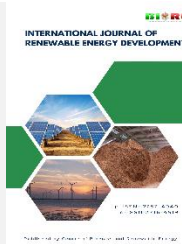




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Research Article

Hard-template synthesis of Ti–V–Mn ternary photocatalysts using gelatine-modified mesoporous silica for efficient methylene blue degradation

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Abstract. The rapid expansion of the textile industry, driven by technological progress, has resulted in substantial dye pollution, particularly from methylene blue effluents, which remain highly recalcitrant in aquatic environments. Photocatalysis offers a sustainable and effective pathway for dye degradation, and in this study, Ti–V–Mn ternary photocatalysts were synthesized using a 20% gelatine-modified mesoporous silica hard template. Comprehensive characterization was carried out to establish the relationship between structural and optical properties and photocatalytic performance. XRD revealed that the G–Ti–Mn sample exhibited the highest crystallinity (19.62%), while SEM–EDX confirmed the uniform distribution of all metal precursors. FTIR spectra displayed characteristic M–O vibrations corresponding to Ti–O, V–O, and Mn–O bonding, and UV–Vis DRS showed reduced band gap energies in the range of 1.005–2.39 eV, favoring visible-light activation. BET analysis indicated a typical type IV isotherm, with the G–V–Mn sample exhibiting the highest surface area of 106.67 m²/g and pore diameters of 3.74–4.94 nm, confirming the mesoporous nature of the materials. Photocatalytic evaluation demonstrated that the G–V–Mn system achieved the highest degradation efficiency, removing up to 67.83% of methylene blue under UV–Vis irradiation. These findings highlight the potential of gelatine-assisted mesoporous templates in engineering ternary metal photocatalysts with enhanced structural and optical features for sustainable wastewater treatment applications.

Keywords: Photocatalyst; Ti-V-Mn; Gelatine; Methylene Blue; Mesopore Silica; Photodegradation



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1. Introduction

The textile industry represents one of the most dynamic manufacturing sectors worldwide, contributing significantly to economic growth, employment opportunities, and international trade (Imran *et al.*, 2021)(Ojha & Roy, 2025). However, its rapid expansion has also intensified environmental challenges, particularly the discharge of dye-containing wastewater into aquatic systems (Blue & Solution, 2023). Synthetic dyes are extensively utilized in textile dyeing, printing, and finishing processes because of their affordability, broad color range, and chemical stability (Rauf *et al.*, 2011). Nevertheless, these characteristics also make them highly persistent pollutants in water environments (Ghosh *et al.*, 2019). The presence of stable chromophoric and auxochromic groups enhances resistance toward biodegradation, oxidation, and photolysis (Jadhav *et al.*, 2025), making dye contamination one of the major concerns in industrial wastewater treatment (Suba *et al.*, 2024).

Among synthetic dyes, methylene blue (MB) is widely employed in textile production due to its intense coloration, relatively low cost, and high solubility (Fajarwati *et al.*, 2011).

Despite these advantages, MB exhibits considerable toxicity toward aquatic ecosystems and human health (Blue & Solution, 2023). Exposure to MB-contaminated water may cause irritation of the eyes and skin, gastrointestinal inflammation, and systemic toxicity at elevated concentrations (Imran *et al.*, 2021). In aquatic environments, the persistence of MB increases chemical oxygen demand (COD) and decreases light penetration, thereby disrupting photosynthesis and ecological balance (Zhang *et al.*, 2019). In addition, its aromatic molecular structure contributes to high chemical stability and poor degradability under natural conditions, while its mutagenic and carcinogenic potential raises further environmental concerns (Thirugnanam *et al.*, 2017). Since only a fraction of dye molecules are effectively fixed onto textile fibers during dyeing processes, substantial quantities are ultimately released into wastewater streams, emphasizing the need for efficient remediation technologies (Krishnan *et al.*, 2024).

Photocatalysis has emerged as a promising approach for degrading organic pollutants in wastewater because it enables the mineralization of contaminants into environmentally benign

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products under light irradiation (Gaya & Abdullah, 2008) (Ulfa & Anggreani, 2022). Among various photocatalysts, titanium dioxide (TiO_2) remains one of the most extensively investigated materials owing to its chemical stability, non-toxicity, abundance, and strong oxidative properties (Ariapad & Zanjanchi, 2011). However, the practical application of TiO_2 is restricted by its wide band gap energy (3.0–3.2 eV), which limits photoactivity mainly to the ultraviolet region of the solar spectrum (Bekena & Kuo, 2020) (Wei *et al.*, 2018). To overcome this limitation, numerous studies have explored Ti-based multimetal oxide systems through doping, heterojunction formation, and semiconductor coupling to enhance visible-light absorption and suppress electron–hole recombination (Rauf *et al.*, 2011) (Zhao *et al.*, 2016).

Among transition metals, vanadium (V) and manganese (Mn) are particularly attractive modifiers for Ti-based photocatalysts because their multiple oxidation states can facilitate electron transfer and improve redox behavior (Krishnan *et al.*, 2024). Vanadium has been reported to promote charge carrier mobility, whereas manganese can enhance visible-light absorption and catalytic activity (Zhao *et al.*, 2016) (Yakout, 2021). Although Ti-based multimetal oxide photocatalysts have been widely studied for methylene blue degradation, most previous reports primarily focused on binary systems or conventional synthesis strategies with limited control over catalyst morphology and active-site distribution (C. Chen *et al.*, 2017). Consequently, the synergistic interaction within a ternary Ti–V–Mn system, particularly when integrated with a tailored mesoporous architecture, remains insufficiently understood. This represents an important scientific gap because the coexistence of Ti, V, and Mn may generate complementary redox pathways, improved charge separation efficiency, and broader visible-light responsiveness compared with single- or bimetallic systems.

Besides chemical composition, the structural morphology of photocatalysts plays a crucial role in determining photocatalytic performance (Kammakam, 2021). Mesoporous silica has attracted considerable attention as a hard template because it provides high surface area, tunable pore structures, and enhanced stability (Deng & Chen, 2017). Its ordered porous architecture facilitates uniform dispersion of active species, improved light harvesting, and more efficient diffusion of reactants and products (Precelia *et al.*, 2018) (Deng & Chen, 2017). Conventional mesoporous materials such as SBA-15 and MCM-41 are commonly synthesized using synthetic surfactants, which may increase production cost and environmental burden (Nur *et al.*, 2023) (Ulfa, 2017). In contrast, naturally derived polymers such as gelatine offer a more sustainable alternative (Ulfa & Apriliani, 2020) (Sachithanadam & Chandrakanth, 2014). Gelatin contains functional groups capable of interacting with metal precursors, thereby influencing nucleation, crystal growth, and metal dispersion during synthesis (Ulfa *et al.*, 2014). Moreover, gelatine is biodegradable, renewable, and environmentally friendly, making it a promising green template for advanced photocatalyst fabrication (Ulfa *et al.*, 2022).

Despite the growing interest in Ti-based multimetal oxide photocatalysts, studies integrating gelatine-modified mesoporous silica templates with ternary Ti–V–Mn systems remain very limited (Nur *et al.*, 2023). To date, no study has specifically investigated the synthesis of Ti–V–Mn ternary photocatalysts using a 20% gelatine-modified mesoporous silica hard-template approach for methylene blue degradation. Therefore, the novelty of this work lies not only in the incorporation of Ti, V, and Mn into a ternary oxide system, but also in the use of a gelatine-assisted mesoporous hard-template strategy to achieve improved structural control, enhanced surface properties, and optimized visible-light photocatalytic

performance. Accordingly, this study aims to synthesize and characterize Ti–V–Mn ternary photocatalysts prepared through a gelatin-modified mesoporous silica hard-template method. The relationship between structural, optical, and morphological properties and photocatalytic activity toward methylene blue degradation is systematically evaluated. This work is expected to provide new insights into the design of sustainable ternary photocatalysts with enhanced visible-light activity for textile wastewater treatment applications.

2. Materials and Method

2.1 Materials

Titanium(IV) ethoxide ($\text{Ti}(\text{OC}_2\text{H}_5)_4$, 99%), vanadium(V) oxide (V_2O_5 , 99%), manganese dioxide (MnO_2 , 99%), hydrochloric acid (HCl, 37%), sodium hydroxide (NaOH, 2 M), citric acid ($\text{C}_6\text{H}_8\text{O}_7$), tetraethyl orthosilicate (TEOS, 98%), commercial gelatin, and methylene blue ($\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}\cdot x\text{H}_2\text{O}$, analytical grade) were used as received without further purification. Deionized water ($18.2 \text{ M}\Omega\cdot\text{cm}$) was employed for all solution preparations.

2.2 Synthesis of Gelatin-Modified Silica (SPG-20)

The mesoporous silica template (SPG-20) was prepared by dissolving Pluronic P123 in 1.6 M HCl under vigorous stirring, followed by the addition of TEOS as the silica precursor and 20 wt% gelatine as a natural pore-directing agent. The mixture was continuously stirred for 24 h at 35 °C and subsequently subjected to hydrothermal treatment at 100 °C for 24 h. The resulting solid was filtered, washed with deionized water, and dried at 60 °C. Finally, the material was calcined at 550 °C for 5 h to remove the organic moieties, yielding the gelatine-modified mesoporous silica template (SPG-20).

2.3 Synthesis of Ti-V-Mn Photocatalysts Using Hard-Template Method

The molar ratio of $\text{Ti}(\text{OC}_2\text{H}_5)_4 : \text{V}_2\text{O}_5 : \text{MnO}_2$ was fixed at 1:0.05:0.05 for the ternary G–Ti–V–Mn sample, while binary counterparts (G–Ti–V, G–Ti–Mn, G–V–Mn) were prepared with the same total metal loading. The pH of the mixed precursor solution was adjusted to 3.5 using 0.1 M HCl to promote controlled hydrolysis and prevent premature precipitation. Hydrolysis was carried out by dropwise addition of the metal precursor solution into 20 mL of SPG-20 suspension under vigorous stirring (800 rpm) for 1 h at room temperature. Subsequently, the mixture was heated to 70 °C under constant stirring (500 rpm) for 2 h to evaporate excess solvent and initiate gelation. Aging was then performed at room temperature for 24 h without stirring to allow complete cross-linking and uniform distribution of metal species within the silica template. Calcination was conducted in a muffle furnace under static air atmosphere (no controlled gas flow) with a heating rate of 2 °C min^{-1} , held at 250 °C for 5 h. The use of 250 °C as a low-temperature calcination strategy intended to preserve mesoporosity and prevent excessive crystal growth.

Following calcination, the silica template was selectively removed by alkaline etching in 2 M NaOH solution at 90 °C under stirring for 10 h. The resulting solid was thoroughly washed with deionized water until the filtrate reached neutral pH, filtered, and dried at 60 °C for 24 h. The final product, denoted as G–Ti–V–Mn, was collected as a dry powder and

used for photocatalytic evaluation and physicochemical characterization.

2.4 Characterization Technique

The crystalline phases of the samples were analyzed using X-ray diffraction (XRD, Panalytical PW 3050/60, Cu K α radiation, $\lambda = 1.5406 \text{ \AA}$). Fourier transform infrared (FTIR) spectra were recorded on a Shimadzu IR-Prestige-21 spectrometer with a resolution of 0.5 cm^{-1} . Morphological and elemental analyses were carried out using scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDX, JEOL JSM-700, 15.0 kV accelerating voltage). Optical absorption properties and band gap energies were determined using UV-Vis diffuse reflectance spectroscopy (UV-Vis DRS, Analytik Jena Specord 200 Plus). Textural properties, including surface area, pore volume, and pore size distribution, were obtained via nitrogen adsorption-desorption measurements using the Brunauer-Emmett-Teller (BET) method.

