



Faculty of Resource Science and Technology

**Adsorption and Photocatalytic Performance of Ternary $\text{TiO}_2/\text{ZnS}/\text{GO}$
Composite for the Removal of Dyes**

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**Master of Science
2024**

Adsorption and Photocatalytic Performance of Ternary TiO₂/ZnS/GO
Composite for the Removal of Dyes

Allysha Riziana Binti Reduan

A thesis submitted

In fulfillment of the requirements for the degree of Master of Science

(Environmental Science)

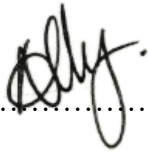
Faculty of Resource Science and Technology

UNIVERSITI MALAYSIA SARAWAK

2024

DECLARATION

I declare that the work in this thesis was carried out in accordance with the regulations of Universiti Malaysia Sarawak. Except where due acknowledgements have been made, the work is that of the author alone. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.



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Date: 15/01/2024

ACKNOWLEDGEMENT

I would like to express my heartfelt gratitude to God Almighty for His unwavering blessings that have illuminated my path and throughout my research journey.

I am incredibly thankful to my supervisor, AP Dr. Devagi Kanakaraju, for her mentorship, guidance, patience and help throughout my master's studies. Her wisdom and encouragement have shaped me both personally and professionally. I would also like to acknowledge the efforts of Pn Dyg Fatimawati Bt. Awg Alli, En Wahap Bin Marni, and En Shahfri Bin Semawi for their guidance in instrumentation analysis. I would also like to acknowledge Dr. Lim Ying Chin from UiTM Shah Alam for her assistance in analysing the samples and contributing her knowledge to my studies.

To my parents, Reduan bin Ahmad, Sarimah binti Rostani and my entire family, your love, support, and sacrifices have been the foundation of my success. Your belief in me has given me the confidence to pursue my dreams. To my friends, Sahlinah, Naylisa, Nisa, Nabilah, Haziah and Easter, for their pillars of support, providing laughter, and companionship during both the highs and lows of life. Our friendship is a cherished gift. To my cat, Mochi, who has been my companion for all the late-night writings.

Finally, I know my 18-year-old self would be incredibly proud of where I am today. We did it.

ABSTRACT

The escalating environmental concerns associated with the widespread use of synthetic dyes in industrial processes necessitate innovative and efficient approaches for their removal from aqueous environments. Ternary composites, with titanium dioxide (TiO_2) as a key component, are recognized for exceptional photocatalytic performance in water treatment. Zinc sulphide (ZnS) and graphene oxide (GO) were added to TiO_2 to enhance its photocatalytic and adsorption properties by promoting charge carrier separation that increases the likelihood of electron transfer reactions, thereby boosting its efficiency in degrading pollutants. This study aimed to assess the efficacy of $\text{TiO}_2/\text{ZnS}/\text{GO}$ composites (1:1:1, 1:2:1, and 2:1:1) in removing single and mixed dye pollutants, including Methylene blue (MB), Methyl orange (MO), and Rhodamine B (Rho B). Various spectroscopic and microscopic techniques comprehensively confirmed the successful creation of $\text{TiO}_2/\text{ZnS}/\text{GO}$ composites. Due to its superior performance, 1.0 g of the $\text{TiO}_2/\text{ZnS}/\text{GO}$ (1:1:1) achieved the highest MB removal rate (98.4%) at an initial concentration of 20 ppm over 150 minutes under UVA irradiation, surpassing other composites. In mixed dyes, the $\text{TiO}_2/\text{ZnS}/\text{GO}$ composite removed 99.1%, 44.3%, and 62.1% of MB, MO, and Rho B, respectively. The presence of different radical scavengers in MB removal showed that the active species in the photocatalytic degradation were $\bullet\text{OH}$ and $\bullet\text{O}_2^-$ radicals. $\text{TiO}_2/\text{ZnS}/\text{GO}$ -CaAlg beads achieved 64.2% for MB and 12.2% for Rho B, while MO showed no removal in mixed medium. The recyclability study revealed superior stability of $\text{TiO}_2/\text{ZnS}/\text{GO}$ -CaAlg beads compared to the $\text{TiO}_2/\text{ZnS}/\text{GO}$ powder. These findings provide valuable insights into its efficiency in addressing multiple pollutants.

Keywords: Photocatalysis, alginate, dyes, wastewater, titanium dioxide

***Penyerapan dan Prestasi Fotokatalitik Komposit Ternary TiO₂/ZnS/GO untuk
Penyingkiran Pewarna***

ABSTRAK

Isu pencemaran akibat daripada penggunaan pewarna sintetik dalam proses oleh industri perlu ditangani dengan pendekatan yang inovatif dan efisien bagi memastikan penyingkirannya daripada persekitaran akuatik. Komposit tiga unsur yang terdiri daripada titanium dioksida (TiO₂) sebagai komponen utama telah diiktiraf untuk prestasinya yang amat memberangsangkan dalam rawatan air. Zink sulfida (ZnS) dan oksida grafin (GO) mengালakkan pemisahan pembawa cas pada TiO₂ yang boleh meningkatkan reaksi pemindahan elektron dan seterusnya meningkatkan prestasinya sebagai bahan fotokatalisis dan penyerapan. Tujuan kajian ini adalah untuk mengkaji keberkesanan komposit TiO₂/ZnS/GO (1:1:1, 1:2:1, dan 2:1:1) menyingkirkan pencemar pewarna tunggal dan campuran, termasuk Metilena biru (MB), Metil oren (MO), dan Rhodamin B (Rho B) dalam bentuk serbuk dan manik. Pencirian menyeluruh dengan menggunakan pelbagai teknik spektroskopi dan mikroskopi mengesahkan pembentukan komposit TiO₂/ZnS/GO. Berdasarkan prestasi perbandingan di antara nisbah TiO₂/ZnS/GO yang dikaji, 1.0 g TiO₂/ZnS/GO (1:1:1) dipilih untuk kajian pelbagai parameter operasi (contohnya dos, kepekatan awal, pH, pemusnah radikal, dan larutan pewarna campuran) kerana ia menghasilkan penyingkiran MB tertinggi iaitu sebanyak 98.4% untuk kepekatan awal 20 ppm MB selepas rawatan 150 min di bawah sinaran UVA. Bagi larutan pewarna campuran, komposit TiO₂/ZnS/GO telah menyingkirkan 99.1% MB, 44.3% MO, dan 62.1%, Rho B. Spesis aktif utama dalam tindak balas degradasi fotokatalisis adalah radikal •OH and •O₂⁻. Keputusan menunjukkan bahawa TiO₂/ZnS/GO-

CaAlg manik mencatat kadar penyingkiran sebanyak 64.2% dan 12.2%, masing-masing untuk MB dan Rho B sementara tiada penyingkiran dicatatkan untuk MO dalam media pewarna campuran. Perbandingan kitaran rawatan diantara $\text{TiO}_2/\text{ZnS}/\text{GO}$ dan $\text{TiO}_2/\text{ZnS}/\text{GO}-\text{CaAlg}$ menunjukkan kestabilan manik berbanding dengan serbuk. Penemuan ini memberikan pandangan yang berharga mengenai aplikasinya yang berpotensi dalam rawatan air sisa, dengan penekanan utama untuk menangani pelbagai pencemar secara serentak.

Kata kunci: Fotokatalisis, alginat, pewarna, air sisa, titanium dioksida

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LIST OF ABBREVIATIONS

Alg	Alginate
BET	Brunauer-Emmett-Teller
e^-	Electron
EDX	Energy-dispersive X-ray
EIS	Electrochemical Impedance Spectroscopy
FTIR	Fourier Transform Infra-Red Spectroscopy
h^+	Hole
$h\nu$	Photon energy
pH_{pzc}	Point of Zero Charge
PL	Photoluminescence
SEM	Scanning Electron Microscope
TEM	Transmission Electron Microscopy
TiO ₂ /ZnS/GO	Titanium dioxide/Zinc sulphide/Graphene oxide
UV	Ultraviolet
UV-Vis DRS	Ultraviolet Visible Diffuse Reflectance Spectroscopy
VB	Valence Band

CHAPTER 1

INTRODUCTION

1.1 General Introduction

In recent years, the contamination of water has emerged as a serious threat to human life, primarily driven by technological advancements, rapid industrialization, and substantial population growth. Moreover, water pollution has intensified due to the continuous introduction of both organic and inorganic pollutants into aquatic ecosystems, resulting in adverse consequences for aquatic habitats. The textile industry, in particular, is a global source of concern due to the unintentional discharge of contaminated wastewater into water bodies, significantly affecting the quality of water resources (Rafiq, 2021). According to World Bank research, operations related to textile dyeing and treatment account for 17–20% of industrial water pollution. The textile industry is widely recognized as one of the most environmentally detrimental sectors due to its release of contaminated effluents into pristine water bodies. An estimated daily treatment of 12 to 20 tonnes of textiles results in the discharge of approximately 1000 to 3000 m³ of water (Hassaan et al., 2017). To effectively address the issue of organic pollutants (OPs), particularly dyes generated by human activities like dyeing processes and industrial discharges, there is a pressing need for stringent regulations and efficient treatment solutions. In light of this, the utilization of semiconductor-based photocatalysts for photodegradation emerges as one of the most promising approaches for remediating dye-laden wastewater. It is commonly known that a number of parameters affect how well photocatalysts work in the treatment of water, including: (1) narrow band gap; (2) adsorption capacity of organic molecules on the

surface area; (3) oxygen vacancies; (4) impurity energy level; and (5) electron trapping ability (Barakat et al., 2013; Cao et al., 2013).

While possessing exceptional photocatalytic properties, titanium dioxide (TiO_2) faces certain constraints that impede its broad and practical utilization in water treatment. The large band gap of TiO_2 (3.2 eV for anatase) and the high rate of photogenerated charge carrier recombination are the reasons behind its low photon efficiency. Moreover, the accumulation of nanosized photocatalysts reduces catalytic effectiveness by obstructing light-induced charge carrier migration to the surface and increasing the probability of recombination (Liu et al., 2015a; Wen et al., 2015). The incorporation of metal sulfides and carbon-based compounds into TiO_2 presents an array of potential solutions for tackling these issues effectively.

Materials derived from carbon, including graphene oxide, carbon nanotubes, fullerenes, and graphene nanosheets, are becoming more sought after for altering and creating composites based on TiO_2 . This is attributed to their distinct structural and electronic characteristics (Thiruvengadathan et al., 2021). Graphene oxide (GO) is typically fabricated from high-purity graphite through oxidation. GO sheets possess oxygenated functional groups, which provide the sheets with distinct properties that set them apart from pure graphene (Priyadharshini et al., 2022). TiO_2 -GO nanocomposite synthesized using the solvothermal method, demonstrated threefold enhanced photocatalytic degradation of gaseous benzene compared to pure anatase TiO_2 nanoparticles (Yadav & Kim, 2016). TiO_2 -GO nanocomposites facilitate a more stable separation of photogenerated charge carriers, thereby amplifying their photocatalytic efficacy when exposed to UV radiation. Another study reported that TiO_2/GO composites displayed excellent adsorption and photocatalytic activity in degrading methylene blue

(MB) as a result of its high surface area allowing more adsorbability of MB molecules (Wang et al., 2019b). Moreover, the addition of GO reduced the recombination of photo-generated electron-hole pairs and enhanced the facilitation of interfacial electron transport. Research indicates that the extensive surface area of GO provides additional sites for the surface adsorption of contaminants, leading to a substantial improvement in surface photocatalytic reactions and consequently enhancing catalytic performance (Singh et al., 2020; Kong et al., 2022).

Zinc sulphide (ZnS), a metal sulphide, is being increasingly recognized as an excellent photocatalyst for photocatalytic degradation in wastewater treatment. ZnS is preferred as a photocatalyst because of its direct band gap (3.7 eV), good mechanical stability, efficient conductivity, and improved electron transfer ability (Wang et al., 2022; Jamal et al., 2023). Thus far, the combination of ZnS with graphene has led to the creation of novel photocatalysts with unique traits. For instance, graphene has been reported to act as an effective electron acceptor and transporter to reduce electron-hole recombination and increase the lifespan of photogenerated charge carriers from ZnS (Cao et al., 2014). The optimized material, ZnS–5 wt% graphene removed 88.33% of MB under UV light as a result of the high surface of graphene and efficient separation of charge carriers' separation. Hu et al. (2011) revealed that ZnS-graphene resulted in complete degradation of MB within 32 min compared to ZnS alone due to the synergistic effect between ZnS and graphene. Hence, these studies have established that the inclusion of graphene on ZnS leads to an enhancement in photo-induced charge separation and transportation (Ibrahim et al., 2017). Furthermore, compared to TiO₂ alone, combining TiO₂ with ZnS has been shown to effectively prevent the recombination of electron-hole pairs, increasing

photocatalytic activity (Franco et al., 2009; Rahmawati et al., 2015; Chandrasekaran et al., 2019).

Currently, there is considerable interest in the emerging trend of creating TiO₂-based ternary composites as this material exhibits exceptional surface and optical properties, along with enhanced photooxidation capabilities (Qin et al., 2019; Maarisetty et al., 2020). Various synthesis techniques can be employed to fine-tune the surface and optical parameters that determine the photocatalytic performance of TiO₂-based ternary composites (Hong et al., 2020). For example, the ZnS-graphene/TiO₂ composite synthesized via the sol-gel method successfully removed 90.1% of MB within 150 min as a result of both adsorption and photocatalytic effects (Park et al., 2014). rGO/ZnS/TiO₂, where rGO is reduced graphene oxide, was synthesized via the combination of the modified Hummers method and ultrasound. It successfully removed 97% of crystal violet dye through adsorption and photodegradation, due to the uniform deposition of rGO on ZnS and TiO₂ nanoparticles (Kale et al., 2020).

