. **Sweety Dahiya:** Writing – original draft, Visualization, Supervision, Conceptualization. **Manju Rani:** Validation, Supervision, Investigation, Formal analysis. **SP Nehra:** Writing – review & editing, Supervision, Methodology, Investigation, Funding acquisition, Formal analysis. **Anshu Sharma:** Writing – review & editing, Visualization, Validation, Supervision, Data curation, Conceptualization. **Sudesh Chaudhary:** Writing – review & editing, Supervision, Formal analysis, Conceptualization.

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.

Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.apsusc.2024.161852>.

Data availability

Data will be made available on request.

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