2.5 Photocatalytic Activity Test

The photocatalytic degradation of methylene blue was evaluated using a Shimadzu UV-Vis spectrophotometer (UV-3600) at a maximum absorption wavelength of 664 nm. In a typical experiment, 50 mg of photocatalyst was dispersed in 200 mL of methylene blue solution ($20 \text{ mg}\cdot\text{L}^{-1}$). Prior to irradiation, the suspension was magnetically stirred in the dark for 30 min to establish adsorption-desorption equilibrium. Photodegradation was carried out under visible-light irradiation using a 300 W Xenon arc lamp equipped with a UV-cutoff filter to restrict the emission to a wavelength range of 420–800 nm. The light intensity at the solution surface was maintained at $100 \text{ mW}\cdot\text{cm}^{-2}$, corresponding to a calculated photon flux of approximately $4.50 \times 10^{-6} \text{ Einstein}\cdot\text{s}^{-1}$. Photodegradation was carried out under visible-light irradiation, and aliquots were collected at regular time intervals, centrifuged to remove photocatalyst particles, and analyzed spectrophotometrically to determine the degradation efficiency.

3. Result and Discussion

3.1. FTIR Analysis and Surface Functional Groups

The SPG-20 Figure 1 presents the FTIR spectra of the synthesized photocatalysts (G-V-Mn, G-Ti-V, G-Ti-Mn, and G-Ti-V-Mn). All samples exhibit broad absorption bands within the region of $3200\text{--}3800 \text{ cm}^{-1}$, which are attributed to O-H stretching vibrations originating from surface hydroxyl groups and adsorbed water molecules (Ulfa & Afif, 2022). The presence of these hydroxyl functionalities suggests strong hydrophilic character, which is beneficial for photocatalytic reactions in aqueous media by facilitating pollutant adsorption and enabling hydroxyl radical ($\cdot\text{OH}$) generation (Gaya & Abdullah, 2008).

The bands detected around $1636\text{--}1648 \text{ cm}^{-1}$ correspond to H-O-H bending vibrations of molecular water adsorbed on the catalyst surface (Litowczenko *et al.*, 2021). The persistence of this feature in all samples confirms the affinity of the ternary and binary oxides for water, a property that can further enhance photocatalytic efficiency under liquid-phase conditions (Ulfa *et al.*, 2024). Distinct absorption peaks observed between $430\text{--}1000 \text{ cm}^{-1}$ are assigned to M-O stretching vibrations, confirming the formation of Ti-O, V-O, and Mn-O bonds within the oxide network (Ulfa & Lestari, 2025). Although the band positions slightly differ among the samples, the overlap of

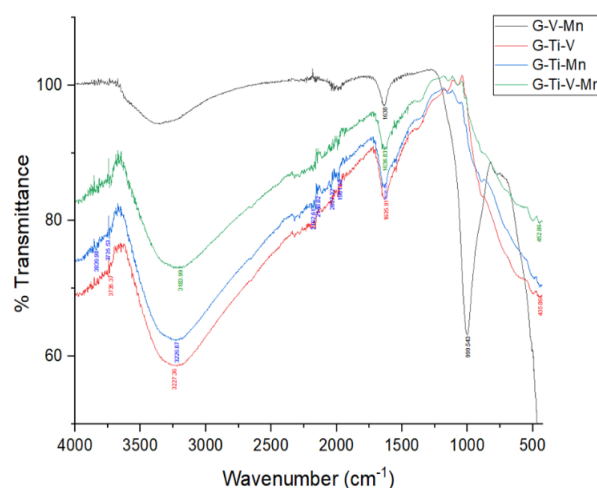


Fig. 1 Spectral characteristics of the sample under FTIR analysis.

features reflects the comparable vibrational modes of these transition-metal oxides. Notably, the broad and intense absorption in this region supports the successful incorporation of Ti, V, and Mn into the oxide lattice.

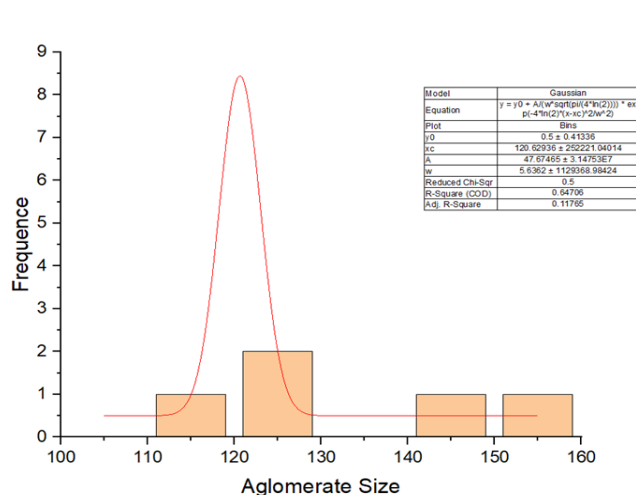
In the G-Ti-Mn sample, an additional weak band near 1981 cm^{-1} was detected, which may be associated with residual carbonyl-containing species (Lambruschi *et al.*, 2015). This feature likely arises from incomplete decomposition of gelatine used as the biotemplate, since the applied calcination temperature (250°C) may not be sufficient to fully remove organic residues. The persistence of this band highlights the influence of gelatine on the final composition and suggests that traces of carbonaceous groups remain embedded in the photocatalyst structure (Mikhailov, 2023).

Overall, the FTIR analysis confirms the successful synthesis of Ti-V-Mn-based photocatalysts, where characteristic M-O, O-H, and H-O-H bands dominate the spectra. The presence of hydroxyl groups and adsorbed water indicates potential active sites for photocatalytic reactions, while minor carbonyl features suggest residual template contributions that may influence surface chemistry.

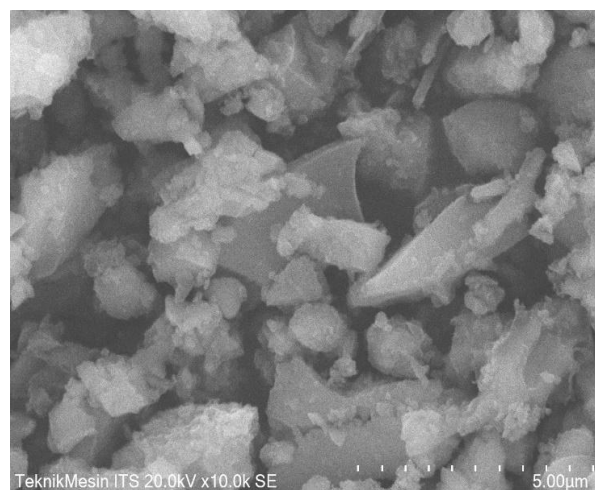
3.2. Morphological and elemental Characteristics

The FTIR analysis confirmed the presence of characteristic M-O vibrations associated with Ti-O, V-O, and Mn-O bonding, as well as surface hydroxyl groups that are crucial for photocatalytic reactions. These functional groups are closely related to the surface structure of the material, which was further investigated by SEM analysis. As shown in Fig. 2, the G-Ti-V-Mn photocatalyst exhibits an irregular and heterogeneous morphology, reflecting the influence of the templating and calcination processes. The irregular crystalline domains observed in the SEM micrograph are consistent with the heterogeneous distribution of organic residues detected by FTIR, particularly the carbonyl-related bands attributed to incomplete decomposition of gelatine during calcination (Sharma *et al.*, 2025).

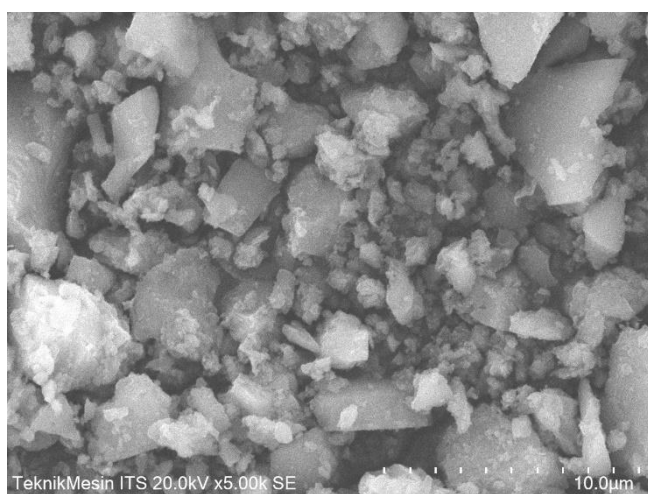
The heterogeneous morphology may also be attributed to non-uniform nucleation during synthesis, which results in particles of varying sizes and shapes (Justyna *et al.*, 2023). The presence of agglomerated structures suggests that, although mesoporous silica and gelatine templating guided the overall framework, partial collapse of pore channels or residual carbonaceous groups likely contributed to the irregular crystal



(a)



(b)



(c)

Fig. 2 Morphological imaging of the G-Ti-V-Mn as visualised by SEM imaging (5000x and 10.000x)

growth (Yan *et al.*, 2019). This structural heterogeneity supports the FTIR evidence of residual organic functionalities and adsorbed water, indicating that both inorganic oxide networks and organic remnants coexist in the final catalyst.

The particle size distribution analysis further confirms this observation, with the majority of particles falling within the range of 120–130 nm, as fitted by Gaussian modeling. The relatively narrow standard deviation indicates a moderately homogeneous nucleation process, although some heterogeneity remains due to incomplete gelatine decomposition as evidenced by FTIR. This good size control effect is greatly influenced by the presence of functional groups in gelatine which act as effective natural pore-directing agents, before being finally removed through calcination. Such nanoscale dimensions provide a relatively high surface-to-volume ratio, which, in combination with surface hydroxyl groups identified by FTIR, may enhance active site availability for photocatalytic degradation of methylene blue. Thus, the combined evidence from FTIR and SEM demonstrates that the G-Ti-V-Mn photocatalyst possesses both the functional groups and the morphological features necessary for effective photocatalysis, albeit with residual heterogeneity that reflects the role of gelatine as a natural biotemplate.

However, in addition to the small particle size variations, SEM micrographs also show the presence of a significant

agglomeration structure in the samples. This agglomeration phenomenon can be explained by two main factors: surface thermodynamics and the residual template effect.

Thermodynamically, nanoparticles have a very high surface energy due to the large fraction of atoms located on the surface. To minimize surface free energy and achieve a more stable condition, these nanoparticles tend to attract each other and group together to form larger aggregates. On the other hand, the formation of these irregular particle clusters is also triggered by the low-temperature calcination strategy (250 °C). Although this low temperature is crucial for maintaining the mesoporous framework and preventing excessive crystal growth, it is proven not high enough to completely decompose all organic components of gelatine. The presence of bound carbon residues (such as carbonyl groups detected in FTIR analysis) acts as carbonaceous bridges between particles, thus locking the nanoparticles into a tight and irregular agglomerate. The SEM-EDX results (Fig. 3-4) and elemental compositions summarized in Table 1 further confirm the successful synthesis and incorporation of the targeted metal components, as evidenced by the simultaneous presence of Ti, V, and Mn in G-Ti-V-Mn, although the EDX-derived ratios deviate from the initial precursor ratio of 2:1:1.