As such, this study embarked on producing TiO₂-based ternary photocatalysts with improved charge separation by combining TiO₂, GO and ZnS as previous studies have not investigated the potential of GO in such composites. No reports are available to explore the inclusion of GO in such composites to improve charge separation or as an adsorbent. The integration of these three components, including GO, as an adsorbent, and a supporting matrix, has the potential to boost the overall adsorption capacity, surpassing what can be achieved with each material in isolation (Tayouri et al., 2022; Suhaimi et al., 2022). The ternary TiO₂/ZnS/GO composite was synthesized using the hydrothermal method, a cost-effective and versatile approach for materials synthesis. The hydrothermally synthesized TiO₂/ZnS/GO was examined for its trifunctional properties including its ability to catalyze

reactions, reusability and ability to operate under various conditions. Another significant contribution of this work is the performance investigation of the immobilized form of $\text{TiO}_2/\text{ZnS}/\text{GO}$ on alginate (Alg). Immobilization of $\text{TiO}_2/\text{ZnS}/\text{GO}$ was focused in this study because suspended form may pose a significant challenge for separation and recycling upon treatment. The application of green support like Alg for immobilization not only addresses these issues but also serves as an adsorbent, offering an additional advantage in water treatment. Alg, a natural polymer derived from various species of brown seaweed, is frequently employed as a polymeric matrix for encapsulating pollutants (Kanakaraju et al., 2022; Ansari et al., 2023). Studies have shown the effectiveness of Alg when combined with TiO_2 -based photocatalysts for pollutant removal (Nouri et al., 2020; Chkirida et al., 2021). The combined effect of adsorption and photocatalysis is expected when using immobilized calcium-alginate (Ca-Alg) $\text{TiO}_2/\text{ZnS}/\text{GO}$ ternary composites. The concurrent process of adsorption and photocatalysis concentrates OPs and establishes a mutual interface between the adsorbent and photocatalyst components. This interface efficiently binds pollutant molecules to the surface of the photocatalyst particles, resulting in their rapid degradation in the presence of UV light (Tu et al., 2016; Yahya, 2018). The efficacy of $\text{TiO}_2/\text{ZnS}/\text{GO}$ -CaAlg beads was assessed as an environmentally friendly system with potential applications for large-scale water treatment.

1.2 Problem Statement

Although TiO_2 functions as a remarkably effective photocatalyst, its extensive application in practical water treatment encounters various constraints. TiO_2 suffers from rapid recombination of photogenerated electron-hole pairs, leading to low efficiency and reduced photocatalytic activity. This limited selectivity often results in the formation of undesired

byproducts or incomplete degradation of target pollutants, limiting its practical application in complex environmental matrices. Additionally, the aggregation of nanoscale photocatalysts diminishes their catalytic efficacy by obstructing the access of light-induced charge carriers to the surface, thereby heightening the likelihood of recombination. To address these challenges effectively, the incorporation of ZnS and/or GO into TiO₂ introduces a variety of potential solutions. The presence of ZnS or GO into TiO₂ leads to a more reliable segregation of photogenerated charge carriers, resulting in an augmented photocatalytic performance when exposed to UV irradiation. However, an excessive quantity of ZnS or GO might elevate the likelihood of interactions between electrons and holes, leading to a higher occurrence of recombination between photogenerated electron-hole pairs. Consequently, this could diminish the overall photocatalytic activity of the catalyst. Hence, there is significant interest in the emerging strategy of fabricating ternary composites that consist of TiO₂, ZnS, and GO. The primary aim of this approach is to produce materials that showcase exceptional surface and optical characteristics, coupled with adsorption capacities and improved photooxidation capabilities. Furthermore, there has been insufficient investigation into the dominant reactive species in photocatalytic reactions within ternary composites. This study will be crucial to understand which reactive species is/are primarily responsible for the degradation of methylene blue (MB) and to grasp the role of different reactive species. Such understanding provides valuable insights into the mechanisms underlying photocatalytic degradation processes. Moreover, the effectiveness of ternary composites in degrading mixed dye solutions and the effect of solution pHs remains largely unexplored due to the complex nature of mixed dye systems. Also, TiO₂/ZnS/GO could be inefficient for separation and recycling as expensive and time-intensive processes are needed to retrieve the composite after treatment. Utilizing

environmentally friendly processes, such as employing Alg for immobilization, is crucial for retrieving the composite after treatment, while also addressing these problems and serving as an adsorbent, thereby presenting an added benefit in water treatment. The synergy between adsorption and photocatalysis is anticipated when employing immobilized calcium-alginate (Ca-Alg) $\text{TiO}_2/\text{ZnS}/\text{GO}$ ternary composites. This concurrent operation of adsorption and photocatalysis aims to concentrate OPs and establish a reciprocal interface connecting the adsorbent and photocatalyst components. Therefore, this study aims to fabricate the $\text{TiO}_2/\text{ZnS}/\text{GO}$ composite and assess its effectiveness in degrading various individual and mixed dyes under UV light. Furthermore, the study also emphasized a comparison of the effectiveness of $\text{TiO}_2/\text{ZnS}/\text{GO}$ -CaAlg beads in their immobilized state versus their powdered form.

1.3 Research Question

The research questions of this study are:

- a. What is the correlation between the surface structure, elemental compositions, electrochemistry and optical properties of $\text{TiO}_2/\text{ZnS}/\text{GO}$ with its photocatalytic activity?
- b. How do the adsorption capacities of TiO_2 , ZnS , GO , TiO_2/ZnS (1:1), and $\text{TiO}_2/\text{ZnS}/\text{GO}$ (1:1:1, 1:2:1, and 2:1:1) differ between each other?
- c. How is the photocatalytic performance of $\text{TiO}_2/\text{ZnS}/\text{GO}$ composite affected by the operational parameters such as dosage, dye concentration, mixed dye solutions, solution pH, and the presence of radical scavenger?
- d. What is the relative photocatalytic efficacy between $\text{TiO}_2/\text{ZnS}/\text{GO}$ composite powder and $\text{TiO}_2/\text{ZnS}/\text{GO}$ -CaAlg beads in the degradation of MB, methyl orange

(MO), rhodamine B (Rho B), and mixed dye solutions?

- e. What is the extent of reusability of both $\text{TiO}_2/\text{ZnS}/\text{GO}$ composite powder and $\text{TiO}_2/\text{ZnS}/\text{GO}-\text{CaAlg}$ beads?

1.4 Objectives

The main objective of this study was to fabricate multifunctional $\text{TiO}_2/\text{ZnS}/\text{GO}$ composites for the removal of MB, MO, Rho B and mixed dyes in aqueous solution. The specific objectives of this study were:

- a. To synthesize and characterize $\text{TiO}_2/\text{ZnS}/\text{GO}$ composites for their surface morphology, elemental compositions, electrochemistry, and optical properties,
- b. To compare and evaluate adsorption capacities between TiO_2 , ZnS, GO, TiO_2/ZnS (1:1), and $\text{TiO}_2/\text{ZnS}/\text{GO}$ (1:1:1, 1:2:1, and 2:1:1),
- c. To evaluate the parameters that affect the photocatalytic performance of $\text{TiO}_2/\text{ZnS}/\text{GO}$ composite namely dosage, concentration of dye, mixed dyes solution, solution pH, and presence of radical scavengers,
- d. To compare the photocatalytic efficiency of $\text{TiO}_2/\text{ZnS}/\text{GO}$ powder and $\text{TiO}_2/\text{ZnS}/\text{GO}-\text{CaAlg}$ beads for the degradation of MB, MO, Rho B and mixed dyes solution, and
- e. To investigate the reusability of $\text{TiO}_2/\text{ZnS}/\text{GO}$ powder and $\text{TiO}_2/\text{ZnS}/\text{GO}-\text{CaAlg}$ beads for up to four cycles.

1.5 Significance of the study

The significance of this study was to explore the possibilities of the trifunctional $\text{TiO}_2/\text{ZnS}/\text{GO}$ photocatalyst, which combines adsorption, photocatalytic reactions, and recyclability. It aims to degrade various dyes simultaneously in contaminated water. In addition, the employment of Ca-Alg onto $\text{TiO}_2/\text{ZnS}/\text{GO}$ for immobilization and recyclability is expected to enhance the material's stability and facilitate its recyclability, making it more practical for applications where repeated use is desired, such as in water treatment processes. The research contributes to nanotechnology, emphasizing the composite's potential for large-scale water treatment and its role in addressing environmental challenges. Overall, the study provides insights into optimizing these composites for practical applications, emphasizing their significance in advancing materials science and environmental science research.

CHAPTER 2

LITERATURE REVIEW

2.1 Titanium dioxide (TiO_2) semiconductor

TiO_2 has attracted increased attention as a photocatalyst due to its nontoxicity, inexpensiveness, resilient oxidation power, and great chemical stability (Alberti et al., 2019). Recent advances in nanotechnology have demonstrated that nanomaterials, such as nanosized TiO_2 photocatalysts, can perform exceptionally well in the purification of the environment. Heterogeneous TiO_2 photocatalysis, which has tremendous potential for environmental purification, is a rapidly growing area of environmental engineering. Fujishima and Honda discovered the performance of photocatalysts with the use of TiO_2 in the hydrolysis of water into hydrogen and gas (Beeldens, 2006; Jang et al., 2020).

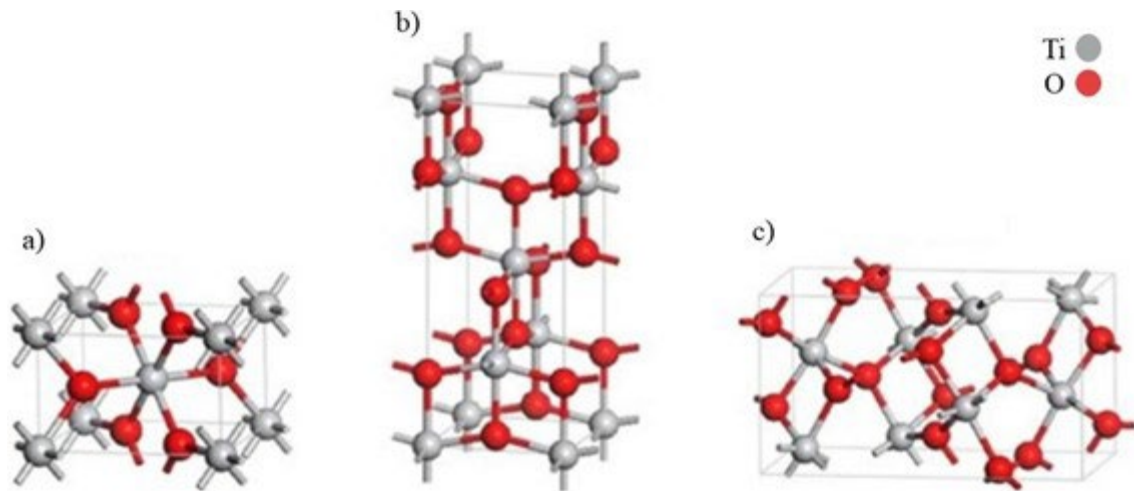


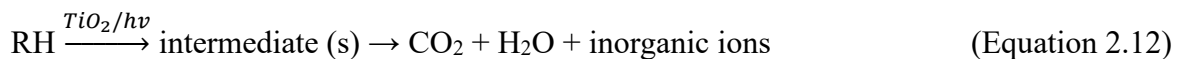
Figure 2.1: Crystalline structures of TiO_2 : (a) rutile, (b) anatase, and (c) brookite (Source: Baranowska-Wójcik, 2020).

TiO_2 possesses distinct crystal structures, namely anatase, brookite, and rutile (Figure 2.1) (Baranowska-Wójcik, 2020). Among these variations, anatase holds particular promise due to its beneficial properties for enhanced photocatalytic activity. These

properties encompass a notable band gap, the presence of hydroxyl groups, extensive surface area, and significant porosity. Rutile exhibits greater stability under regular conditions, but anatase surpasses rutile stability when particle diameters decrease to less than 14 nm (Peiris et al., 2021). A commonly available TiO_2 form is Degussa P25 titania, containing a composition of 75% anatase and 25% rutile. The structures of these polymorphs hinge on the spatial arrangement of TiO_6 octahedra. Their distinctions arise from their 3D octahedral assembly and degrees of distortion. The standard unit cell of tetragonal anatase consists of 12 atoms, with its octahedron displaying orthorhombic distortion and interconnections with 10 surrounding octahedra. On the other hand, the tetragonal rutile structure is comprised of 6 atoms, featuring a slightly orthorhombic octahedron attached to 8 surrounding octahedra. These distinct lattice structures lead to differences in electronic band arrangements and mass densities. Due to these structural characteristics, coupled with the notable mobility of electron-hole pairs, anatase displays superior photocatalytic efficiency under UV irradiation, as compared to the rutile and brookite phases. This insight is supported by research references (Daghrir et al., 2013; Kolesova et al., 2021). In terms of crystalline anatase morphology, the dominant faces are (011) and (001). Particularly, the (001) face exhibits high reactivity, significantly influencing catalytic activity, stability, and absorptive properties (Daghrir et al., 2013).