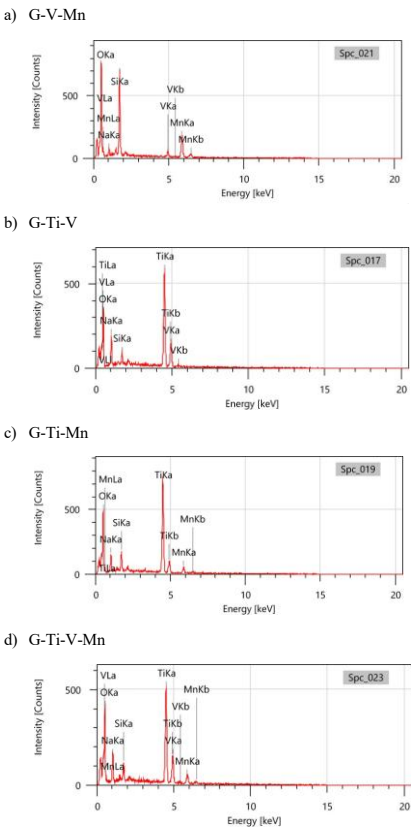


Fig 3. EDX mapping all sample

Table 1. Elemental Composition (EDX) and Metal Ratios of Synthesized Samples

Sample	Ti (%)	V (%)	Mn (%)	O (%)	Na (%)	Si (%)	Metal Ratio (EDX)	Initial Metal Ratio
G-V-Mn	–	4.88	31.78	41.68	2.20	19.46	1 : 6.51	1 : 1
G-Ti-V	41.53	6.08	–	44.94	6.20	1.24	6.83 : 1	2 : 1
G-Ti-Mn	40.84	–	5.32	47.52	4.06	2.25	7.67 : 1	2 : 1
G-Ti-V-Mn	35.48	6.90	6.69	43.55	5.53	1.85	5.14 : 1.03 : 1	2 : 1 : 1

3.3. Textural Properties and Nitrogen Adsorption–Desorption Analysis

Figure 4 shows the nitrogen adsorption–desorption isotherms of the synthesized photocatalysts, which all conform to type IV isotherms according to the IUPAC classification. This pattern is characteristic of mesoporous materials with pore diameters in the range of 2–50 nm. A distinctive feature of type IV isotherms is the presence of a hysteresis loop, which reflects capillary condensation within mesopores. The observation of this behavior in all samples confirms that the templating approach, assisted by gelatine-modified mesoporous silica, successfully yielded materials with mesoporous frameworks. Understanding the isotherm classification is crucial for elucidating the interaction between adsorbates and the porous structure, as it provides insight into whether the material contains predominantly micropores, mesopores, or macropores and how these structural features influence adsorption and catalytic performance.

As summarized in Table 2, the BET surface area values vary considerably among the samples. The G–V–Mn photocatalyst exhibited the highest surface area of 106.67 m²/g,

followed by G–Ti–Mn (76.62 m²/g), G–Ti–V–Mn (35.30 m²/g), and G–Ti–V (8.41 m²/g). The relatively higher surface area of G–V–Mn and G–Ti–Mn suggests that binary systems containing Mn favor the development of larger accessible surfaces, possibly due to improved pore formation during template removal. In contrast, the ternary G–Ti–V–Mn sample displayed an intermediate surface area, lower than its binary counterparts but still substantially higher than G–Ti–V. Since BET surface area represents the total active sites available for adsorption and photocatalytic reactions, these results indicate that the variations in surface area may directly influence photocatalytic efficiency, with G–V–Mn expected to provide the greatest number of active sites for pollutant degradation.

The average pore diameters of the samples ranged from 3.74 to 4.94 nm, confirming their classification as mesoporous according to the IUPAC definition (2–50 nm). These pore sizes are favorable for photocatalytic applications, as they allow efficient diffusion of methylene blue molecules into the porous network while simultaneously providing a high density of accessible active sites. The combination of mesoporous structure and suitable pore diameters enhances molecular transport, thereby facilitating improved contact between the

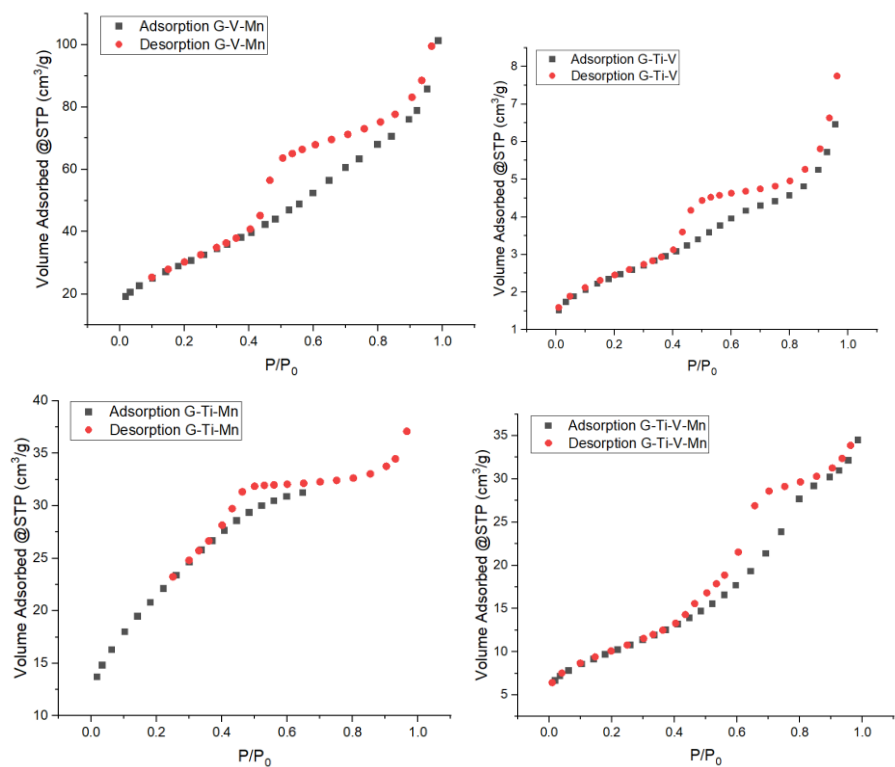


Fig. 4 The N2 adsorption-desorption isotherm of all sample

Table 2
Textural characteristics of the sample

Sample	BET surface area, S_{BET} (m ² /g)	Total pore volume , V_{tot} (cm ³ /g)	Average pore size, D_p (nm)
G-V-Mn	106.67	0.1570	4.09552
G-Ti-V	8.41	0.0124	4.11578
G-Ti-Mn	76.62	0.0591	3.74192
G-Ti-V-Mn	35.30	0.0535	4.93691

photocatalyst surface and dye molecules. Together, the isotherm profiles, surface area data, and pore size distribution provide compelling evidence that the synthesis strategy successfully produced mesoporous Ti–V–Mn-based photocatalysts with tunable textural properties, which are expected to play a decisive role in determining their photocatalytic performance.

The continuous capillary condensation phenomenon without any sharp desorption stagnation confirms that the hard-template method using gelatine-modified mesoporous silica successfully replicates an interconnected pore network. This spatial connectivity between pores is crucial to prevent the formation of dead-end pores, which are often a limiting factor in conventional bulk metal oxide materials. The presence of an interconnected pore network ensures that most of the measured specific surface areas—especially in the G–V–Mn (106.67 m²/g) and G–Ti–Mn (76.62 m²/g) samples—are fully accessible active sites for external molecules, rather than isolated empty spaces within the crystal interior.

This superior pore connectivity directly affects the efficiency of reactant diffusion pathways across the catalyst mesoporous channels. Methylene blue (MB) molecules are known as cationic dyes with a relatively large planar geometry (molecular dimensions of approximately 1.43 nm × 0.61 nm).

With an average pore diameter range of 3.74–4.94 nm, the resulting mesoporous channels provide ample mobility, thus minimizing steric hindrance and the risk of pore clogging during the adsorption process. Within this open mesoporous architecture, the tortuosity of the pore channels is significantly suppressed, which in turn changes the intraparticle transport regime from highly restricted Knudsen diffusion to bulk-like diffusion of liquid-phase molecules. This short diffusion pathway facilitates rapid penetration of methylene blue molecules into the innermost active centers of the catalyst, while accelerating the desorption of degradation products into the bulk solution.

The synergy between pore connectivity and efficient diffusion pathways plays a crucial role in dictating the kinetics of the photocatalytic reaction of methylene blue degradation. Based on the Langmuir-Hinshelwood kinetic model, the rate constant of a pseudo-first-order reaction in a heterogeneous reaction is highly dependent on the rate of mass transfer of the reactants to the active site. The mesoporosity characteristics developed in this study not only provide a large contact area for the adsorption of the initial MB molecules, but also ensure a continuous supply of reactants to the catalyst surface through

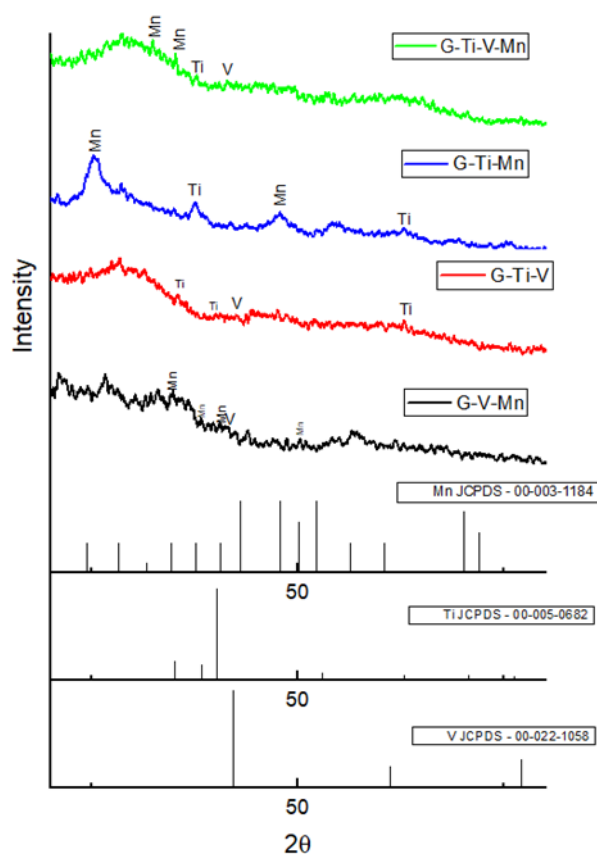


Fig. 5 XRD patterns of all sample

accelerated diffusion, thus preventing local concentration polarization phenomena that can decrease the reaction kinetics.

In addition, the nanometer-scale thickness of the mesoporous walls acts as a very short migration path for photogenerated charge carriers (electrons and electron holes) to move from within the crystal phase to the pore surface. This very short charge travel distance radically suppresses the probability of exciton recombination (electron-hole recombination), ensuring that most of the active charges can interact with the adsorbed species to form hydroxyl radicals. Therefore, the highest degradation performance achieved by the G-V-Mn system (67.83%) is linearly correlated with the optimization of its mesoporosity which is able to accelerate the mass transport kinetics of reactants and interfacial charge transfer kinetics simultaneously.

3.4. Crystal Structure and Phase Composition

Diffraction data can be used to calculate the crystal size of mesoporous silica nanoparticles using the Debye Scherrer formula as in the equation below.

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

The crystallinity of a sample can also be calculated using X-Ray Diffraction characterization data using the following formula.

$$\text{Crystallinity} = \frac{\text{crystalline peak area}}{\text{crystalline and amorphous peak areas}} \times 100\%$$

Figure 5 presents the XRD diffraction patterns of the synthesized photocatalysts. For the G-V-Mn sample, the main diffraction peaks were observed at $2\theta = 34.74^\circ$, 37.60° , 40.61° , 42.17° , and 50.08° , which match well with the reference patterns of vanadium (JCPDS No. 00-022-1058) and manganese (JCPDS No. 00-003-1184) (Al *et al.*, 2021)(Falsafi *et al.*, 2020). The strong reflections indicate that the crystalline structure of this sample is predominantly governed by the manganese phase. In the case of G-Ti-V, the characteristic peaks appeared at $2\theta = 35.07^\circ$, 40.15° , 42.17° , and 62.97° , consistent with titanium (JCPDS No. 00-005-0682) and vanadium phases, confirming that titanium is the dominant crystalline species (Khodaei *et al.*, 2017). For G-Ti-Mn, the major peaks detected at $2\theta = 24.44^\circ$, 35.07° , 47.84° , and 62.97° correspond to both titanium and manganese phases, suggesting that these two metals collectively contribute to the crystalline framework. Finally, the G-Ti-V-Mn ternary system exhibited diffraction peaks at $2\theta = 31.07^\circ$, 34.74° , 35.07° , and 42.17° , aligning with reference patterns for Ti, V, and Mn, although the manganese phase was found to be dominant.