Furthermore, the presence of oxygen vacancies within TiO_2 imparts the distinctive characteristics of an n-type semiconductor material (Etacheri et al., 2015). These oxygen vacancies are balanced out by Ti^{3+} centers. The overlap of oxygen's 2p orbitals forms the valence band, whilst the 3d orbitals of Ti^{4+} create the lower part of the conduction band (Daghrir et al., 2013). The measured optical absorption thresholds for anatase, brookite, and rutile were 388.7 nm, 398.6 nm, and 413.3 nm, respectively. These values correspond

to optical band gaps of 3.19 eV, 3.11 eV, and 3.0 eV, which are in line with previously published research (3.2 eV for anatase, 3.37 for brookite, and 3.0 eV for rutile) (Cao et al., 2016). The generation of a positive hole in the valence band and the process of exciting electrons from the valence band to the conduction band are shown in Figure 2.2 (Sujatha et al., 2020). The primary process of photocatalysis involves the ejection of an electron from the valence band (VB) of the TiO₂ semiconductor into the conduction band (CB), creating a hole (h⁺) in the semiconductor's valence band. When TiO₂ absorbs UV (photon) irradiation with energy equivalent to or more than its band gap (>3.2 eV), electron-hole pairs are formed, initiating the photocatalytic activity. The photocatalytic mechanism of TiO₂ can explained as follows (Eq. 2.1 – 2.12):



Electron-hole pairs ($e^- - h^+$) are produced when photonic stimulation results in the formation of an unfilled valence band (Eqs. 2.1 – 2.3). The surface-trapped valence band electron is represented by the e^-_{TR} , and the conduction band hole by the h^+_{TR} . The photoexcited electron recombines with the valence band hole in the absence of electron scavengers (Eq. 2.4), concurrently releasing heat energy. The surface OH^- groups on the TiO_2 particle are reacted with the positive hole, producing surface-adsorbed hydroxyl radicals ($\bullet OH_{ads}$) (Eqs. 2.5 – 2.6). Recombination of the electron-hole pair is inhibited in the presence of oxygen, resulting in the formation of superoxide radical anions (O_2^-), which can then protonate to create hydroperoxyl radicals ($HO_2\bullet$) and H_2O_2 (Eqs. 2.7 – 2.9). The decomposition of OPs is aided by photogenerated holes and the reactive oxygen species (ROS), such as $\bullet OH$ radicals (Banerjee et al., 2014) (Eqs. 2.10 – 2.11). The organic chemicals in the liquid phase may degrade into their corresponding intermediates as the duration of irradiation increases. These intermediates then mineralize into carbon dioxide, water, and inorganic ions (Eq. 2.12).

Various precursors are utilized to generate TiO_2 nanoparticles via the sol-gel method, with titanium alkoxides being the most commonly employed. Titanium isopropoxide (TTIP), titanium ethoxide, and titanium butoxide (TBT) are among the frequently used titanium alkoxides for TiO_2 synthesis via the sol-gel route. As TTIP synthesis often requires rigorous conditions (high temperatures and extended reaction times) to achieve desired nanoparticle properties, TBT offers better control over the synthesis process, allowing for the formation of uniform nanoparticles with desired size and morphology under milder reaction conditions (Szoldra et al., 2021).

TiO_2 -based photocatalysis has been studied for approximately five decades, but its successful commercialization has remained elusive due to its limited efficiency (Dharma et

al., 2022). The prominent rate of charge recombination and the material's large band gap are the main causes of this inefficiency. As a result, it can only utilize UV radiation, which accounts for 4% of solar radiation. Increasing light absorption is essential to increasing the capacity of photogenerated charge carriers (Dharma et al., 2022).

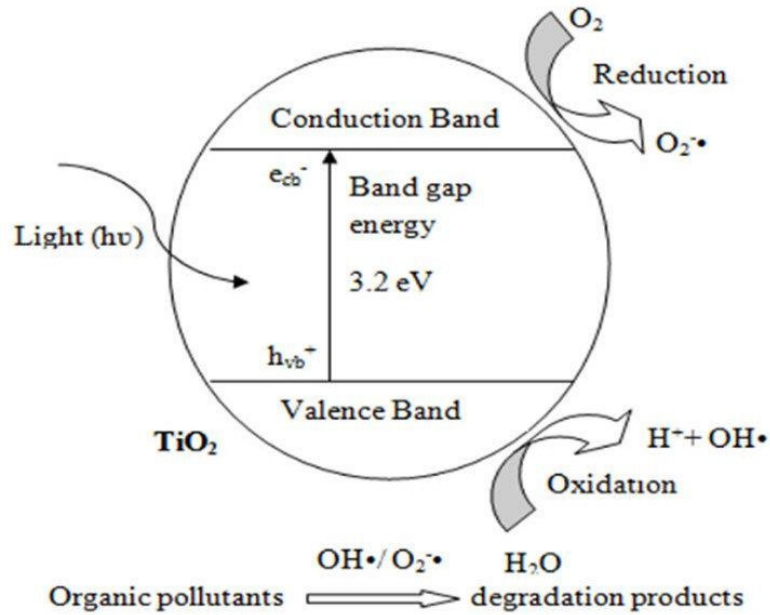


Figure 2.2: Principle of TiO₂ photocatalysis in the presence of pollutant (Source: Sujatha et al., 2020).

Various techniques have been developed to overcome these restrictions, such as immobilisation on support structures to increase the photocatalytic efficiency of TiO₂ and the creation of binary and ternary composites with metals, non-metals, and semiconductors (Li & Feng, 2016; Szkoda et al., 2016; Nguyen et al., 2020; Gong et al., 2021).

2.2 Zinc sulphide (ZnS)

ZnS is a well-known semiconductor photocatalyst in the II-VI group. Its unique photocatalytic activities, excellent physical properties, and various nanoscale morphologies have garnered significant attention (Sharma et al., 2021). Of all the inorganic

semiconductor photocatalysts, ZnS possesses one of the widest ranges of nanoscale morphological types. Light-emitting diode (LEDs), electroluminescence, flat panel displays, infrared windows, sensors, lasers, and biodevices have all historically shown remarkable versatility and promise for distinct basic characteristics and a broad range of uses (Zheng et al., 2020). Examples of the remarkable photocatalytic activity of ZnS nanostructures include photoreduction of CO₂, photocatalytic dehalogenation of halogenated benzene derivatives, photocatalytic degradation of organic contaminants, and photocatalytic splitting of water to form H₂. More benefits that ZnS provides include high electrical mobility, low cost, water insolubility, nontoxicity, and superior thermal stability. Additionally, it has superior transport qualities, which lessen carrier scattering and recombination (Zhang et al., 2013).

ZnS is present in two primary crystalline structures. One is cubic, referred to as sphalerite, while the other one is hexagonal, known as wurtzite (Figure 2.3). In both of these crystalline configurations, the coordination geometry around the zinc (Zn) and sulfur (S) atoms takes on a tetrahedral arrangement within the crystal system. The respective band gaps for cubic ZnS and hexagonal ZnS are 3.72 eV and 3.77 eV, respectively (Zheng et al., 2020). This implies that when exposed to UV light, ZnS only reacts at 340 nm to separate electrons from holes. Additionally, in the absence of sacrificial electron donors, ZnS could photochemically disintegrate into its component elements when exposed to radiation (Fajrina & Tahir, 2019).

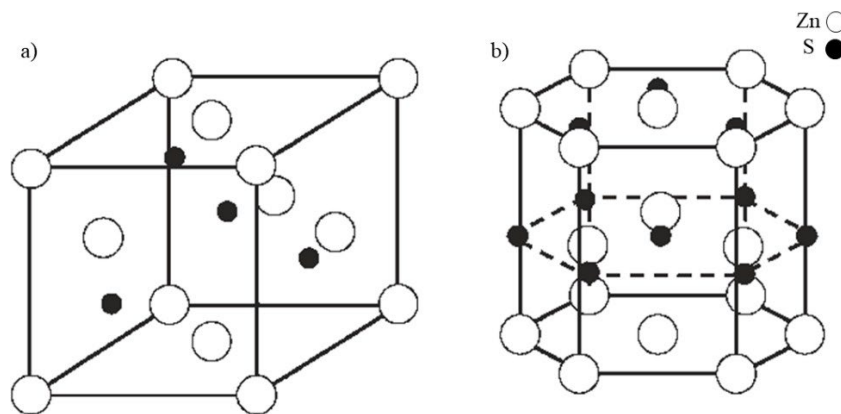


Figure 2.3: The (a) sphalerite and (b) wurtzite crystal structures of ZnS (Source: Jamal et al., 2020).

However, there are a few issues which prevent it from becoming more catalytically active which include poor visible-light sensitivity due to its broad band gap (Yu et al., 2021) and low photon efficiency due to its quick electron-hole recombination (Ahluwalia et al., 2016). Numerous approaches have been investigated to address these issues by developing composites and combining them with other semiconductors such as ZnO, CdS, MoS₂, and WO₃ to increase the photogenerated carriers' transmitting efficiency and widen the spectral response range (Xu et al., 2015; Palanisamy et al., 2018).

2.3 Graphene oxide (GO)

Graphene, composed of a single carbon atom layer arranged in a honeycomb lattice, exhibits remarkable strength and can be manipulated into various dimensional forms such as 0D, 1D, and 3D structures (Khan et al., 2016). Its exceptional transparency, high crystallinity, and impressive electronic properties further enhance its appeal. An effective strategy to broaden graphene's application spectrum involves the creation of graphene derivatives. For example, the introduction of epoxy, hydroxyl, and carboxyl groups onto the basal planes of the graphite layers by strong oxidising agents results in the

creation of GO (Figure 2.4). These oxygen-rich functional groups give GO great hydrophilicity, which allows for efficient dispersion in a variety of solvents, particularly water. These oxygen-based functional groups also provide reactive sites for GO's chemical modification or functionalization, which makes the development of products based on GO simple. According to Lee et al. (2021), GO is a carbon substance made up of a layer of separate sp² hybrid carbon atoms. It is a two-dimensional carbonaceous material with a hexagonal honeycomb crystal structure (Yu et al., 2022).

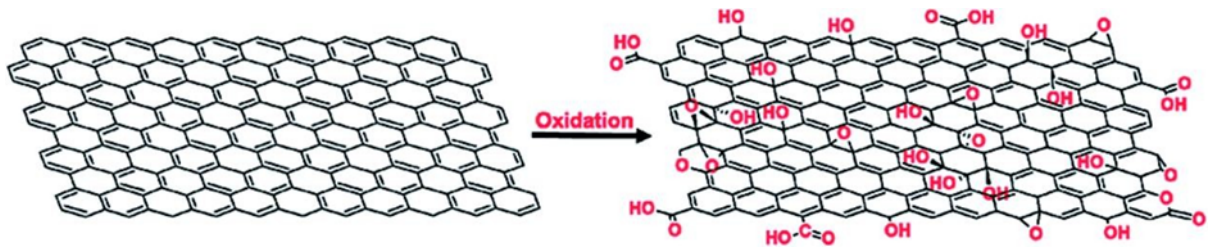


Figure 2.4: Graphene sheet oxidation to form GO (Source: Yu et al., 2022).

GO has several advantages over graphene, including lower production costs, mass production feasibility, and easier processing. Recent comprehensive research on GO has revealed that it possesses remarkable characteristics and a wide range of active functional groups, including oxygen (Papageorgiou et al., 2017). Depending on the requirements of application domains, oxygen-containing groups or decreased doping components can be employed as catalytic active centres for covalent or non-covalent modification design. The GO interlayer gap can be functionalized by small molecules or polymer intercalations, and it can be further increased by oxygen-containing groups. Graphene and GO possess exceptional mechanical, electrical, and thermal properties due to their distinct structural and morphological characteristics (Zhang et al., 2013b; Yi and Shen, 2015; You et al., 2020). Graphene is hydrophobic, while GO is hydrophilic and readily diffused in water because of the clear differences between the two materials caused by the presence of

oxygen bound with some carbons. Furthermore, GO's large surface area provides more adsorption sites for pollutants, greatly boosting surface photocatalytic reactions and raising catalytic activity (Kong et al., 2022).

2.4 Binary TiO₂/ZnS composites

One major obstacle to obtaining the required properties for photocatalytic treatment with a single photocatalyst is the recombination rate of photogenerated electron-hole pairs (Asadzadeh-Khaneghah & Habibi-Yangjeh, 2020). Binary composites consist of two separate components with varying characteristics. These components are commonly denoted as the matrix and the reinforcement. When these components are combined, it creates a material with distinctive properties that diverge from those of its elements (Peng et al., 2016). A single photocatalyst may struggle to attain the essential attributes needed for photocatalytic treatment, largely because of the rapid recombination of electron-hole pairs generated during the process (Ahmed and Haider, 2018). To overcome this constraint, the configuration of the conduction and valence bands in a semiconductor is crucial in determining the capabilities of photogenerated electrons for reduction and oxidation (Li et al., 2021).

The combination of TiO₂ with metal sulphides can significantly improve the photocatalytic activity of the resultant material. When TiO₂ is paired with semiconductors like TiO₂/XS (where X can be Pb, Zn, or Cd), the resulting nanocomposites exhibit improved optical characteristics, such as enhanced absorption and photoluminescence, when compared to their larger bulk counterparts (Zheng et al., 2020). For example, Xiaodan et al. (2006) discovered that the photocatalytic activity of the TiO₂/ZnS nanocomposite surpassed that of both individual TiO₂ and ZnS, particularly under visible

light conditions. TiO_2/ZnS nanoparticles' synergistic effect on the surface of TiO_2 anatase and the interaction between methyl parathion ions and the binary compound can be attributed to significantly greater separation of charges that results in enhanced efficiency. Additionally, Zheng et al. (2020) noted that binary and ternary photocatalysts offer advantages over single photocatalysts. This advantage was due to their ability to modify band bending at interfaces and generate a motive force for the separation of charge carriers. Consequently, they mitigate the rate of charge carrier recombination, resulting in enhanced photocatalytic efficiency.

The introduction of ZnS, onto TiO_2 , can have multiple effects on the final photocatalyst product, effectively preventing electron-hole recombination and enhancing its photocatalytic performance (Zhang et al., 2022). For instance, ZnS traps electrons in the conduction band of TiO_2 when they are excited. Because ZnS promotes electron transport, there is less likelihood of electron-hole recombination. Furthermore, by utilising the principles of quantum confinement, the combined TiO_2/ZnS composite aids in the degradation of OPs (Wang & Zhang, 2014). ZnS, possessing an excess of electrons, broadens the spectrum of light absorption (Sharma et al., 2021). The photocatalytic degradation mechanism using TiO_2/ZnS nanocomposite is illustrated in Figure 2.5. When exposed to radiation, the light supplies the necessary photons for the creation of electron and hole pairs (Eq. 2.13). TiO_2 's conduction band (CB) is more positive than that of ZnS, whereas ZnS's valence band (VB) is more negatively positioned than TiO_2 . According to Qu et al. (2014), the transfer of photogenerated holes can occur from the valence band of TiO_2 to the valence band of ZnS, indicating the efficient separation of photogenerated electrons and holes. The band structure facilitates the separation of excited electron-hole pairs and promotes redox reactions. Electrons can reduce dissolved molecular oxygen to

produce $\bullet\text{O}_2^-$ radical anions (Eq. 2.14), while holes can oxidize H_2O molecules, yielding $\text{HO}\bullet$ radicals on the TiO_2/ZnS surfaces (Eq. 2.15). Ultimately, organic dye pollutants are oxidized by these highly active species to form CO_2 and H_2O products (Eq. 2.16). The elemental steps that occur during the degradation mechanism of dye using TiO_2/ZnS nanocomposite are represented by the following equations:

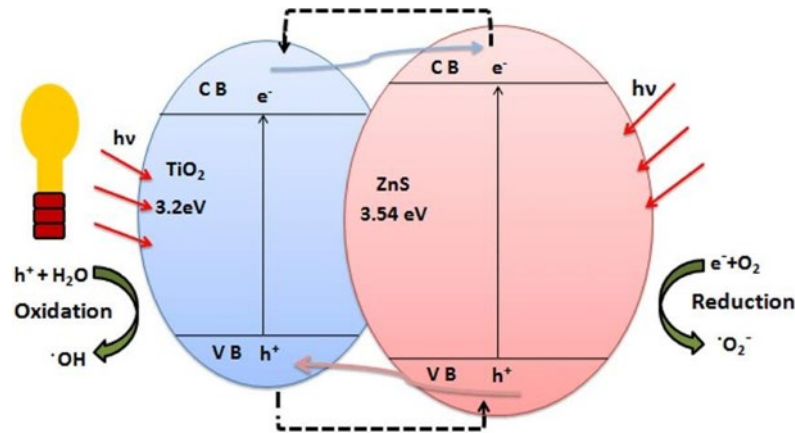
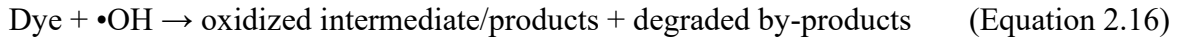
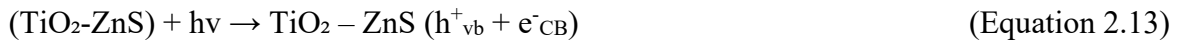


Figure 2.5: Schematic illustration of the photodegradation process using a binary TiO_2/ZnS (Source: Priya et al., 2021).

Furthermore, the method of synthesis for TiO_2/ZnS composites can have a substantial impact on the structural, morphological, and optical aspects of the final material. Different synthesis methods can lead to variations in the crystallinity, particle size, surface area, and overall performance of the composite. Table 2.1 summarizes the effect of synthesis methods of binary TiO_2/ZnS composites on their properties and performance.

2.4.1 Fabrication methods of TiO₂/ZnS composites

2.4.1.1 Sol-gel method

The sol-gel method offers numerous benefits that make it an attractive choice for composite synthesis. Initially, the sol-gel process is regarded as environmentally friendly because it does not necessitate severe synthesis conditions or the utilization of intricate equipment. It involves the transformation of a sol (a stable colloidal suspension) into a gel by a series of chemical reactions. This simplicity and ease of operation make the sol-gel method cost-efficient and accessible for composite fabrication. Furthermore, the sol-gel method provides greater control over the consistency and purity of the final product. By carefully adjusting the precursor concentrations and reaction parameters, such as temperature and time, it is possible to achieve precise control over the composition, morphology, and structure of the TiO₂/ZnS composite. For instance, Sattar et al. (2019) annealed TiO₂/ZnS nanocomposites at different temperatures namely 100°C, 450°C, 750°C, and 1050°C, using TBOT as the precursor for TiO₂ and zinc acetate for ZnS. It was found that the applied temperatures and their resulting morphologies affected the degradation of MB. TiO₂/ZnS annealed at 100°C displayed a rapid decrease in the concentration of MB, attributed to reduced agglomeration and increased active sites. Microscopic characterization showed variation in morphology, transitioning from flower flakes at 100°C to nanorods at 450°C, and agglomerations of nanocomposites at higher temperatures. Moreover, ZnS is uniformly distributed throughout the TiO₂ matrix, improving the composite's overall stability and preventing phase separation or component agglomeration during photocatalytic processes (Rauf et al., 2022).

Prasannalakshmi and Shanmugam (2017) investigated the effect of varying degrees of ZnS-loaded on TiO₂/ZnS composites on the removal of brilliant green (BG) and MB

dyes under solar light irradiation using the sol-gel method (Table 2.1). In the case of high ZnS loading (referred to as TZ4), the TiO₂ particles exhibited uneven distribution, with ZnS aggregating on the TiO₂ surface. In contrast, when ZnS loading was low (referred to as TZ1), the amalgamation of TiO₂ particles and ZnS exhibited a more uniform combination, facilitated by heterogeneous nucleation. With a decrease in the amount of ZnS content, there is an increase in surface area. This augmented surface area is highly beneficial for photocatalytic activity, as it facilitates the creation of additional active sites capable of absorbing dye molecules and generating free radicals, which play a major role in the degradation of dyes. As a result, TZ1 exhibited the most rapid degradation rate, reaching $0.110 \pm 0.001 \text{ min}^{-1}$ for MB and $0.102 \pm 0.001 \text{ min}^{-1}$ for BG, surpassing the performance of other ZnS loadings (Figure 2.6(a)). However, excessive concentrations may result in a decrease in visible light penetration due to an enhanced light scattering impact by catalyst particles, whilst concentrations that are too low may be ineffective in producing a higher degradation rate of pollutants (Habib et al., 2021).

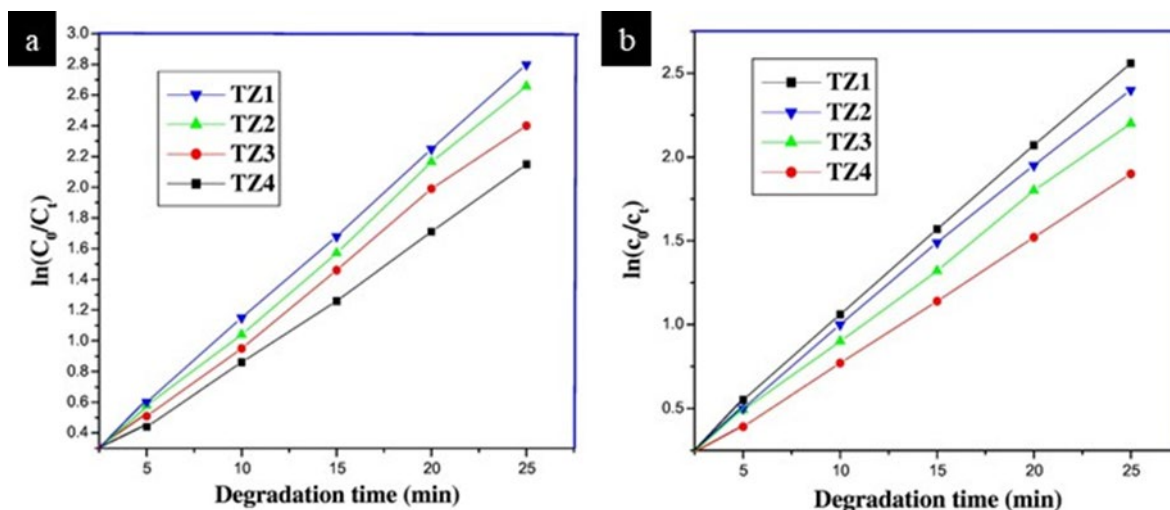


Figure 2.6: (a) Photocatalytic rate constant of binary TiO_2/ZnS on MB (b) BG (Source: Prasannalakshmi and Shanmugam, 2017).

Nevertheless, a study conducted using an optimal range from different wt% of ZnS loading was successfully synthesized by Dhatshanamurthi et al. (2014) via the sol-gel method. The study showed that the pseudo-first-order rate constants obtained for ZnS loadings of 3.4%, 10.7%, and 14.3% were 0.0074, 0.0398, and 0.0301 min^{-1} , respectively. The morphology of TiO_2/ZnS (10.7%) showed that the particles were not aggregated as compared to bare TiO_2 . Hence, ZnS modification preferably retarded the TiO_2 aggregation. Another study reported that TiO_2 -ZnS loading particularly less and beyond 18.0 wt.%, can induce a screening effect that diminishes the catalyst's specific activity (Kuzhalosai et al., 2013). The surface area of ZnS/ TiO_2 (133 m^2/g) loaded with 18.0 wt.% was higher than that of the commercial TiO_2 (50 m^2/g). The particles exhibit a size of approximately 0.1 μm and possess an almost spherical shape. The geometric and electrical properties of the ZnS atoms added to the TiO_2 surface are significant, improving the catalyst's photocatalytic activity. The 18.0 wt% of TiO_2/ZnS degraded 97.9% of Sunset Yellow (SY) within 90 min under UV radiation compared to 82.3% of removal by the commercial TiO_2 under the same reaction time.

2.4.1.2 Hydrothermal method

Hydrothermal synthesis is a method used to cultivate crystals from a water-based solution within an autoclave by employing heightened temperatures resulting in the formation of superior-quality crystals of the intended nanomaterial (Yang & Park, 2019). Kong et al. (2017) synthesized TiO₂ nanotube arrays/ZnS (TNAs/ZnS) nanocomposites via the hydrothermal method (Table 2.1). It was observed that the amounts of zinc source and sulfur influenced the morphology of the synthesized composites. The hydrothermal method employed in creating TNAs/ZnS, incorporating a moderate quantity (10 mmol) of ZnS nanospheres, improved the capacity to absorb MB molecules owing to the extensive surface area of the nanocomposite. Moreover, the photodegradation rate was higher as the amounts of Zn²⁺ and S²⁻ increased. However, when the amount exceeded 10 mmol, the photocatalytic rate was reduced because too much ZnS may prevent TNAs from absorbing enough sunlight. As a result, an excess of ZnS would influence the adsorption and photocatalytic activity of MB while also causing electron-hole pair recombination. Priya et al. (2021) synthesized TiO₂/ZnS via the hydrothermal method by varying the molar concentration of Zn. It is observed that as the Zn content in TiO₂/ZnS increased, the nanocomposite shows a non-uniform distribution of densely arranged particles. It is also shown that the TiO₂/ZnS nanocomposite with the lowest content of Zn had excellent adsorption capacity compared to the higher Zn content because as the crystallite size decreased, the surface area increased.

2.4.1.3 Solvothermal method

Solvothermal synthesis involves generating crystalline materials by elevating the temperature above the boiling point of the reactants within a sealed reaction system,

resulting in the creation of a high-pressure environment (Huo et al., 2023). Furthermore, the underlying principle of solvothermal synthesis primarily lies in the variation of solubility within the pressure vessel, leading to the transformation of chemical substances from precursors to crystals. This solubility discrepancy is a consequence of the temperature gradient established between the dissolution and crystallization regions (Demazeau & Largeteau, 2015). In addition to the solvent system, the solvothermal method closely mirrors the hydrothermal technique. Figure 2.7 illustrates the fundamental steps involved in the solvothermal and hydrothermal synthesis of the TiO₂/ZnS-based composite. Harish et al. (2017) impregnated ZnS quantum dots on the surface of the TiO₂ mesosphere by a soft template-assisted hydrothermal approach (Table 2.1). The morphological analysis revealed that the ZnS quantum dots were effectively immobilized on the TiO₂ mesosphere ensuring strong interfacial interactions between the two materials. The presence of a higher concentration of ZnS is found to be able to decrease the pore size of mesoporous spheres by filling the pores within the network. This effectively diminishes the interaction between OPs and the photocatalyst. Furthermore, the ideal ZnS content must be determined since the TiO₂/ZnS photocatalyst's performance in photocatalytic activity depends on the atomic arrangement at the catalyst surface-to-OPs interface (Xu et al., 2018). As a result, ZnS concentration is essential for heterojunction formation in TiO₂/ZnS nanocomposites, which inhibits electron-hole pair recombination.

Overall, while both hydrothermal and solvothermal synthesis have their advantages and limitations, hydrothermal synthesis may be preferred for its cost-effectiveness, environmental friendliness, broader applicability, uniformity, purity, and ease of handling.