The crystallite sizes and degrees of crystallinity calculated using the Debye-Scherrer equation are summarized in Table 3. Among the samples, G-Ti-Mn exhibited the smallest crystallite size (4.83 nm) but the highest crystallinity (19.62%). In contrast, G-V-Mn displayed the largest crystallite size (19.80 nm) yet with very low crystallinity (0.85%), suggesting that while larger crystallites were formed, their arrangement was relatively disordered. The ternary G-Ti-V-Mn system exhibited intermediate values with a crystallite size of 9.87 nm and a crystallinity degree of 8.14%, indicating that the coexistence of three metals promoted a mixed phase with moderate ordering.

Generally, higher crystallinity values reflect a more ordered atomic arrangement, which often translates into enhanced mechanical stability and improved thermal resistance. However, in photocatalysis, excessively high crystallinity may reduce the number of structural defects, which are often beneficial as active sites for charge trapping and reactive radical formation. Thus, the relatively moderate crystallinity observed in the ternary G-Ti-V-Mn catalyst may be advantageous, providing a balance between structural stability and defect-induced photocatalytic activity. These findings suggest that the interplay between crystallite size and crystallinity degree is a key factor in determining the photocatalytic performance of the synthesized Ti-V-Mn-based materials.

The phase composition characteristics of this multimetallic system are strongly influenced by the low-temperature calcination strategy (250°C) applied during the template removal process. Thermodynamically, a temperature of 250°C is below the activation energy threshold required for long-range crystalline phase transformation for some single transition oxides, such as the pure anatase TiO_2 phase, which generally requires temperatures above $350\text{--}400^\circ\text{C}$. Due to this thermal limitation, the phase composition of the G-Ti-V-Mn ternary material is not a uniform single crystalline phase, but rather a hybrid system in which nanocrystalline domains are dispersed within an amorphous-rich matrix. The dominance of manganese phase reflections in the ternary diffraction pattern indicates that manganese species have a lower nucleation free energy under these synthesis conditions, thus forming short-range order more quickly compared to titanium and vanadium species, which tend to maintain their amorphous structure at these temperatures.

Viewed from a crystallographic perspective, the close ionic radius sizes between Ti^{4+} (0.0605 nm), V^{5+} (0.054 nm), and various manganese oxidation states such as Mn^{4+} (0.053 nm) or Mn^{3+} (0.0645 nm) allow for isomorphous atomic substitution interactions or interstitial insertions in the crystal lattice. These

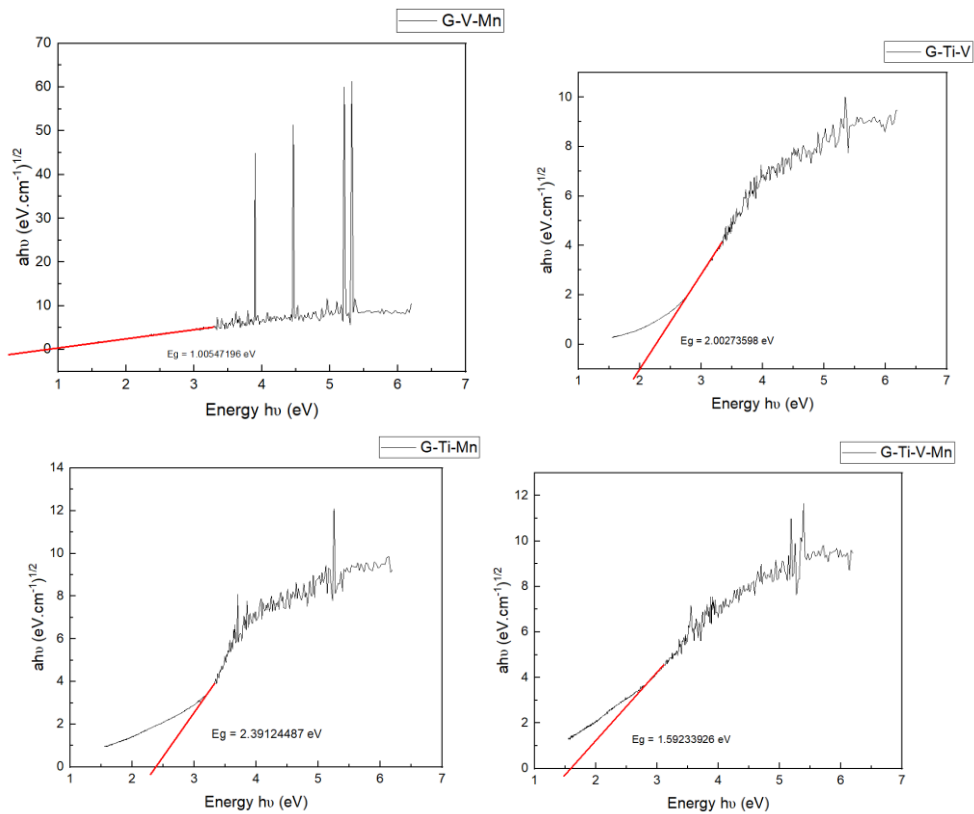


Fig. 6 Band gap of all sample by UV-DRS

Table 3
Crystallite size and degree of crystallinity of the synthesized photocatalysts

Sample	Crystallite size, D (nm)	Degree of crystallinity (%)
G-V-Mn	19.80	0.85
G-Ti-V	13.75	0.25
G-Ti-Mn	4.83	19.62
G-Ti-V-Mn	9.87	8.14

intermetallic interactions induce significant lattice strains due to the crystallographic mismatch. These internal mechanical stresses act as a barrier to crystal growth kinetics along the principal lattice planes, which directly explains why the crystallite sizes of the samples are limited to a very narrow nanometer range (4.83–19.80 nm). The minor shift in the angular position 2θ and the peak broadening phenomenon observed in the diffraction pattern of the multimetal sample compared to its pure phase are physical manifestations of the lattice distortion, which confirms the disruption of atomic periodicity due to the penetration of foreign atoms into the host unit cell.

Regarding the possibility of mixed-metal oxide formation, the low calcination temperature of 250 °C thermodynamically limits the formation of stoichiometrically ordered binary or ternary solid solutions (such as pure TiMnO_3 or TiVO_4 crystalline phases) due to limited interatomic thermal diffusion. However, at the grain boundaries between the amorphous and semicrystalline phases, intensive chemical interactions occur, leading to the formation of disordered mixed-metal oxide networks via heteronuclear oxygen bridges, such as Ti-O-Mn and Ti-O-V bonds. This primitive, non-

stoichiometric mixed-oxide structure is highly advantageous for photocatalytic applications; the random hybrid phase creates intimate electronic contacts at the atomic level that facilitate the formation of an interfacial internal electric field. This local electric field radically accelerates the spatial separation of photogenerated charges (electrons and electron-holes), thus minimizing energy losses due to premature exciton recombination.

3.5. Optical Properties and Band Gap Energy

As illustrated in Fig. 6, the calculated band gap energies using the Tauc plot method reveal that the synthesized photocatalysts exhibit distinct variations depending on the metal composition. The G–V–Mn sample demonstrated the lowest band gap of approximately 1.00 eV, while G–Ti–V and G–Ti–Mn displayed higher band gap energies of 2.20 eV and 2.39 eV, respectively. Interestingly, the ternary G–Ti–V–Mn composite exhibited a band gap of 1.59 eV, which lies between the values of the binary systems. These results suggest that the incorporation of multiple transition metals introduces electronic

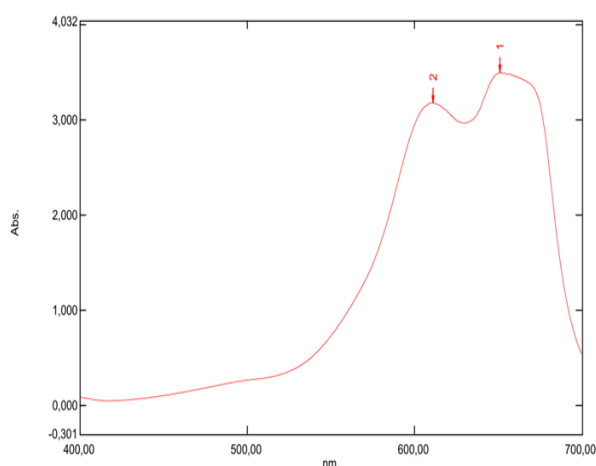


Fig. 7 UV-Vis spectra of treated MB solution by photocatalytic degradation

interactions that significantly modify the band structure, thereby enhancing visible-light absorption.

The very low band gap value (~ 1.00 eV) in the G-V-Mn binary sample is due to the dominance of manganese oxide phase which has an intrinsically narrow band gap (1.0–2.0 eV), without the influence of the wide band gap of TiO_2 . The incorporation of electrons from the V and Mn orbitals triggers electronic crowding that introduces intermediate energy states (intermediate energy states) within the original forbidden band. Another important factor is the very low crystallinity of the sample (0.85%), where the dominance of the amorphous phase results in abundant lattice defects and oxygen vacancies (oxygen vacancies). In the electronic structure, these defects create localized energy levels that induce the band tailing phenomenon. This phenomenon shifts the optical absorption edge towards lower energies, resulting in a very narrow band gap value when plotted using the Tauc plot method.

The electronic interactions between Ti, V, and Mn species in G-Ti-V-Mn ternary photocatalysts are driven by the proximity of ionic radii (Ti^{4+} , V^{5+} , and $\text{Mn}^{4+}/\text{Mn}^{3+}$), which induce isomorphic substitution and interstitial insertion into the crystal lattice. These phenomena induce lattice distortion and internal mechanical stress that contribute to the limitation of the crystallite size in the nanometer scale. From the band structure aspect, the multimetallic coupling modifies the density of states (DOS) by introducing intermediate energy states or impurity bands within the original forbidden band gap. The presence of these sublevels reduces the minimum transition energy, thus narrowing the band gap drastically to 1.59 eV. In addition, the dominance of amorphous phase due to low-temperature calcination increases the density of localized surface defect states in the DOS profile.

This DOS modification significantly alters the charge transfer pathway through a multi-stage excitation mechanism under visible light irradiation, where the V/Mn sub-band energy acts as an electronic bridge for electrons from the valence band (VB) to the conduction band (CB). Furthermore, the high density of structural defects serves as temporal charge trapping centers that effectively suppress the recombination rate of photogenerated charge carriers. The presence of complementary redox pairs ($\text{V}^{5+}/\text{V}^{4+}$ and $\text{Mn}^{4+}/\text{Mn}^{3+}$) on the catalyst surface simultaneously enhances electron mobility and facilitates multi-stage charge transfer. Electrons in the CB reduce adsorbed oxygen to superoxide radicals, while holes in the VB oxidize water and surface hydroxyl groups to hydroxyl radicals. This synergy of charge transfer pathways and the

formation of reactive species efficiently accelerates the degradation of methylene blue-conjugated structures.

Previous studies have reported that the intrinsic band gap values of individual oxides are typically around 3.0–3.2 eV for TiO_2 , 2.18–2.8 eV for V_2O_5 , and 1.0–2.0 eV for MnO_2 . The lower band gap values observed in the synthesized composites compared to pure TiO_2 indicate a synergistic effect of V and Mn incorporation, which introduces intermediate energy states within the forbidden band. These localized states facilitate electronic transitions under visible-light irradiation, thereby extending the photocatalytic response beyond the ultraviolet region. Moreover, the observed variations also reflect the influence of crystallite size, electronic coupling among the metals, and the presence of structural defects that were previously evidenced by XRD and FTIR analyses.