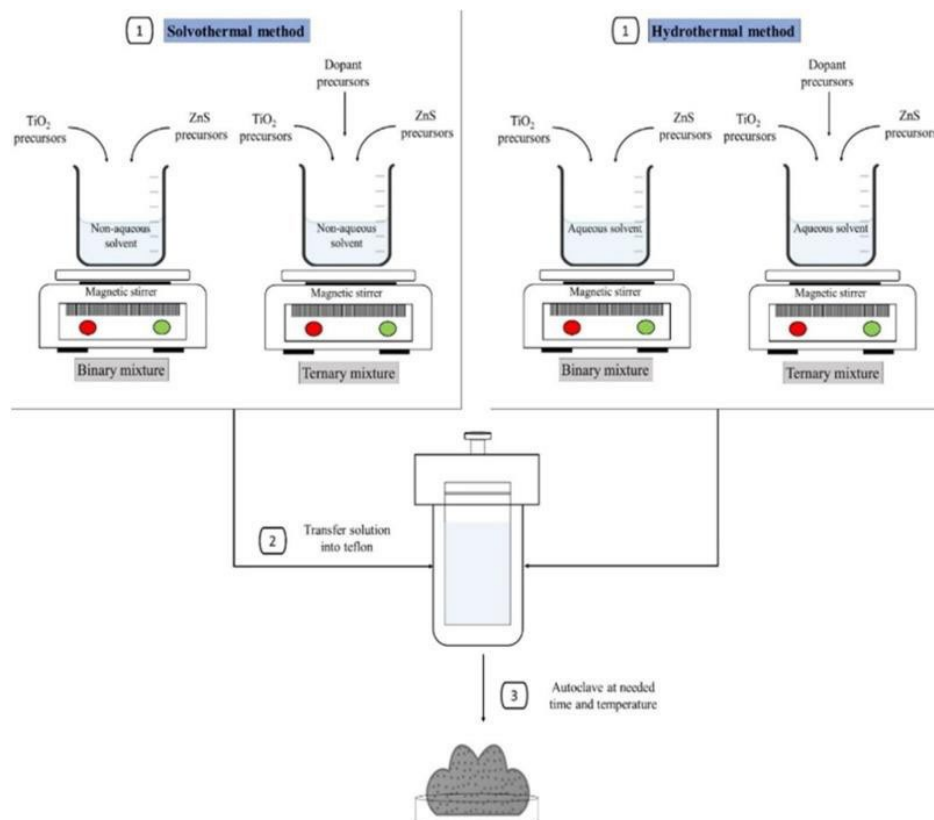


Figure 2.7: Schematic illustration of the synthesis of binary TiO_2/ZnS composites via the hydrothermal and solvothermal methods (Source: Kanakaraju et al., 2023).

Table 2.1: Effect of synthesis methods of binary TiO₂/ZnS composites on their properties and performance

Methods	Precursors used	Phase composition (XRD), crystallite size, BET, TEM	Morphology (SEM/FESEM)	Removal (%) or kinetic rate (min ⁻¹)	References
Sol-gel	40 mL acetic acid, 10 mL ethanol solution, 2.196 g zinc Acetate, 20 mL TBOT, 100 mL glycerol	XRD: TiO ₂ Anatase (450 °C), rutile (750 °C) and brookite (1050 °C)	Flower flakes like particles (100°C), nanorods (450°C) and agglomerations	Almost complete removal of MB solution	Sattar et al., 2019
	5 mL TTIP, 0.25 MZnC ₄ H ₆ O ₄ , 0.5 MNa ₂ S	XRD: Anatase TiO ₂ , 25 ± 0.2 nm, BET: 15.07 ± 0.1 m ² /g, TEM: 15–20 nm	Spherical TiO ₂ nanocrystal surrounded with ZnS	Degradation rates: 0.110 ± 0.001 min ⁻¹ and 0.102 ± 0.001 min ⁻¹ for MB and BG, respectively after 25 min.	Prasannalakshmi and Shanmugam, 2017

Table 2.1: Continued

	12.5 mL TTIP (99 %) and 0.005 M Zinc nitrate ($\text{Zn}(\text{NO}_3)_2$), 0.005 M Na_2S	XRD: Anatase TiO_2 , cubic ZnS , 31.8 nm, BET: 133 m^2/g	Particles almost spherical TiO_2	Achieved 85.5% removal of (Sunset Yellow) SY dye after 75 min.	Rajamanickam and Shanthi, 2016
	12.5 mL TTIP, 0.03 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.03 M Na_2S	XRD: Anatase TiO_2 , 15.2 nm, BET: 133.3 m^2/g , TEM: 3–20 nm	Slightly aggregated nanoparticles	The degradation rate of Phenol red sodium salts (PRSS) increased from 0.0149 to 0.0352 min^{-1} after 60 min	Dhatshanamurthi et al., 2014
Solvothermal method	1 mL TTIP, 0.025 M $\text{Zn}(\text{CH}_3\text{CO}_2)_2$, 0.025 M $\text{C}_2\text{H}_5\text{NS}$	XRD: Anatase TiO_2 , TEM: 2–6 nm	Mesoporous spheres with a rough surface decoration	Achieved 98.40% of MB removal after 32 min.	Harish et al., 2017
Hydrothermal method	Ti plate, Zn acetate, $\text{CH}_4\text{N}_2\text{S}$	XRD: Anatase TiO_2	Stratiform or flaky flower-like sheet	The photodegradation rate of MB rose to	Kong et al., 2017

Table 2.1: Continued

			91.6% after 240 min.		
TTIP, 0.25 M	XRD: Anatase TiO ₂ ,	Non-uniform dense spherical-shaped	Removal efficiency up		Priya et al., 2021
Zn(CH ₃ CO ₂) ₂ , 0.5 M	BET: 9.41 nm, TEM:		to 70.07% of CV after		
CH ₄ N ₂ S	4.41 nm		60 min.		

2.5 Binary of TiO₂/GO composites

Since its discovery in 2004, graphene has exerted a substantial influence on various scientific and technological domains, owing to its remarkable physicochemical properties. High specific surface area (2630 m²/g for single-layer graphene, theoretically), remarkable electronic qualities and electron transport capacities, unparalleled flexibility and impermeability, strong mechanical strength, and superior thermal and electrical conductivities, are some of the key features of graphene (Chen et al., 2012a; Julkapli and Bagheri, 2015). The combination of TiO₂ and GO nanosheets is believed to offer several advantages in terms of photocatalytic activity: (i) GO can effectively capture and transport charge carriers, preventing the recombination of electron-hole pairs, (ii) the composite can be easily recovered from aqueous solutions because of the large GO sheets, (iii) the new composite provides a sufficient number of active sites, ensuring high catalytic efficiency, (iv) the band gap of the composite can be tuned or extended, allowing for better utilization of visible light due to the creation of a hybrid orbital just below the conduction band of TiO₂ (Leary & Westwood, 2011; Jia et al., 2016). Table 2.2 summarizes the selected studies of TiO₂/GO composites. The fabrication methods (e.g. hydrothermal, solvothermal, colloidal blending, and sol-gel) applied for the synthesis have been discussed along with their effect on the material's properties and performance.

2.5.1 Fabrication methods of TiO₂/GO composites

2.5.1.1 Hydrothermal method

TiO₂/GO composites were frequently synthesized via the hydrothermal method which has extensive applications in wastewater purification, particularly in the fields of photocatalytic degradation and disinfection. The hydrothermal method employed for the

synthesis of TiO₂/GO at 120°C resulted in the formation of spherical TiO₂ particles along the wrinkles and edges of GO sheets (Mahima et al., 2018) (Table 2.2). Consequently, 65% of CV dye removal was obtained. The spherical TiO₂ accumulated along the wrinkles and edges of the GO sheet was also attained via the hydrothermal method (Sharma et al., 2018). An overall removal efficiency of 63% for CV was achieved. The notable removal of CV dye was ascribed to an increase in the surface area and improved charge separation within TiO₂/GO. Additionally, the inclusion of GO in the TiO₂/GO composite contributed to a considerably reduced band gap, decreasing from 3.14 eV to 2.98 eV compared to TiO₂. The interaction between the unpaired π electrons of GO and the electrons on the surface of TiO₂ has been determined as the cause of this reduction. Additionally, Wang et al. (2019b) revealed that the results showed a substantial influence of GO on the optical features of TiO₂, wherein the composite's band gap decreased with the presence of GO. This resulted in an extension of the light absorption range. The small band gap of TiO₂/GO was beneficial as the degradation of MB increased over time, and the degradation rate was 97.5%, as compared to lone TiO₂ (27.7%) in 140 min. The increased absorption of visible light can be attributed to the development of Ti-O-C chemical bonds within the produced composites, a conclusion supported by the results of FTIR and XRD analyses.

2.5.1.2 Solvothermal method

Typically, when employing the hydro/solvothermal method to synthesize semiconductor/GO photocatalysts, chemical bonds are established between the semiconductors and GO (Li et al., 2022). This creates a synergistic effect between the two components, leading to an enhancement in the photocatalytic properties of the composite compared to the individual semiconductor or GO alone (Jianwei et al., 2013). The

solvothermal method has gained widespread use due to its ability to produce TiO₂/GO with a high specific surface area. Nevertheless, there is variation in the choice of solvent among different studies.

For example, when TiO₂/GO was synthesised using isopropyl alcohol (IPA) in solvothermal conditions, the GO created a thick layer of graphene on the TiO₂ surface, suppressing the formation of TiO₂ crystals (Natarajan et al., 2021) (Table 2.2). Moreover, the TiO₂/GO displayed a much higher BET-specific surface area of 97.08 m²/g compared to only 1.06 m²/g for pristine TiO₂. Under UV radiation, TiO₂/GO accomplished complete degradation of 2,4-dichlorophenoxyacetic acid (2,4-D), highlighting that the elevated specific surface area plays a role in augmenting photooxidation. Similarly, Zhen et al. (2018) also synthesized TiO₂/GO using the solvothermal method, but they used glycerin as their preferred solvent. The glycerin aided in the formation of a significant number of TiO₂ nanoflakes with a thickness of 20 nm that are interconnected laterally on the graphene sheets. An 80% degradation level of oxytetracycline (OTC) was attained within a 60 min timeframe.

Thus, the choices of solvent are often dependent on the specific requirements of the synthesis process, such as the solubility of precursors, the desired reaction temperature and pressure, and the properties of the resulting material. The selected solvents required optimized reaction conditions to achieve the desired characteristics of the synthesized materials.

2.5.1.3 Colloidal blending method

The colloidal blending method, known for creating composite photocatalysts, encompasses the mixing of GO suspension with semiconductor solution (or semiconductor precursors)

followed by subsequent steps such as drying and calcination (Ahmed & Mohamed, 2023). In contrast to the hydro/solvothermal methods, the solution mixing method offers advantages such as mild reaction conditions, facile, and cost-effectiveness. However, one limitation of this method is the difficulty in forming chemical bonds between the semiconductors and GO due to the gentle reaction conditions, which can affect the overall performance of the resulting photocatalysts (Jianwei et al., 2013).

Nguyen-Phan et al. (2011) produced TiO₂/GO composites through colloidal blending for the photodegradation of MB. When exposed to UV light, the composites performed better for both adsorption and photocatalysis, with a 90% removal efficiency as opposed to 50% for pure TiO₂ (Table 2.2). In a separate study, the photodegradation efficiency of TiO₂/GO to MO is up to 87.2% in 15 min, as compared to Degussa P25 powders at 38.4% under the irradiation of UV light (Zhang et al., 2011). In general, this was linked to the fact that the blending process promotes intimate contact between TiO₂ nanoparticles and GO sheets. This close interaction can create a network structure with increased interfacial areas, potentially leading to a higher overall surface area (Padmanabhan et al., 2021). The excellent photocatalytic performance seen in the TiO₂/GO composite systems can be attributed to the increase in specific surface area that GO facilitates, as well as the formation of both π - π conjugations between dye molecules and aromatic rings and ionic interactions (Mandal et al., 2019). One significant drawback of colloidal blending was the agglomeration of TiO₂ nanoparticles on GO sheets occurred during the blending process, which led to non-uniform distribution (Zhang et al., 2011). This may result in the loss of active sites and compromise the desired properties of the nanocomposites, which affects the photocatalytic activity of TiO₂/GO.

2.5.1.4 Sol-gel method

Sol-gel method is also frequently used in the synthesis of TiO₂/GO to enable the creation of a composite with a distinct advantage, achieved at comparably lower temperatures. There are multiple steps in the sol-gel process: sol fabrication, gelling, gel synthesis, calcination, and drying. This approach provides uniform molecule doping, resulting in improved photocatalytic properties. In this technique, two different approaches have been used: the synthesis of sol-gel from precursor solutions of titanium and carbon nanomaterials, and the preparation of sol-gel from TiO₂ alone, followed by the addition of dispersed carbon material.

Cao (2013) used the sol-gel route to prepare a uniform distribution of TiO₂ onto GO sheets by introducing TBOT to GO dispersion. The TiO₂/GO was found to enhance the degradation rate of Reactive Brilliant Red X-3B (X-3B dye) by 96.3% as compared to TiO₂ (87.6%) under UV irradiation. Ramos et al. (2020) used a similar approach but applied titanium (IV) isopropoxide (Ti(OC₄H₉)₄) solution as the TiO₂ precursor. They discovered that the addition of GO resulted in a 20% degradation rate under UV irradiation and a 63% degradation rate under solar radiation. Since GO enhances dye adsorption and charge carrier transport, the TiO₂/GO composites demonstrated higher photocatalytic activity towards the photodegradation of tartrazine dye when exposed to UV and visible light irradiation than pure TiO₂. Additionally, the TiO₂ nanoparticles adhere to the GO sheet, increasing the nanocomposite's specific surface area and pore structure while also inhibiting TiO₂ particle aggregation (Khavar et al., 2018). The increased specific surface area of the composites leads to higher adsorptive capabilities. Thus, the reaction conditions help to promote the formation of a stable and dispersed sol, which leads to increased specific surface area and higher adsorptive capabilities.

Table 2.2: Effect of synthesis methods applied for the synthesis of binary TiO₂/GO composites on their properties and performance.

Methods	Precursors	Phase composition (XRD), crystallite size, BET, TEM	Morphology (SEM/FESEM)	Removal (%) or kinetic rate (min ⁻¹)	References
Hydrothermal method	TTIP, graphite powder	XRD: Anatase TiO ₂ , GO, 10.7°	Accumulation of TiO ₂ on wrinkles and edges of GO.	63% of CV degradation after 150 min	Mahima et al., 2018
	17 mL tetrabutyl titanate, graphite powder	XRD: Anatase TiO ₂ , 11.7°, GO, BET: TGO-20%, 83.6 m ² /g, TEM: Anatase TiO ₂ , 0.354 nm	Small and uniform TiO ₂ particles on GO sheets	97.5% of degradation of MB after 35 min	Wang et al., 2019b
	TTIP, graphite powder, algal extract (<i>C. pyrenoidosa</i>)	XRD: Anatase TiO ₂ , 10.7°, GO, Size: 50 nm TiO ₂	TiO ₂ accumulated along the wrinkles and edges of GO sheets	63% of CV removal was observed after 150 min	Sharma et al., 2018

Table 2.2: Continued

	TTIP, graphite powder, algal extract (<i>C. pyrenoidosa</i>)	XRD: Anatase TiO ₂ , 10.7°, GO, Size: 50 nm TiO ₂	TiO ₂ accumulated along the wrinkles and edges of GO sheets	63% of CV degradation was observed after 150 min	Sharma et al., 2018
Solvothermal method	TTIP, GO, glycerin	XRD: Anatase TiO ₂ , TEM: 0.351 nm, TiO ₂	TiO ₂ nanoflakes on graphene sheets, interconnected laterally	80% degradation of oxytetracycline (OTC) in 60 min	Zhen et al., 2018
	TTIP, graphite powder	XRD: Anatase TiO ₂ , 11.09°, TiO ₂ , ~5.15 – 7.25 nm, TiO ₂ /GO, ~13 – 15 nm, BET: 97.08 m ² /g, TiO ₂ /GO	Sphere-like structure of TiO ₂ distributed uniformly on wrinkled GO sheets	Complete degradation of 2,4-D after 240 min.	Natarajan et al., 2021

Table 2.2: Continued

Colloidal blending method	Commercial TiO ₂ (P25, Degussa), graphite powder	XRD: TiO ₂ , 25.5°, BET: 66.92 m ² /g, TiO ₂ /GO	Uniform dispersion/embedding of TiO ₂ between GO layers	More than 90% and 95% removal of MB under UV and visible light, respectively	Nguyen-Phan et al., 2011
	Titanium (IV) sulfate (Ti(SO ₄) ₂), graphite powder initial reactants.	XRD: Mixed of anatase and rutile TiO ₂ , crystallize size of TiO ₂ , 9 nm, 11°, GO, TEM: 10 nm, TiO ₂ /GO	Agglomerated TiO ₂ particles embedded on GO sheets	The photodegradation efficiency of MO was 87.2% after 15 min.	Zhang et al., 2011

Table 2.2: Continued

Sol-gel	Titanium (IV) isopropoxide, graphite powder	XRD: Anatase TiO ₂ , no characteristics peak of GO, crystallite size: >20 nm	Agglomerated TiO ₂ incorporated onto GO sheets	Degradation of tartrazine dye was 20% under UV radiation conditions and 63% with solar radiation.	Ramos et al., 2020
	Tetrabutyl titanate (TBOT), graphite	XRD: Anatase TiO ₂ , 10.4° and 41.7°, GO, crystallite size of TiO ₂ /GO, 12 nm	Spherical TiO ₂ loaded uniformly on a thin GO layer	Achieved 96.3% of X- 3B removal in 60 min.	Cao, 2013

2.6 Photocatalytic Performance of TiO₂/ZnS-based ternary composites

The utilization of TiO₂/ZnS binary composites is constrained by specific drawbacks, such as difficulties in transferring separated charges and the necessity for UV light (400 nm) activation (Wu et al., 2017). To address these limitations, significant scientific focus has been directed towards engineering ternary composites with modified intrinsic characteristics. Ternary composites can be defined as a composite substance formed by three distinct components or phases, and this fusion results in the creation of a composite material that possesses distinctive and exceptional properties and attributes (Hong et al., 2020). Ternary composites, as opposed to binary compounds, have a lower band gap energy, which allows OPs to be photodegraded by light sources with longer wavelengths ($\lambda > 400$ nm) and effectively inhibits electron-hole recombination (Prasad et al., 2019). The powdered forms of both binary and ternary-based TiO₂/ZnS nanocomposites face challenges such as (i) separation problems, limiting their usability in large-scale water treatments, (ii) the inclination of particles to leach and release in continuous flow systems, and (iii) the aggregation of the nanoparticles. These challenges have rendered the recovery and reusability of the composite difficult. Table 2.3 summarizes the selected studies on the photocatalytic performance of TiO₂/ZnS-based ternary composites. These studies have performed modification on TiO₂/ZnS with carbonaceous materials such as rGO, activated carbon (AC), and graphene (Maarisetty et al., 2020; Kale et al., 2020; Meng et al., 2012; Park et al., 2014).

It has been discovered that materials like carbonaceous material enhance the production of ROS and facilitate efficient electron transfer, hence increasing the photocatalytic efficacy of TiO₂/ZnS. rGO is one such substance. Visible light is more readily absorbed when carbon atoms are added to the TiO₂/ZnS structure because this

reduces the band gap. According to Maarisetty et al. (2020), rGO is a good choice for altering TiO₂/ZnS because it provides homogeneous, smooth sheets with a large surface area (Table 2.3). The resulting composite of TiO₂/ZnS/rGO exhibited a substantial surface area of 460.1 m²/g and effectively degraded 20 mg/L of MB under solar radiation.

Four cycles of photocatalytic experiments were also carried out where the results proved the composite was able to degrade MB gradually, up to 80%. Additionally, the FTIR measurements demonstrate that the catalysts did not significantly change following the fourth recycling cycle, which helps to explain the consistent photocatalytic effectiveness throughout many cycles. According to another study, ultrasonication of rGO with TiO₂ and ZnS increased the ternary composite's specific surface area and thus increased the amount of available active sites for CV adsorption (Kale et al., 2020). As a result, under UV irradiation, photodegradation of CV attained degradation rates of 97.02%, 96.34%, and 96.14% from initial concentrations of 50, 70, and 100 ppm, respectively.

In addition, by altering binary TiO₂/ZnS with activated carbon simultaneously, materials with unique features, like an exceptionally high specific surface area, can be produced by utilizing relatively inexpensive synthetic methods (Li et al., 2023). For example, when AC was added to TiO₂/ZnS, the specific surface area of the resulting ternary composite, TiO₂/ZnS-AC, increased to 52.11 m²/g, while that of pure TiO₂ was only 18.85 m²/g (Meng et al., 2012). The degradation of Rho B using TiO₂/ZnS-AC under visual irradiation produced over 70% removal within 120 min, surpassing the performance of pristine TiO₂ because of the larger specific area and more reactive sites in the former.

Numerous carbon compounds, including graphene, have positive effects on heterogeneous semiconductor photocatalytic activity because of their effective electron transport and interaction effects. TiO₂/ZnS/graphene composites were developed by Park et

al. (2014) to improve TiO₂'s photocatalytic efficiency for the degradation of MB. When exposed to visible light, graphene may produce electrons, absorb and transfer the photogenerated electrons of ZnS and TiO₂, which lowers the rate at which electron-hole pairs recombine. In comparison with ZnS/graphene composites, the degradation rate of MB with TiO₂/ZnS-graphene was roughly 16–30% greater (Table 2.3). The increased photocatalytic activity indicates that the composites absorb a substantial amount of light in the visible spectrum, and the addition of graphene increases the visible range of light absorption.

The incorporation of transition metals such as iron (Fe), copper (Cu), and bismuth (Bi) as dopants in binary TiO₂/ZnS has the effect of diminishing the rate of interfacial charge transfer while concurrently enhancing light and surface absorption capacity (Khalid et al., 2017). This is explained by a redshift of the TiO₂ band edge caused by Ti (3d) overlapping with the d levels of transition metals at the conduction band. Moreover, because Zn²⁺ tends to replace the cation site, its valence in ZnS easily accepts a variety of 3d transition metal ions. The approximately same ionic radii of host Ti⁴⁺ (0.75 Å) and Zn²⁺ (0.74 Å) ions allow Zn²⁺ ions to easily replace Ti⁴⁺ in the TiO₂ lattice without changing the crystal structure (Rauf et al., 2011). Its absorption is expanded into the visible region by this substitution. Under visible light, the ternary combination TiO₂/ZnS/Fe efficiently broke down paracetamol and Rho B dye, obtaining degradation rates of 88% and 94%, respectively (Danish et al., 2020) (Table 2.3). The addition of Fe created a new state beneath the TiO₂/ZnS composite's conduction band, resulting in greater light absorption in the longer wavelength range. Similarly, the addition of Bi as a modification to TiO₂/ZnS resulted in a considerable increase in the rate of degradation of MO dye (Dong et al., 2014) (Table 2.3). When compared to the recorded 0.0029 min⁻¹ for bare TiO₂, the degradation

rate of MO improved significantly to 0.0141 min^{-1} . Furthermore, the composite demonstrated that there was no significant decrease in photocatalytic activity even after four cycles under solar light. The stability of the photocatalytic activity in TiO_2/ZnS -Bi remained constant. The absorption edge of TiO_2/ZnS is extended into the visible spectrum by the presence of Bi. Additionally, upon exposure to irradiation, the modified ternary compound tends to accumulate electrons in the conduction band of the binary TiO_2/ZnS , with holes accumulating in the valence band of Bi. Consequently, these investigations have demonstrated that the performance of binary TiO_2/ZnS -based photocatalysts improves when doped with appropriate transition metals.

It is commonly recognized that metal sulphides, such as CdS and In_2S_3 , can effectively absorb a broad spectrum of visible and/or UV light. This characteristic is attributed to their electrical composition, charge transport capabilities, and the endurance of their excited states (Ayodhya & Veerabhadram, 2018). Mittal et al. (2019) discovered that the $\text{TiO}_2/\text{ZnS}/\text{CdS}$ ternary system effectively decomposed 99% of Rho B within 200 min under visible light (Table 2.3). Conversely, because of its large band gap, which limits its ability to absorb longer wavelengths in the visible spectrum, pure TiO_2 's photocatalytic activity was significantly decreased when exposed to visible light. Additionally, Liu et al. (2015b) observed that the ternary $\text{TiO}_2/\text{ZnS}/\text{In}_2\text{S}_3$ exhibited better responsiveness to visible light and displayed effective separation of charge carriers. Under visible light exposure, the degradation of Rho B azo dye increased from 27.2% for pure TiO_2 to 93.8% for the ternary $\text{TiO}_2/\text{ZnS}/\text{In}_2\text{S}_3$ after the metal sulphide, In_2S_3 , was added to the binary TiO_2/ZnS (Table 2.3). When comparing the influence of metal sulfide doping, In_2S_3 demonstrated a notably quicker degradation time of 80 min compared to CdS, which took 200 min (Liu et al., 2015b; Mittal et al., 2019). The distinction is that, in comparison to the ternary

TiO₂/ZnS/CdS composite, the ternary TiO₂/ZnS-In₂S₃ composite absorbs light more efficiently. In₂S₃ typically has a narrower band gap compared to CdS. A narrower band gap allows a semiconductor to absorb photons with lower energy, which corresponds to longer wavelengths in the visible spectrum. A removal efficiency of 98% for Rhodamine B was attained through three consecutive cycles using TiO₂/ZnS-In₂S₃. The hydrothermal method resulted in a highly stable ternary TiO₂/ZnS-In₂S₃ photocatalyst suitable for practical applications.

Nevertheless, integrating carbonaceous materials, metal oxides, and metal sulfides can lead to significant expenses, while the chemical synthesis procedure might require sophisticated equipment, rendering these modifications impractical and economically unfeasible (Al Jitan et al., 2020). Moreover, using such altered TiO₂/ZnS is not recommended for wastewater treatment facilities striving to generate purified water, as it can give rise to issues such as photocorrosion, pollution, and the release of metals into the treated water through leaching (Liu et al., 2015b). Lastly, recycling studies can be complicated, requiring systematic investigations into the degradation, regeneration, and performance changes of the material over multiple cycles. Thus, challenges in developing effective recycling processes might contribute to the lack of studies.

Table 2.3: Selected studies of TiO₂/ZnS-based ternary composites for dye removal.

TiO ₂ /ZnS-based ternary composites	Synthesis method	Pollutant	Parameters used	Removal efficiency (%)	Recyclability efficiency (cycles)	References
TiO ₂ /ZnS-rGO	Solvothermal method	Methylene blue (MB)	Catalyst: 15 mg [MB]: 20 mg/L Irradiation time: N/A Light source: 80 min	Achieved a complete removal of MB under solar sunlight after 80 min	>80% removal after 4 cycles under sunlight	Maarisetty et al., 2020
TiO ₂ /ZnS-rGO	Ultrasound-assisted method	Crystal violet (CV)	Catalyst: 0.4 mg [MB]: 50 mg/L	Almost 97% of CV was removed after 80 min	N/A	Kale et al., 2020

Table 2.3: Continued

Irradiation time: 50 min						
Catalyst: 0.01 g/L						
[Rho B]: 1×10^{-5} mol/L						
TiO ₂ /ZnS/AC	Sol-gel method	Rhodamine B (Rho B)	Irradiation time: 2 h	Removed 70% of Rho B dye after 2 h	N/A	Meng et al., 2012
Light source: Visible light						
Catalyst: 0.01 g						
TiO ₂ /ZnS-graphene	Sol-gel method	Methylene blue (MB)	[MB]: 0.355 mg/L Irradiation time: 150 min	Removed 90% of MB after 150 min	N/A	Park et al., 2014

Table 2.3: Continued

Light source:						
Visible light						
TiO ₂ /ZnS/Fe	Ultrasound-assisted method	Rhodamine B (Rho B)	Catalyst: 1.0 g [Rho B]: 10 mg/L Irradiation time: 75 min Light source: Visible light	Achieved 94% of Rho B removal during 75 min irradiation	N/A	Danish et al., 2020
TiO ₂ -ZnS-Bi	Sol-gel method	Methyl orange (MO)	Catalyst: 0.4 g [MO]: 20 mg/L Irradiation time: 120 min Light source: UV light	Degradation rate of 0.0141 min ⁻¹ for MO after 120 min	The rate of degradation, 0.0141 min ⁻¹ remained the same after 4 cycles under solar light	Dong et al., 2014