Notably, the G-Ti-V-Mn photocatalyst exhibited a moderate band gap (1.59 eV) alongside an intermediate crystallinity of 8.14%. This relatively amorphous character suggests the presence of numerous disordered sites, which, although potentially reducing long-range structural order, may increase the density of surface defects that act as charge trapping centers. Such features are advantageous for photocatalysis because they can prolong the lifetime of photogenerated electron-hole pairs, thereby enhancing the formation of reactive oxygen species. Consequently, the reduction in band gap energy observed for the ternary system is not only a direct result of compositional tuning but also a reflection of its structural and electronic disorder, both of which play a critical role in driving photocatalytic performance.

3.6. Photocatalytic Degradation Performance

The photocatalytic degradation tests were conducted to evaluate the efficiency of the synthesized Ti-V-Mn-based photocatalysts toward methylene blue (MB) removal. Prior to illumination, the suspensions containing MB and the photocatalyst were stirred in the dark for 5 minutes to establish adsorption-desorption equilibrium between the dye molecules and the catalyst surface. This step ensures that subsequent decreases in absorbance can be attributed primarily to photocatalytic activity rather than physical adsorption alone, in agreement with previously reported methodologies (Yuniar *et al.*, 2022).

Upon irradiation with UV light, photocatalytic degradation was monitored at various time intervals (5, 10, 15, 20, 25, 30, and 120 minutes). The UV-Vis spectra (Fig. 7) confirmed that methylene blue exhibits a maximum absorption peak at 664 nm, which corresponds to the $n \rightarrow \pi^*$ transition of the aromatic C=N bonds within the dye structure. This observation is consistent with earlier reports indicating that MB typically absorbs in the 660–670 nm range depending on the solvent and experimental conditions. The identification of this characteristic λ_{max} value was critical for quantifying the concentration of residual dye during photocatalytic testing.

The progressive decline in absorbance at 664 nm during the irradiation process reflects the photodegradation of MB molecules facilitated by the Ti-V-Mn photocatalysts. The reduction of this band intensity indicates the disruption of chromophoric groups and cleavage of the conjugated aromatic structure, ultimately leading to mineralization of the dye. These findings confirm that the ternary metal combination is effective in harnessing photo-induced charge carriers to generate reactive oxygen species (ROS), which play a pivotal role in the oxidative breakdown of MB. The consistency between λ_{max} values and literature benchmarks further validates the accuracy of the experimental approach employed in this study.

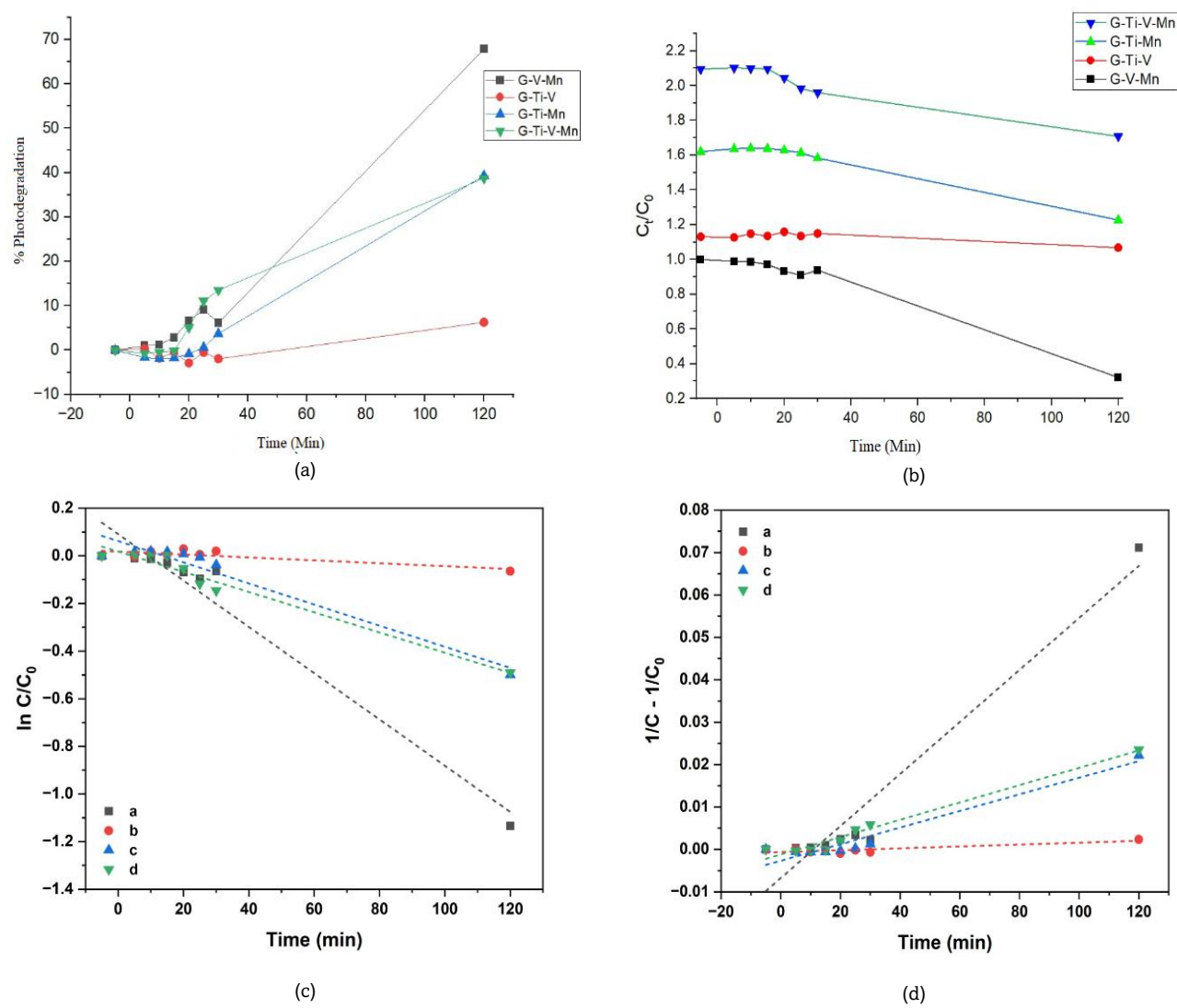


Fig. 8 Photocatalytic degradation of methylene blue by G-V-Mn, G-Ti-V, G-Ti-Mn, and G-Ti-V-Mn photocatalysts: (a) degradation percentage, (b) concentration decay profile (C/C_0), (c) PFO kinetic model, and (d) PSO kinetic model under visible-light irradiation.

Table 4
Photocatalytic degradation efficiency of methylene blue by T-V-Mn-based photocatalysts

Sample	Degradation efficiency (%)
G-V-Mn	67.83
G-Ti-V	6.27
G-Ti-Mn	39.32
G-Ti-V-Mn	38.73

As shown in Fig. 8, the photocatalytic degradation profiles of methylene blue (MB) exhibited fluctuations during the initial irradiation stages, particularly between 5 and 25 minutes. This behavior can be attributed to the adsorption-desorption dynamics of MB molecules on the catalyst surface, which had already been initiated during the preliminary 5-minute dark adsorption step. The establishment of adsorption equilibrium ensures that the subsequent decline in MB concentration is primarily due to photocatalytic activity. The observed fluctuations are consistent with the presence of amorphous phases identified by XRD, especially in G-Ti-V-Mn (crystallinity 8.14%), where the disordered structure provides abundant adsorption sites but can also promote desorption events, thereby causing non-linear degradation trends.

From 30 to 120 minutes of irradiation, all photocatalysts displayed a continuous increase in degradation efficiency, corresponding to the progressive fading of MB solution color and enhanced light penetration to the catalyst surface. The FTIR spectra confirmed the presence of hydroxyl groups and adsorbed water, which act as active sites for hydroxyl radical generation. SEM images revealed irregular morphologies with nanoscale particle sizes, further supporting the existence of heterogeneous active surfaces. Meanwhile, BET analysis demonstrated that the G-V-Mn photocatalyst possessed the highest surface area ($106.67 \text{ m}^2/\text{g}$), significantly larger than G-Ti-Mn ($76.62 \text{ m}^2/\text{g}$), G-Ti-V-Mn ($35.30 \text{ m}^2/\text{g}$), and G-Ti-V ($8.41 \text{ m}^2/\text{g}$). This correlation is directly reflected in the degradation efficiency trend ($\text{G-V-Mn} > \text{G-Ti-Mn} > \text{G-Ti-V-Mn} > \text{G-Ti-V}$), confirming that surface area plays a critical role

Table 5
Performance Comparison of Ti-Based Photocatalysts

Photocatalyst	Catalyst Dose (g/L)	Irradiation Conditions	Degradation Time (min)	Degradation Efficiency (%)	Reference
0.05% Mn-TiO ₂	0.10	Halogen Lamp	35	86	(Latif <i>et al.</i> , 2022)
V-TiO ₂ (Film Tipis)	0.01 (estimasi)	UV Lamp	120	~80	(W. Chen <i>et al.</i> , 2017)
Cu-C/TiO ₂	1.00	Visible Light	120	100	(Kavil <i>et al.</i> , 2020)
V,Co-TiO ₂	1.50	Xenon Lamp	60	92.12	(V & Tio, 2018)
TiO ₂ P25	1.50	Xenon Lamp	60	56.55	(V & Tio, 2018)
G-Ti-V-Mn	0,25	Xenon Lamp	120	38,73%	This Study
G-V-Mn	0,25	Xenon Lamp	120	67,83%	This Study

in determining photocatalytic activity by providing abundant adsorption and reaction sites.

Interestingly, the photocatalytic performance does not strictly follow the band gap trend obtained from UV-Vis DRS. Although G-Ti-V-Mn exhibited a relatively low band gap (1.59 eV), its degradation efficiency (38.73%) was lower than G-V-Mn (67.83%), which had a slightly higher band gap (1.00 eV) but a much larger surface area and higher density of accessible active sites. This finding highlights that band gap narrowing alone is insufficient to guarantee superior photocatalytic performance; rather, it must be accompanied by optimized surface properties and appropriate crystallinity. Collectively, the integration of XRD, FTIR, SEM, BET, and UV-DRS results confirms that high photocatalytic efficiency arises from a synergistic combination of moderate crystallinity, the presence of surface hydroxyl groups, nanoscale morphology, and especially high surface area, which together enhance light absorption, charge separation, and reactive oxygen species (ROS) formation.

To provide a deeper understanding of the effectiveness of the developed Ti-V-Mn-based catalyst system, the photocatalytic performance of G-V-Mn and G-Ti-V-Mn samples was compared with various Ti-based photocatalysts previously reported in the literature for the degradation of methylene blue (MB). A comprehensive comparison including catalyst dosage, light source conditions, contact time, and degradation efficiency is summarized in Table 5.

3.7 Kinetic Analysis of Photocatalytic Degradation

To further evaluate the photocatalytic performance of the Ti-V-Mn-based catalysts, the degradation kinetics of methylene blue (MB) were analyzed using the pseudo-first-order (PFO) model, expressed as $\ln(C_0 + C_t) = kt$ where C_0 is the initial concentration, (C_t) is the concentration at irradiation time t , and k is the apparent rate constant (min^{-1}). The linear fitting of $\ln(C_0 + C_t)$ versus time (Fig. 8b) showed good agreement with the PFO model for all samples, indicating that the rate of degradation is primarily governed by the availability of active sites and photon absorption under UV illumination. The calculated kinetic parameters are summarized in Table 6. The G-V-Mn photocatalyst exhibited the highest rate constant ($k=0.0123 \text{ min}^{-1}$), consistent with its highest surface area ($106.67 \text{ m}^2/\text{g}$) and strongest degradation efficiency (67.83%). In comparison, G-Ti-Mn and G-Ti-V-Mn showed moderate

values of $k=0.0078 \text{ min}^{-1}$ $k = 0.0078 \text{ min}^{-1}$ and 0.0069 min^{-1} respectively, reflecting their intermediate surface areas and crystallinity. Meanwhile, G-Ti-V presented the lowest rate constant ($k=0.0015 \text{ min}^{-1}$, which is in line with its poor degradation efficiency (6.27%) and limited surface area ($8.41 \text{ m}^2/\text{g}$). These findings confirm that photocatalytic activity is not solely dictated by band gap narrowing, as suggested by UV-Vis DRS, but is instead controlled by a synergy of structural, morphological, and electronic factors. Specifically, high surface area (BET), the presence of hydroxyl groups (FTIR), moderate crystallinity (XRD), and nanoscale particle dimensions (SEM) collectively enhance the adsorption of dye molecules and the generation of reactive oxygen species, thereby accelerating degradation kinetics. The kinetic analysis thus provides a quantitative validation of the characterization-performance relationship established in this study.

In addition to the pseudo-first-order (PFO) model, the photocatalytic degradation kinetics of methylene blue (MB) were also analyzed using the pseudo-second-order (PSO) model, which is described by the following equation: $t/q_t = (1/k^2 q_e^2) + (t/q_e)$ where q_t (mg g^{-1}) is the adsorption capacity at time t , q_e (mg g^{-1}) is the equilibrium adsorption capacity, and k^2 ($\text{g mg}^{-1} \text{ min}^{-1}$) is the PSO rate constant. While the PFO model assumes that the degradation rate is proportional to the concentration of MB in solution, the PSO model accounts for chemisorption processes and surface interactions between MB molecules and the photocatalyst active sites.

The fitting results (Table 7) demonstrate that the experimental data are generally better described by the PFO model, as evidenced by higher R^2 values (>0.97). However, the PSO model provides additional insight into the role of surface chemistry. For instance, the G-V-Mn photocatalyst exhibited the highest equilibrium adsorption capacity ($q_e = 171.2 \text{ mg g}^{-1}$) and the largest PSO rate constant ($k^2=1.42 \times 10^{-3} \text{ g mg}^{-1} \text{ min}^{-1}$), confirming that its superior photocatalytic activity arises from the combined effects of high surface area and efficient chemisorption. In contrast, G-Ti-V showed the lowest values for both q_e and k^2 , consistent with its poor photocatalytic performance.

These results underline that photocatalytic efficiency cannot be solely attributed to electronic properties such as band gap narrowing. Instead, a balance between structural order (XRD), surface functional groups (FTIR), morphology (SEM), surface area and porosity (BET), and light-harvesting capacity (UV-DRS) is essential to achieving optimal photocatalytic activity. The dual kinetic modeling (PFO and PSO) validates the conclusion that surface adsorption and active site availability play equally critical roles as charge carrier dynamics in determining degradation efficiency.

The comprehensive characterization of Ti-V-Mn-based photocatalysts reveals that their photocatalytic performance arises from a synergistic interplay of structural, morphological, electronic, and surface properties. FTIR analysis confirmed the presence of M-O vibrations (Ti-O, V-O, Mn-O) and abundant

Table 6
Pseudo-first-order kinetic parameters for MB degradation

Sample	K (min ⁻¹)	R ²
G-V-Mn	0.0123	0.985
G-Ti-Mn	0.0078	0.978
G-Ti-V-Mn	0.0069	0.972
G-Ti-V	0.0015	0.961

Table 7
Pseudo-second-order kinetic parameters for MB degradation

Sample	q_e (mg g ⁻¹)	k^2 (g mg ⁻¹ min ⁻¹)	R^2
G-V-Mn	171.2	1.42×10^{-3}	0.972
G-Ti-Mn	128.4	9.65×10^{-4}	0.961
G-Ti-V-Mn	117.6	8.81×10^{-4}	0.956
G-Ti-V	64.3	5.27×10^{-4}	0.947

surface hydroxyl groups, which provide active sites for hydroxyl radical ($\bullet$ OH) generation during photodegradation. XRD results indicated low crystallinity for most samples, with G-Ti-Mn exhibiting the highest degree of crystallinity (19.62%). The amorphous-rich phases (e.g., G-Ti-V-Mn) introduce structural disorder and defect sites that facilitate charge trapping, thereby suppressing electron-hole recombination.

SEM imaging revealed irregular morphologies with heterogeneous nanoscale particle distributions, consistent with the observed adsorption-desorption fluctuations during early degradation stages. BET analysis highlighted that G-V-Mn possessed the highest surface area (106.67 m² g⁻¹), significantly exceeding the ternary G-Ti-V-Mn (35.30 m² g⁻¹) and G-Ti-V (8.41 m² g⁻¹). This high surface area directly correlated with its superior degradation efficiency (67.83%), underscoring the pivotal role of surface-driven adsorption and reaction kinetics. UV-Vis DRS analysis demonstrated band gap narrowing in all multimetal systems compared to pure TiO₂, with G-Ti-V-Mn (1.59 eV) and G-V-Mn (1.00 eV) effectively extending light absorption into the visible range. However, photocatalytic activity was not dictated by band gap alone, as G-Ti-V-Mn, despite its narrowed band gap, showed lower efficiency than G-V-Mn due to its reduced surface area.

Kinetic modeling further reinforced these observations. The pseudo-first-order (PFO) model provided the best fit ($R^2 > 0.97$), confirming that the reaction rate is primarily governed by active site availability and photon absorption. Nevertheless, the pseudo-second-order (PSO) model revealed complementary insights into surface interactions, with G-V-Mn exhibiting the highest equilibrium adsorption capacity ($k^2=171.2$ mg g⁻¹) and rate constant ($k^2=1.42 \times 10^{-3}$ g mg⁻¹). These findings establish that while electronic properties (band gap) enable efficient light harvesting, adsorption capacity and surface area are decisive for sustaining high photocatalytic efficiency.

Overall, the integration of FTIR, XRD, SEM, BET, UV-DRS, and kinetic analyses demonstrates that the most efficient photocatalyst (G-V-Mn) benefits from a unique combination of high surface area, abundant hydroxyl functionalities, moderate band gap narrowing, and defect-rich structures. These features collectively promote efficient charge separation, enhanced ROS generation, and sustained photodegradation of methylene blue. This study highlights that the rational design of multimetallic photocatalysts requires a balanced optimization of band structure, crystallinity, and surface textural properties to maximize photocatalytic activity under practical conditions.

3.8. Thermal Stability and Decomposition Behavior by TGA

Thermogravimetric analysis (TGA) was performed on the Ti-V-Mn samples synthesized with and without gelatin to evaluate their thermal behaviour (Fig 9). The gelatin-assisted sample (G-Ti-V-Mn) exhibited a total weight loss of approximately 7.73%, comprising an initial mass loss below 450 °C (3.07%) and a second weight-loss stage between 600 and 900 °C (4.66%). These mass-loss events are attributed to the removal of physically adsorbed water, surface hydroxyl groups, and thermally unstable surface species associated with the porous structure generated during the gelatine-assisted synthesis process. In contrast, the Ti-V-Mn sample prepared without gelatin displayed only minor mass variation over the entire temperature range, indicating higher thermal stability of the inorganic framework. EDX analysis revealed no detectable carbon in the G-Ti-V-Mn sample, indicating that gelatine was effectively removed during calcination at 550 °C and that the observed weight loss was not associated with residual organic species (Fig 3, Table 1). The greater mass change observed for G-Ti-V-Mn is therefore attributed to differences in surface chemistry and pore structure resulting from gelatine-assisted templating. These findings suggest that gelatine can be employed as a sustainable pore-directing agent for mesoporous silica synthesis, reducing reliance on synthetic structure-directing agents while preserving the structural integrity and photocatalytic functionality of the Ti-V-Mn ternary system. The overall characterization results indicate that the enhanced photocatalytic performance is closely related to the combined effects of favorable surface textural properties, abundant accessible active sites, and improved charge-transfer characteristics imparted by the gelatine-assisted synthesis route.

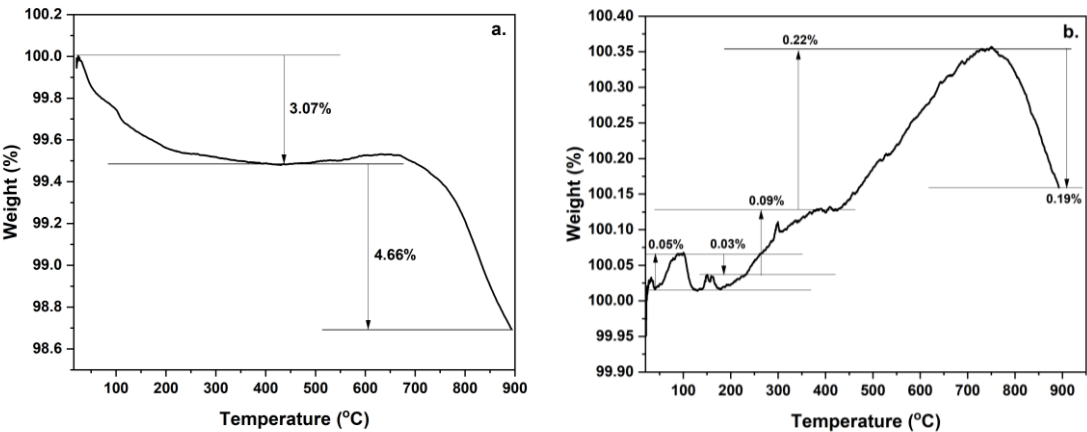


Fig 9. TGA curves of Ti-V-Mn photocatalysts prepared (a) with gelatine-assisted mesoporous silica (G-Ti-V-Mn) and (b) without gelatine template.

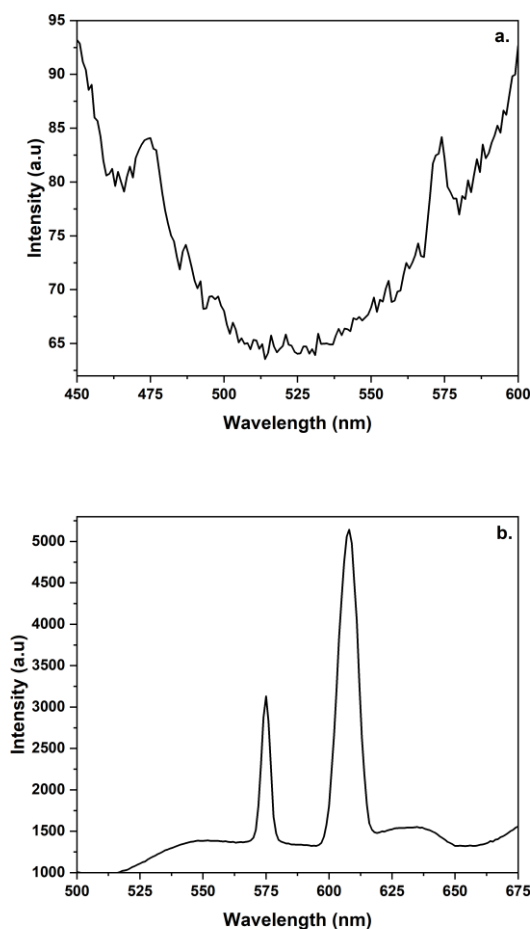


Figure 10. Photoluminescence spectra of Ti-V-Mn photocatalysts synthesized (a) with gelatine-assisted mesoporous silica (G-Ti-V-Mn) and (b) without gelatine template.