Table 2.3: Continued

TiO ₂ /ZnS-CdS	Hydrothermal method	Rhodamine B (Rho B)	Catalyst: 50 mg [Rho B]: 4.10 mg/L Irradiation time: 140 min Light source: UV light	Increasing degradation efficiency of Rho B under visible light: > 99% after 140 min	N/A	Mittal et al., 2019
TiO ₂ /ZnS-In ₂ S ₃	Hydrothermal method	Rhodamine B (Rho B)	Catalyst: 10 mg [Rho B]: 10 mg/L Irradiation time: 120 min Light source: Visible light	Achieved nearly 100% removal after 80 min under visible light	98% removal after 3 cycles	Liu et al., 2015b

2.7 Photocatalytic Performance of TiO₂/GO-based ternary composites

Graphene, a material renowned for its unique electronic properties, consists of six carbon atoms forming a flat hexagonal lattice with a honeycomb architecture through sp² hybridization (Draper et al., 2022). Currently, graphene can be produced as a single sheet or multiple layers using various methods. The most common approach involves the chemical exfoliation of graphite, which introduces oxygen functional groups and leads to the development of GO due to its cost-effectiveness and ease of use. GO has been used in conjunction with TiO₂ to improve MB's photocatalytic degradation in aqueous solutions. The enhanced photodegradation performance is a result of GO's exceptional properties, which include its large surface area, strong mechanical strength, superior thermal stability, and effective electron transport capabilities. In the case of the TiO₂/GO composite, it achieved nearly complete MB degradation in approximately 4 hours, a feat that could not be achieved using TiO₂ alone (Kurniawan et al., 2020). Nonetheless, it is noteworthy that the degradation process for a ternary composite does not necessitate an extended duration. For instance, the TiO₂/GO/WO₃ composite exhibits superior absorptivity and photocatalytic activity compared to TiO₂, achieving approximately 80% degradation within 60 min (Liu et al., 2018). The addition of WO₃ quantum dots effectively served as electron receptors preventing the recombination of electrons and holes, thereby broadening the TiO₂'s capacity to respond to visible light irradiation. Moreover, an additional investigation indicated that TiO₂/Ag₃PO₄@GO displays high responsiveness to visible light, as evidenced by its small band gap (2.36 eV) and photoluminescence (PL) analysis, which demonstrates a consistent decrease in the probability of electron-hole pair recombination (Al Kausor, M., & Chakraborty, 2020). Figure 2.8 (a) illustrates the proposed photodegradation mechanism by the ternary TiO₂/Ag₃PO₄@GO composite which

was mainly driven by visible light irradiation. The composite showed an outstanding photocatalytic efficiency with no discernible decline after five recycles, in contrast to the bare Ag_3PO_4 . The structure of $\text{TiO}_2/\text{Ag}_3\text{PO}_4@\text{GO}$ has no visible structural changes in morphology and particle size as shown by the TEM micrograph (Figure 2.8(b)). The recyclability of $\text{TiO}_2/\text{Ag}_3\text{PO}_4@\text{GO}$ has a critical aspect that determines its practical feasibility and sustainability in various applications.

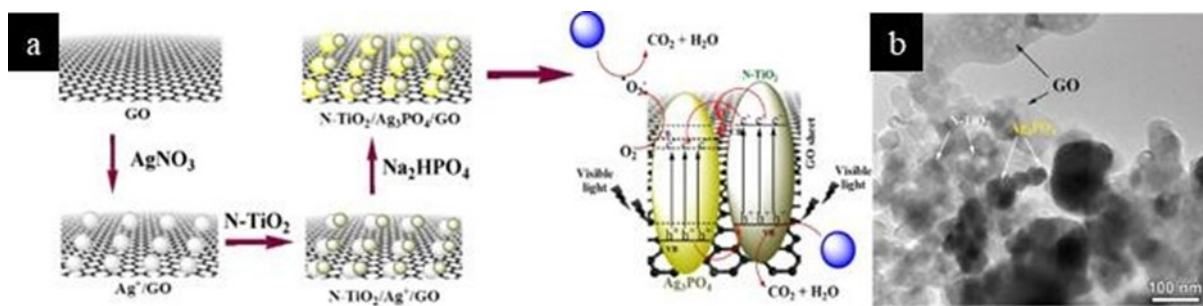


Figure 2.8: (a) Proposed photodegradation mechanism of $\text{TiO}_2/\text{Ag}_3\text{PO}_4@\text{GO}$ and (b) TEM micrograph of the recycled $\text{TiO}_2/\text{Ag}_3\text{PO}_4@\text{GO}$ composite (Source: Al-Kausor and Chakraborty, 2020).

Furthermore, the considerable specific surface area of GO and enhanced electron mobility make it viable to develop a ternary catalyst with a high photodegradation rate through its integration with another composite. For example, Kaur and Kaur (2019) employed a simple ultrasonication technique to fabricate $\text{MgFe}_2\text{O}_4\text{-TiO}_2\text{NPs}@\text{GO}$. This composite exhibited enhanced efficacy in the degradation of MB under UV light compared to the MgFe_2O_4 composite. The notable factors contributing to the disparities in photocatalytic activity were identified as its greater surface area and distinctive nanostructure. Another study which reported an enhancement in the photocatalytic activity of TiO_2/GO involved the fabrication of $\text{TiO}_2/\text{CuO}/\text{GO}$ (Noor et al., 2020). Based on the increased surface area of the composite, it was discovered that the ternary composite had greater photocatalytic activity in the degradation of MO than single and binary composites.

The enhanced photocatalytic activity of the nanocomposite was caused by its mesoporous structure and comparatively large surface area, which promoted the interaction between photogenerated radicals and MB dye molecules (Wang et al., 2015). The recombination rate of photogenerated charge carriers leads to the development of oxygen vacancies, which can be attributed to the reduced form of CuO and the π electrons of GO. Thus, the formation of TiO₂ heterojunction with other binary semiconductors heterojunction would be a suitable method to maximize its environmental applications.

Most research concerns specifically focus on the behaviour and removal of individual dyes instead of the simultaneous removal of dyes. For instance, Rosu et al. (2017) investigated the photodegradation of azo dyes (amaranth, SY and tartrazine) using TiO₂-Pt/rGO under UV and natural sunlight irradiation. Comparatively, amaranth (99.56%) showed faster removal of degradation than SY (99.15%) and tartrazine (96.23%). The aromatic groups (benzene and naphthalene) of dyes are linked to sulphonic groups (SO³⁻), which make the dyes more soluble in water and encourage the interaction of dye molecules with hydroxyl radicals, which improves photocatalytic activities. Moreover, azo dyes with anionic groups exhibit a negative charge in solution, a result of the hydrolysis of sulfonic groups (Anku et al., 2016). Consequently, in an acidic environment, electrostatic interactions may occur with the positively charged surface of TiO₂. The pH level of the solution containing the organic dye affects the catalyst's ability to degrade. As an example, the TiO₂/Cr₂S₃/GO heterojunction showed superior photocatalytic activity compared to MO (86.3%) in the degradation of MB (98.3%) and Rho B (96.6%) (Hasan et al., 2020). Changes in pH affected the surface electric charge of TiO₂, which in turn affected the organic dye's ability to adhere to the TiO₂ surface. This in turn affected the rate of

elimination and caused fluctuations in the photocatalyst's degrading performance (Kumar and Pandey, 2017).

The mechanism of TiO₂/GO-based ternary composites has been illustrated in several studies (Jo et al., 2017; Kaur and Kaur, 2019; Al-Mamun et al., 2021; Hasan et al., 2020). Figure 2.9 illustrates the mechanism of TiO₂/Cr₂S₃/GO composite in degrading OPs of MB, Rho B, and MO (Hasan et al., 2020). The catalyst generates electron-hole pairs and becomes active when exposed to light. The superoxide radicals $\bullet\text{O}_2^-$ are formed when the electrons react with adjacent O₂ atoms. In addition, additional electrons, superoxide ions, and $\bullet\text{OH}$ radicals are produced when light is absorbed by the GO surface. Dyes decompose into CO₂ and H₂O when OH⁻ and $\bullet\text{OH}$ radicals are present. The resulting nanocomposite exhibited enhanced photocatalytic activity and a higher photodegradation rate, achieving 98.3%, 96.6%, and 86.3% degradation of MB, Rho B, and MO, respectively, in 120 min under visible light irradiation. These results outperformed those of Cr₂S₃/GO and TiO₂ photocatalysts. The synergistic effect of Cr₂S₃ and GO significantly contributes to the enhanced photoactivity of TiO₂, making it a promising solution for pollutant degradation and creating a contaminant-free water environment. Furthermore, Liu et al. (2017) discovered that the RGO/Ag₂S/TiO₂ nanocomposite significantly enhanced the photoresponsiveness of reduced graphene when combined with Ag₂S. The results were contrasted with the separate applications of Ag₂S and Ag₂S/TiO₂. Among these, the composite containing 3% by weight of rGO, Ag₂S, and TiO₂ displayed the most amazing photocatalytic performance under both UV and near-infrared (NIR) light. The reason for this improvement was a greater distance between electron-hole pairs (Liu et al., 2017). Impressively, it only took 30 min to achieve 98.5% degradation of MB, signifying efficient photocatalytic activity.

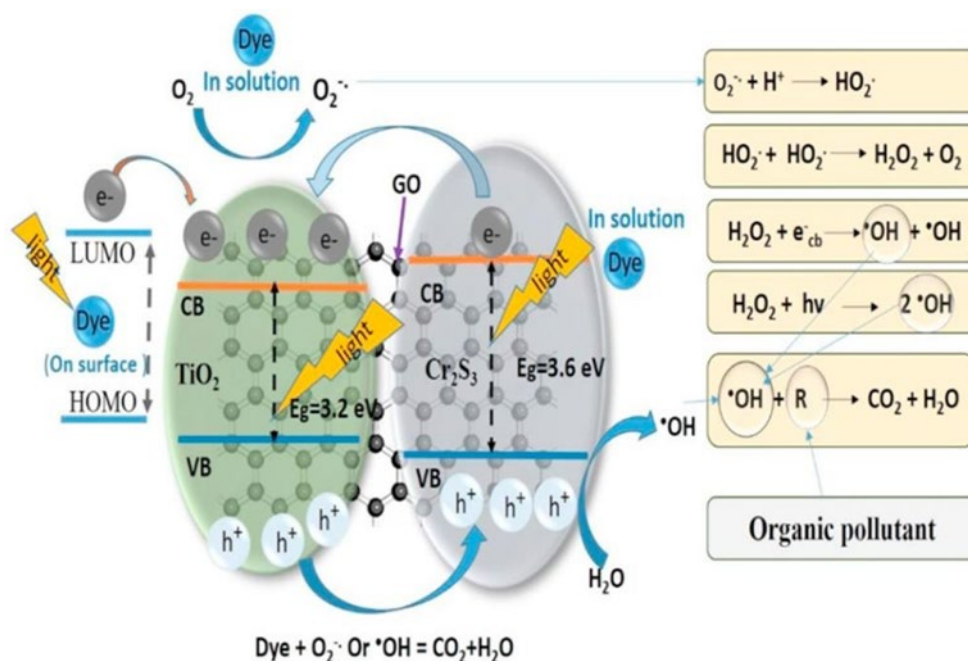


Figure 2.9: Mechanism of the TiO₂/Cr₂S₃/GO photocatalyst to degrade OPs (MB, Rho B, and MO) (Source: Hasan et al., 2020).

2.8 Immobilization of TiO₂-based materials on Alginate

Alginate (Alg) is a naturally occurring polysaccharide derived from brown seaweed. The chemical structure of Alg is made up of 1,4-linked β -D-mannuronic acid (M) and 1,4 α -L-guluronic acid (G) residues, as depicted in Figure 2.10. These residues can be paired in different ways to create different types of Alg with distinct properties (Wang et al., 2019a). Due to its special properties, including biocompatibility, biodegradability, and gel-forming ability, Alg is widely used in a range of industrial, biomedical, and environmental applications, including wastewater treatment and pollutant degradation. The abundant surface functional groups (e.g., carboxyl and hydroxyl) in Alg have the potential to trap cationic ions via ion exchange between the crosslinking cations and target contaminants such as dyes (Raus et al., 2021).

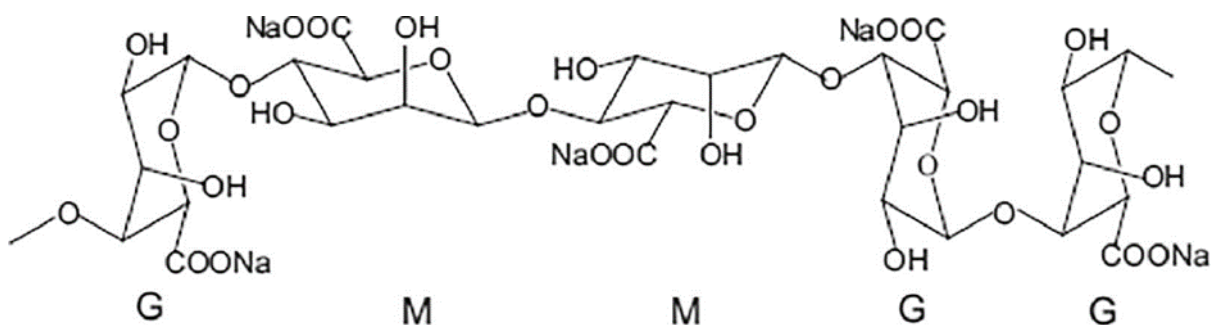


Figure 2.10: Chemical structure of alginate composed of 1,4-linked β -D-mannuronic acid M and 1,4 α -L-guluronic acid G residues. (Source: Wang et al., 2019a).

Gong et al. (2021) synthesized GO-P25@Sodium alginate (SA) beads, which demonstrated increased UV light degrading activity of Rho B. The hybrid nanostructures combining GO and TiO_2 have excellent photocatalytic capacity due to their synergistic effects in reducing the recombination of photo-generated electron-hole pairs, improving the charge transfer rate, and increasing surface adsorption molecules. SA provided a larger surface area, which produced high adsorption capacity and superior conductivity of GO-P25@SA. The combination of components in this composite exhibited remarkable efficiency in degrading Rho B. Throughout the reaction, the crucial species involved were O_2 and $\cdot\text{O}_2^-$. This research highlights the distinctive advantages of utilizing GO and SA to create a functionalized photocatalyst, offering an affordable and easily recyclable approach to removing organic dyes.