Photoluminescence (PL) analysis was conducted to evaluate the recombination behavior of photogenerated charge carriers in the Ti-V-Mn photocatalysts (Fig. 10). The gelatine-assisted sample (G-Ti-V-Mn) exhibited a broad emission band with significantly lower intensity compared to the non-templated Ti-V-Mn sample, which displayed two intense emission peaks at approximately 575 and 607 nm. Since PL intensity is directly related to the radiative recombination of electron-hole pairs, the suppressed emission observed for G-Ti-V-Mn indicates more efficient charge separation and a lower recombination rate. This behavior can be attributed to the formation of defect-rich structures and enhanced interfacial charge-transfer pathways promoted by gelatine-assisted mesoporous templating, which facilitate charge migration and prolong carrier lifetime. The PL results are in good agreement with the BET, UV-DRS, and photocatalytic degradation data, confirming that the superior activity of G-Ti-V-Mn originates from the synergistic effects of improved porosity, defect engineering, and enhanced visible-light-induced charge utilization.

Electrochemical impedance spectroscopy (EIS) was employed to evaluate the charge-transfer characteristics and interfacial resistance of the Ti-V-Mn photocatalysts (Fig. 11). As shown in Fig. 10a and 10b, both samples exhibit the typical frequency-dependent behavior of semiconductor photocatalysts, where the impedance decreases with increasing frequency, followed by a relatively stable region and a slight increase at higher frequencies. Notably, the gelatine-assisted

sample (G-Ti-V-Mn) displays lower impedance values throughout the measured frequency range compared to the non-templated Ti-V-Mn sample, indicating reduced charge-transfer resistance and enhanced electrical conductivity. The lower impedance response suggests that the mesoporous structure generated by gelatine-assisted synthesis facilitates more efficient electron transport across the catalyst surface and minimizes charge accumulation at grain boundaries. Furthermore, the improved conductivity is consistent with the PL results, which demonstrated suppressed electron-hole recombination, and with the UV-DRS analysis showing enhanced electronic interactions among Ti, V, and Mn species. The combination of reduced interfacial resistance and improved charge mobility promotes faster migration of photogenerated electrons and holes to active surface sites, thereby increasing the formation of reactive oxygen species (ROS) and enhancing photocatalytic degradation efficiency. These EIS results further confirm that gelatine-assisted mesoporous engineering effectively improves the charge-transfer dynamics of the Ti-V-Mn system, contributing significantly to its superior photocatalytic performance.

3.9. Charge Recombination and Transfer Properties

Chronoamperometry (CA) measurements were performed to evaluate the photoresponse stability and charge-separation efficiency of the Ti-V-Mn photocatalysts under repeated light on/off irradiation cycles (Fig. 12). Both samples exhibit rapid and reproducible photocurrent responses upon illumination, indicating good photoelectrochemical reversibility and stable

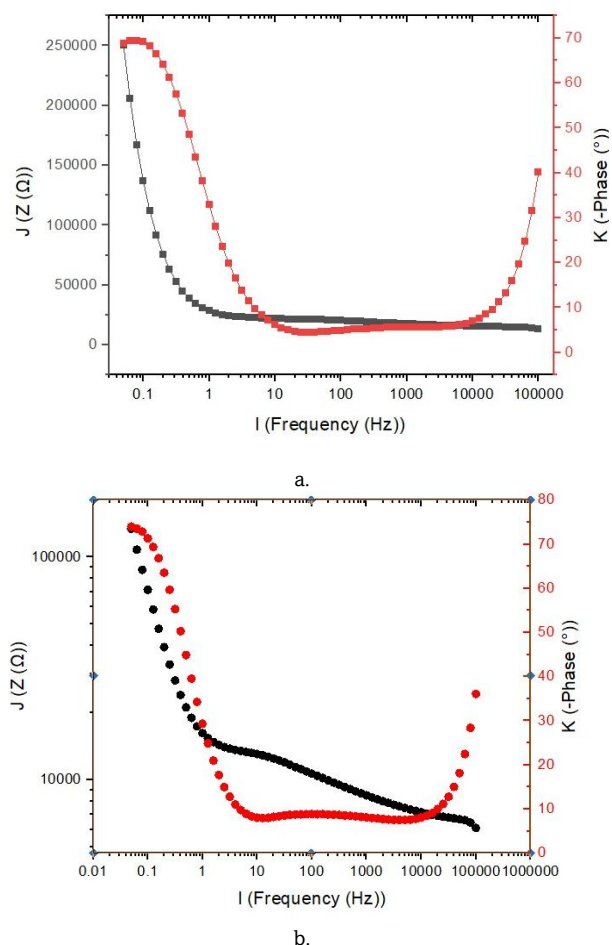


Fig 11. Electrochemical impedance spectroscopy (EIS) plots of Ti-V-Mn photocatalysts synthesized (a) with gelatin-assisted mesoporous silica (G-Ti-V-Mn) and (b) without gelatin template.

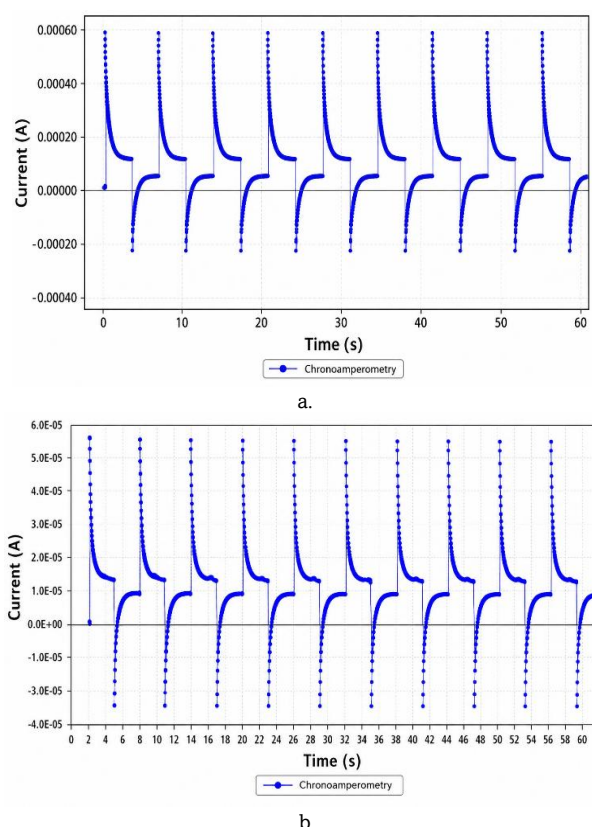


Fig 12. Chronoamperometric responses of Ti-V-Mn photocatalysts synthesized (a) with gelatine-assisted mesoporous silica (G-Ti-V-Mn) and (b) without gelatine template under repeated light on/off irradiation cycles.

charge-generation behavior. However, the gelatine-assisted sample (G-Ti-V-Mn) shows a noticeably higher photocurrent density than the non-templated Ti-V-Mn sample throughout all irradiation cycles. The sharp increase in photocurrent upon light exposure reflects the efficient generation of electron-hole pairs, while the rapid decay when the light is switched off indicates the recombination of charge carriers in the absence of photoexcitation. The enhanced photocurrent response of G-Ti-V-Mn suggests more effective separation and transport of photogenerated charges, which can be attributed to its higher surface area, improved mesoporous architecture, and defect-mediated charge-transfer pathways generated during gelatine-assisted synthesis. Furthermore, the nearly identical photocurrent intensity observed over successive cycles demonstrates excellent photoelectrochemical stability and resistance to photocorrosion. These findings are consistent with the PL and EIS results, confirming that gelatine-assisted mesoporous engineering significantly suppresses charge recombination, reduces charge-transfer resistance, and promotes efficient carrier migration, thereby contributing to the superior photocatalytic degradation performance of the G-Ti-V-Mn photocatalyst.

4. Conclusion

Ti-V-Mn-based photocatalysts were successfully synthesized using a gelatin-modified mesoporous silica hard-template and comprehensively characterized. FTIR confirmed the presence of M-O bonds and surface hydroxyl groups as active sites, while XRD revealed predominantly low crystallinity with varying crystallite sizes. SEM showed irregular nanoscale morphologies, and BET analysis highlighted that G-V-Mn

possessed the highest surface area ($106.67 \text{ m}^2 \text{ g}^{-1}$). UV-Vis DRS analysis demonstrated band gap narrowing, extending visible-light absorption across all multimetal systems. Photocatalytic tests against methylene blue showed that performance was not solely governed by band gap but strongly influenced by surface area and adsorption capacity. G-V-Mn achieved the highest degradation efficiency (67.83%), consistent with its superior surface area and adsorption properties, while G-Ti-V exhibited the lowest efficiency (6.27%). Kinetic modeling confirmed pseudo-first-order behavior with high correlation ($R^2 > 0.97$), while pseudo-second-order analysis emphasized the role of chemisorption, with G-V-Mn showing the highest equilibrium adsorption capacity. These results indicate that synergistic optimization of surface area, hydroxyl functionality, and structural disorder, in addition to band gap engineering, is essential for enhancing photocatalytic performance. Among the tested systems, G-V-Mn emerged as the most promising photocatalyst for methylene blue degradation.

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References

- Al, A. F., Afify, N. N., & Ibrahim, S. S. (2021). Structural morphology and nonlinear behavior of pure and co - doped - $\text{Zn}^{1-x}\text{Fe}^x\text{M}_y\text{O}$ varistors with ($\text{M}=\text{Cu}, \text{Ni}$). *Applied Physics A*. <https://doi.org/10.1007/s00339-021-04560-3>

- Ariapad, A., & Zanjanchi, M. A. (2011). Superlattices and Microstructures Effect of successive incorporation of tungstophosphoric acid into TiO₂ on the activity of photocatalysts for the degradation of methylene blue. *Superlattices and Microstructures*, 49(4), 422–432. <https://doi.org/10.1016/j.spmi.2010.12.012>
- Bekena, F., & Kuo, D. (2020). 10 nm sized visible light TiO₂ photocatalyst in the presence of MgO for degradation of methylene blue. *Materials Science in Semiconductor Processing*, 116, Article 105152. <https://doi.org/10.1016/j.mssp.2020.105152>
- Alhogbi, B. G., & Al Balawi, G. S. (2023). An Investigation of a Natural Biosorbent for Removing Methylene Blue Dye from Aqueous Solution. *Molecules*, 28(6), 2785. <https://doi.org/10.3390/molecules28062785>
- Chen, C., Jaihindh, D., Hu, S., & Fu, Y. (2017). Magnetic recyclable photocatalysts of Ni-Cu-Zn ferrite @ SiO₂ @ TiO₂ @ Ag and their photocatalytic activities. *Journal of Photochemistry and Photobiology A: Chemistry*, 334, 74–85. <https://doi.org/10.1016/j.jphotochem.2016.11.005>
- Chen, W., Koshy, P., Adler, L., & Sorrell, C. C. (2017). Photocatalytic activity of V-doped TiO₂ thin films for the degradation of methylene blue and rhodamine B dye solutions. *Journal of the Australian Ceramic Society*, 569–576. <https://doi.org/10.1007/s41779-017-0068-0>
- Deng, X., & Chen, K. (2017). Protocol for the Nanocasting Method: Preparation of Ordered Mesoporous Metal Oxides. *Chem. Mater.* (2017) 29 (1): 40–52. <https://doi.org/10.1021/acs.chemmater.6b02645>
- Fajarwati, F. I., Sugiharto, E., & Siswanta, D. (2016). Film of chitosan-carboxymethyl cellulose polyelectrolyte complex as methylene blue adsorbent. *Eksakta: Jurnal Ilmu-Ilmu MIPA*, 16(1).
- Falsafi, S. R., Rostamabadi, H., & Jafari, S. M. (2020). X-ray diffraction (XRD) of nanoencapsulated food ingredients. *Characterization of Nanoencapsulated Food Ingredients*. <https://doi.org/10.1016/b978-0-12-815667-4.00009-2>
- Gaya, U. I., & Abdullah, A. H. (2008). Heterogeneous photocatalytic degradation of organic contaminants over titanium dioxide: A review of fundamentals, progress and problems. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*, 9(1), 1–12. <https://doi.org/10.1016/j.jphotochemrev.2007.12.003>
- Ghosh, R. K., Ray, D. P., Debnath, S., Tewari, A., & Das, I. (2019). Optimization of Process Parameters for Methylene Blue Removal by Jute Stick Using Response Surface Methodology. *Environmental Progress & Sustainable Energy*, 38(5), 13146. <https://doi.org/10.1002/ep.13146>
- Imran, M., Khalid, R., Najeeb, J., & Hussain, Z. (2021). Fundamentals and photocatalysis of methylene blue dye using various nanocatalytic assemblies- a critical review. *Journal of Cleaner Production*, 298, 126567. <https://doi.org/10.1016/j.jclepro.2021.126567>
- Jadhav, V., Dhanwate, Y., Raut, P., Shinde, S., Sawant, R., & Bhagare, A. (2025). Efficient photocatalytic methylene blue dye degradation from green - synthesized silver - doped iron oxide (Ag@Fe₂O₃) nanostructures. *Discover Nano*. <https://doi.org/10.1186/s11671-025-04242-6>
- Justyna, L., Kroczevska, M., Baluk, M., Sowik, J., & Zaleska-medynska, A. (2023). Morphology control through the synthesis of metal-organic frameworks. *Advances in Colloid and Interface Science*, 314. <https://doi.org/10.1016/j.cis.2023.102864>
- Kammakakam, I. (2021). Nanomaterials: a review of synthesis methods, properties, recent progress, and challenges *Materials Advances*. 2 (6), 1821–1871; <https://doi.org/10.1039/d0ma00807a>
- Kavil, Y. N., Shaban, Y. A., & Alelyani, S. S. (2020). The removal of methylene blue as a remedy of dye - based marine pollution : a photocatalytic perspective. *Research on Chemical Intermediates*, 46(1), 755–768. <https://doi.org/10.1007/s11664-019-03988-w>
- Khodaei, M., Valanezhad, A., Watanabe, I., & Youse, R. (2017). Surface and mechanical properties of modified porous titanium scaffold. *Surface & Coatings Technology*, 315, 61–66. <https://doi.org/10.1016/j.surfcoat.2017.02.032>
- Krishnan, A., Swarnalal, A., Das, D., Krishnan, M., Saji, V. S., & Shibli, S. M. A. (2024). A review on transition metal oxides based photocatalysts for degradation of synthetic organic pollutants. *Journal of Environmental Sciences*, 139, 389–417. <https://doi.org/10.1016/j.jes.2023.02.051>
- Lambruschi, E., Aliatis, I., Mantovani, L., Tribaudino, M., Bersani, D., Redhammer, G.J., and Lottici, P.P. (2015). Raman spectroscopy of CaM₂+Ge₂O₆ (M₂+ = Mg, Mn, Fe, Co, Ni, Zn) clinopyroxenes. *J. Raman Spectrosc.*, 46, 586–590. <https://doi.org/10.1002/jrs.4681>
- Latif, S., Tahir, K., Ullah, A., Abdulaziz, F., & Arooj, A. (2022). Green synthesis of Mn-doped TiO₂ nanoparticles and investigating the influence of dopant concentration on the photocatalytic activity. *Inorganic Chemistry Communications*, 146(September), 110091. <https://doi.org/10.1016/j.inoche.2022.110091>
- Litowczenko, J., Wieszczycka, K., Staszak, K., Woz, M. J., Maciejewska, B. M., & Jurga, S. (2021). The way for advanced applications of smart materials. *Surface functionalization*, 436. <https://doi.org/10.1016/j.ccr.2021.213846>
- Mikhailov, O. V. (2023). Gelatin Matrix as Functional Biomaterial for Immobilization of Nanoparticles of Metal-Containing Compounds. *Journal of Functional Biomaterials*, 14(2), 92. <https://doi.org/10.3390/jfb14020092>
- Nur, W., Habiddin, H., Ulfa, M., Trisunaryanti, W., Bahruji, H., Holilah, H., Awinatul, A., Amalia, N., Abdul, A., Santoso, E., & Prasetyoko, D. (2023). South African Journal of Chemical Engineering Dual template using P123-gelatin for synthesized large mesoporous silica for enhanced adsorption of dyes. *South African Journal of Chemical Engineering*, 43, 312–326. <https://doi.org/10.1016/j.sajce.2022.11.011>
- Ojha, S., & Roy, S. (2025). Unlocking the potential of metal vanadates for energy , environment and biomedicine: Pioneering developments and perspectives. *Coordination Chemistry Reviews*, 534(March), 216553. <https://doi.org/10.1016/j.ccr.2025.216553>
- Precelia, S. C., Dirgarini, R. R., Nurlianti, J., & Saleh, C. (2018). Sintesis silika mesopori tersulfonasi dari abu daun bambu petung (*Dendrocalamus asper*). *Jurnal Atomik*, 03(1), 61–67. <https://jurnal.kimia.fmipa.unmul.ac.id/index.php/JA/article/view/525/413>
- Rauf, M. A., Meetani, M. A., & Hisaindee, S. (2011). An overview on the photocatalytic degradation of azo dyes in the presence of TiO₂ doped with selective transition metals. *Desalination*, 276(1–3), 13–27. <https://doi.org/10.1016/j.desal.2011.03.071>
- Sachithanadam, M., & Chandranth, S. (2014). A New Phenomenon of Compressive Strain Recovery in Gelatin- Silica Aerogel Composites with SDS. *Procedia Engineering*, 75, 51–55. <https://doi.org/10.1016/j.proeng.2013.11.010>
- Sharma, S., Bharti, R., Verma, M., Sharma, R., Charmier, A. J., & Sutradhar, M. (2025). Sharma, S., Bharti, R., Verma, M., Sharma, R., Charmier, A. J., & Sutradhar, M. (2025). Calcium Oxide Nanoparticles as Green Nanocatalysts in Multicomponent Heterocyclic Synthesis: Mechanisms, Metrics, and Future Directions. *Catalysts*, 15(10), 970. <https://doi.org/10.3390/catal15100970>
- Suba, K., Padmavathy, V., Anishia, S. R., Malini, S., Kavitha, R., & Sasikruba, S. (2024). Biogenic Photodegradation of Methylene Blue Dye using Azadirachta Indica (Neem) Leaf Extract : A Novel Green Catalyst Approach. *J. Environ. Nanotechnol.*, 13(4), 191–201. <https://doi.org/10.13074/jent.2024.12.2441093>
- Thirugnanam, N., Song, H., & Wu, Y. (2017). Photocatalytic degradation of Brilliant Green dye using CdSe quantum dots hybridized with graphene oxide under sunlight irradiation. *Chinese Journal of Catalysis*, 38(12), 2150–2159. [https://doi.org/10.1016/S1872-2067\(17\)62964-4](https://doi.org/10.1016/S1872-2067(17)62964-4)
- Ulfa, M. (2017). Mini Review Karbon Mesopori Dalam Dunia Global. *Jurnal Kimia dan Pendidikan Kimia*, 2(1), 54–65. <https://jurnal.uns.ac.id/jpkp/article/viewFile/8522/9944>
- Ulfa, M., & Afif, H. Al. (2022). Adsorption kinetics of methylene blue with 1 % TiO₂ / SBA-15 using Lagergren , Ho Mckay , and Pandey kinetic model. *AIP Conf. Proc.* 2645, 030021. <https://doi.org/10.1063/5.0112641>
- Ulfa, M., & Anggreani, C. N. (2022). Review on metal oxide for photocatalysis based green strategies for organic pollutant removal from aquatic environment Review on Metal Oxide for Photocatalysis Based Green Strategies for Organic Pollutant Removal from Aquatic Environment. *AIP Conf. Proc.* 2645, 030023. <https://doi.org/10.1063/5.0112636>
- Ulfa, M., Anggreani, C. N., Mulyani, B., & Sholeha, N. A. (2024). Hexagonal TiO₂/SiO₂ Porous Microplates for Methylene Blue

- Photodegradation. *Bulletin of Chemical Reaction Engineering and Catalysis*, 19(1), 149–159. <https://doi.org/10.9767/bcrec.20120>
- Ulfa, M., & Apriliani, W. (2020). Physico-chemical characteristics of gelatin as green template for nanomaterial production. *AIP Conference Proceedings*, 2237(June). <https://doi.org/10.1063/5.0006142>
- Ulfa, M., & Lestari, S. (2025). Design of Bi-and Tri-metal Oxide Photocatalysts via Gelatin-Directed Mesoporous Silica Hard Templating for Advanced Dye Degradation. *Bulletin of Chemical Reaction Engineering & Catalysis*, 20(4), 661–671. <https://doi.org/10.9767/bcrec.20460>
- Ulfa, M., Nikmah, Y., & Nurcahyo, I. F. (2022). Green capping agent and green sensitizer of TiO₂ for photocatalytic activity : Mini review Green Capping Agent and Green Sensitizer of TiO₂ for Photocatalytic Activity : Mini Review. *AIP Conf. Proc.* 2645, 030019. <https://doi.org/10.1063/5.0112645>
- Ulfa, M., Trisunaryanti, W., Falah, I. I., Kartini, I., & Sutarno, S. (2014). Synthesis of mesoporous carbon using gelatin as source of carbon by hard template technique and its characterizations. *IOSR Journal of Applied Chemistry*, 7(5), 01–07. <https://doi.org/10.9790/5736-07530107>
- Lv, T., Zhao, J., Chen, M., Shen, K., Zhang, D., Zhang, J., Zhang, G., & Liu, Q. (2018). Boosted Visible-Light Photodegradation of Methylene Blue by V and Co Co-Doped TiO₂. *Materials*, 11(10), 1946. <https://doi.org/10.3390/ma11101946>
- Wei, J., Wen, X., & Zhu, F. (2018). Influence of Surfactant on the Morphology and Photocatalytic Activity of Anatase TiO₂ by Solvothermal Synthesis. *Journal of Nanomaterials*, 2018. <https://doi.org/10.1155/2018/3086269>
- Yakout, S. M. (2021). Robust ferromagnetism and active visible-near infrared photocatalytic properties : Fe based Mn , Co and Ni codoped CuO nanostructures. *Optical Materials*, 112(December 2020), 110769. <https://doi.org/10.1016/j.optmat.2020.110769>
- Yan, Y., King, S. C., Li, M., Galy, T., Marszewski, M., Kang, J. S., Pilon, L., Hu, Y., & Tolbert, S. H. (2019). Exploring the Effect of Porous Structure on Thermal Conductivity in Templated Mesoporous Silica Films. *The Journal of Physical Chemistry C*, 123 (35), 21721–21730 ; <https://doi.org/10.1021/acs.jpcc.9b03767>
- Zhang, D., Dai, F., Zhang, P., An, Z., Zhao, Y., & Chen, L. (2019). Materials Science & Engineering C The photodegradation of methylene blue in water with PVDF / GO / ZnO composite membrane. *Materials Science & Engineering C*, 96, 684–692. <https://doi.org/10.1016/j.msec.2018.11.049>
- Zhao, Y. F., Li, C., Lu, S., Liu, R. X., Hu, J. Y., Gong, Y. Y., & Niu, L. Y. (2016). Journal of Solid State Chemistry Electronic , optical and photocatalytic behavior of Mn , N doped and co-doped TiO₂ : Experiment and simulation. *Journal of Solid State Chemistry*, 235, 160–168. <https://doi.org/10.1016/j.jssc.2016.01.002>



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