Although research on TiO_2/ZnS and TiO_2/GO alginate-based ternary composites is limited, Alg is a significantly promising material used for the removal of heavy metals, liquid wastes from textiles, and other pollutants that can be utilised with other composites, making it useful in eliminating various water pollutants. It uses reaction mechanisms such as electrostatic attraction and chelating gels to improve the adsorption characteristics of a variety of contaminants (Benettayeb et al., 2022). This natural biopolymer can be

employed in nanomaterial hydrogels to treat both inorganic and organic aqueous solutions effectively.

2.9 Parameters affecting photocatalytic degradation

2.9.1 Dosage of photocatalyst

Several studies have been conducted to investigate the influence of photocatalyst dosage on the photocatalytic degradation of dyes in wastewater (Al-Mamun et al., 2021; Potle et al., 2020; Kale et al., 2020; Rajamanickam & Shanthi, 2016). The efficacy of photocatalytic degradation can be impacted by the quantity of photocatalyst used in the treatment. Generally, an increase in the dosage of photocatalysts results in an overall improvement in the photocatalytic degradation process. This phenomenon is attributed to the higher number of active sites available for pollutants to be adsorbed and subsequently degraded by $\bullet\text{OH}$ radicals. However, when the quantity of active sites becomes saturated with pollutants to a certain extent, there is a possibility that the photodegradation rate could decrease. This reduction may occur because the excessive pollutant load inhibits the penetration of light through the photocatalyst.

For instance, a study reported that photocatalytic elimination of MO dye using $\text{TiO}_2/\text{GO}/\text{Ag}$ nanocomposite resulted in increased removal percentages from 43.67% to 97.67% as the doses increased (0.025 – 0.1 g) (Al-Mamun et al., 2021). The enhancement stems from the creation of numerous sites because of the absorption of dye molecules and photons, consequently boosting the photocatalytic performance (Kurniawan et al., 2020; Shende et al., 2018). A similar trend was discovered in another investigation. The degradation rate rose from 70.70% to 89.63% when the loading of $\text{TiO}_2\text{-ZnO-rGO}$ was

raised from 0.02 to 0.2 g/L over 20 min (Potle et al., 2020). This is related to an increase in TiO₂-ZnO-rGO particle density, which aids in contaminant adsorption and photoelectron absorption. Furthermore, when concentration increases, more active sites on the photocatalyst's surface become available, leading to an increase in ROS production and, as a result, increased CV dye degradation performance.

However, exceeding the optimal level of photocatalyst dosage results in a decline in the removal rate. For instance, the degradation increased from 94.38% to 97.02% when the TiO₂- ZnS-rGO catalyst was raised from 0.3 g/L to 0.4 g/L. Nevertheless, increasing the loading of the TiO₂-ZnS-rGO nanocomposite to 0.5 g/L led to a marginal decrease in degradation, reaching 96.30% and indicating a saturation point in the photocatalytic treatment (Kale et al., 2020). Another investigation revealed that a photocatalyst dosage of more than 250 mg did not affect the photocatalytic activity of SY (Rajamanickam & Shanthi, 2016). An excessive number of catalysts used during photocatalytic treatment may cause significant turbidity and raise the risk of nanoparticle agglomeration. This will impede the penetration of photons, causing a slowdown in the process of photocatalytic degradation (Pouretedal et al., 2016).

2.9.2 Concentration of dye

The effectiveness of a photocatalyst in eliminating pollutants can be enhanced through the adsorption of the pollutant molecules onto its surface. Pollutant adsorption is proportional to the initial concentration of pollutants in the solution (Okab et al., 2023). As a result, the initial pollutant concentrations exert an influence on the photodegradation process. The pollutants adhere to the surface rather than being dispersed throughout the solution's bulk

(Akeremale et al., 2023). Elevated pollutant concentrations can increase water turbidity and mask a larger number of active sites. This, in turn, diminishes the photon exposure to the surface and subsequently reduces the production of $\bullet\text{OH}$ radicals, ultimately causing the degradation efficiency to decline (Kong et al., 2022).

Reza et al. (2017) discovered that the degradation rate is determined by the generation of $\bullet\text{OH}$ radicals on the catalyst surface and the reactivity with dye molecules. As the initial amount of dye was increased, more dye molecules became available for excitation and energy transfer. This association is most likely connected to the production of numerous monolayers of the adsorbed dye on the photocatalyst's surface, which is preferred at high dye concentrations. For example, Dhatshanamurthi et al. (2014) discovered that using the binary TiO_2/ZnS photocatalyst reduces the degradation rate constant from 0.1107 min^{-1} to 0.0203 min^{-1} while increasing the concentration of phenol red sodium salts dye from $2 \times 10^{-4} \text{ M}$ to $6 \times 10^{-4} \text{ M}$. Several factors can be attributed to this decrease pattern. The quantity of $\bullet\text{OH}$ radicals generated on the binary photocatalyst's surface dictates the degradation rate. Lower photon penetration into the solution during photocatalytic degradation is caused by higher initial concentrations of phenol red, which lowers the generation of $\bullet\text{OH}$ radicals. Conversely, lower initial dye concentrations lead to enhanced photon absorption, yielding a greater generation of $\bullet\text{OH}$ radicals.

2.9.3 Solution pH

The pH of the solution has a significant influence on the photocatalytic degradation of organic pollutants because it determines the surface charge of the catalyst and the size of aggregations. Understanding how pH affects photodegradation efficiency is extraordinarily

complex due to the presence of three potential reaction mechanisms that could result in dye decolorization — hydroxyl radical attack, direct oxidation by the positive hole, and direct reduction by the electron in the conducting band. The extent to which each process contributes can be influenced by substrate type and pH levels (Reza et al., 2017).

Pinto da Costa et al. (2015) demonstrated that the TiO₂/ZnS binary composite achieves complete Safranin-T elimination under solar light at pH 6.2, which is close to neutral. The choice of this pH proves that higher pH levels enhance dye molecule adsorption but also hinder light penetration to the composite surface, thereby diminishing photodegradation. Likewise, Mittal et al. (2019) observed that the ternary TiO₂/ZnS/CdS composite demonstrated superior degradation under acidic conditions with a pH of 3. This is primarily due to the significant impact of carboxyl acid group-based physisorption on positively charged TiO₂, which initiates the photosensitization process by injecting charge (Merka et al., 2011). Thus, in the presence of visible light, the ternary TiO₂/ZnS/CdS composite achieves over 99% Rho B degradation, displaying excellent Rho B degradation under acidic conditions (Mittal et al., 2019). Thus far, studies have reported that TiO₂/GO and TiO₂/ZnS-based photocatalysts exhibit optimal performance within slightly acidic to neutral environments (Labiadh et al., 2014; Mittal et al., 2019; Al Kausor et al., 2020). This is presumably due to the positive charge on the photocatalyst's surface, which aids in the adsorption of negatively charged OPs.

2.9.4 Presence of radical scavengers

Research has examined how several radical scavengers, including •OH, •O₂⁻, and h⁺, contribute to the degradation of OPs when used with TiO₂/ZnS and TiO₂/GO-based

photocatalysts. The objective is to discover more concerning the photocatalytic mechanism and the roles of these active species. Commonly employed radical scavengers include substances such as isopropyl alcohol (IPA), tert-butyl alcohol (t-BuOH), and methanol as scavengers for $\bullet\text{OH}$ radicals; EDTA as a scavenger for h^+ ; and benzoquinone (BQ) as a scavenger for $\bullet\text{O}_2^-$ radicals.

In the context of a photocatalytic setup involving $\text{TiO}_2/\text{ZnS}/\text{In}_2\text{S}_3$, the introduction of EDTA and t-BuOH led to a decrease in Rho B degradation to 92.4% and 89.7%, respectively, in comparison to complete degradation in the absence of scavengers. This suggests that both $\bullet\text{O}_2^-$ and h^+ played a significant role in influencing the dye degradation rate (Liu et al., 2015c). Liu et al (2016) revealed that h^+ and $\bullet\text{OH}$ radicals are the most prominent for $\text{TiO}_2/\text{graphene}$ in the degradation of naphthenic acids as the main attribution was due to the photogenerated holes in TiO_2 surface rather than the electrons transferred to graphene sheets. When using the $\text{TiO}_2/\text{ZnS}/\text{CdS}$ photocatalyst, Mittal et al. (2019) discovered that the presence of EDTA had a negligible impact on the rate of photodegradation of Rho B. On the other hand, the degradation rates of Rho B were considerably reduced when IPA and BQ were used as $\bullet\text{OH}$ and $\bullet\text{O}_2^-$ scavengers. This indicates that both $\bullet\text{OH}$ and $\bullet\text{O}_2^-$ radicals primarily acted as the major active species in the photocatalytic degradation process, in contrast to h^+ . The rate was found to inhibit the degradation rate from 94 to 51% when BQ ($\bullet\text{O}_2^-$ scavenger) was used. This suggests that in the presence of $\text{TiO}_2/\text{ZnS}/\text{Fe}$, the superoxide radical anion is the primary reactive species causing photooxidation. However, other studies showed that IPA exhibits any restraining effect on the degradation of AB 25 using $\text{TiO}_2/\text{Ag}_3\text{PO}_4@\text{GO}$. Al-Kausor and Chakraborty, 2020 revealed that both h^+ and $\bullet\text{O}_2^-$ radicals significantly control the photodegradation

rather than the $\bullet\text{OH}$ radicals. The $\bullet\text{O}_2^-$ and the resulting holes intentionally degrade organic dye or phenol due to their enhanced oxidizing ability.

2.10 Model Pollutants

2.10.1 Dyes

Dye pollutants produced in industrial wastewater garner a lot of attention because of their colour and toxicity. Their disposal has caused major contamination in several countries throughout the world. Even minute quantities of dye contaminants (as little as 1 ppm for some dyes) are regarded as an important class of contaminants in wastewater because they may be visually recognised in water by human eyes (Shakoor & Nasar, 2016). Over 10,000 commercially available dyes are inevitably used in a variety of industries, including dyestuffs, textiles, paper, plastics, rubber, cosmetics, tanneries, paints, and leather (Peng et al., 2016). Around 7×10^7 tonnes of synthetic dyes are generated worldwide each year, with over 10,000 tonnes of such colours used by the textile industry (Al-Tohamy et al., 2022). The dyes produced by the 151 industries pose significant harm to aquatic life species (Al-Tohamy et al., 2022). Furthermore, colours may cause gastrointestinal discomfort, nausea, vomiting, diarrhoea, and irritation in people and animals (Shakoor & Nasar, 2016). In this study, MB, Rho B and MO are selected as the model pollutants due to their large consumption in various industries (Figure 2.11).

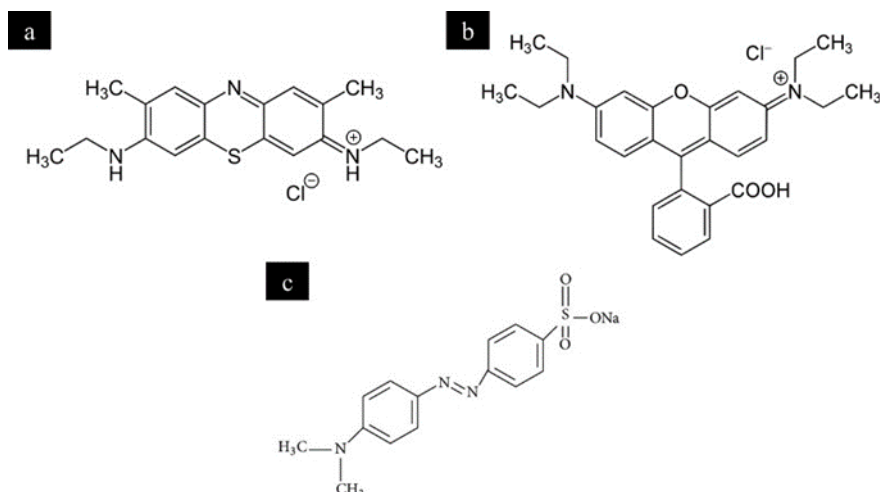


Figure 2.11: Chemical structures of (a) Methylene blue, (b) Rhodamine b, (c) Methyl orange.

2.10.1.1 Methylene blue

The chemical formula of MB is $\text{C}_{16}\text{H}_{18}\text{N}_3\text{ClS}$, and its maximum absorption wavelength is 663 nm. When paired with water at room temperature, it forms a stable solution because of its high-water solubility (Sabar et al., 2020). MB is a positively charged molecule that corresponds to the polymethine dye class and has an amino autochrome unit (Anushree and Philip, 2019). When oxidised, MB has a characteristic deep blue colour and when reduced, it is colourless; leucoMB (Kazemi et al., 2016). The chromophoric and auxochrome groups determine the colour of MB. The chromophore group of MB is the N-S conjugated system in the core of the aromatic heterocycle, whereas the auxochrome group contains N-containing groups with lone pair electrons on the benzene ring (Yang et al., 2017).

Because of the potential negative effects on water quality, addressing the treatment of wastewater containing MB dye prior to discharge into the environment is critical. Numerous methods for removing MB and other textile dyes from industrial effluent have been documented. Adsorption/biosorption (Hameed & Lin, 2020; Li & Yin, 2020),

phytoremediation (Imron et al., 2019), coagulation (Liu et al., 2015c), electrocoagulation (Tir et al., 2015), liquid-liquid extraction (El-Ashtoukhy & Fouad, 2015), ultrafiltration (Kim et al., 2020), nanofiltration (Kong et al., 2019), hybrid systems (Naresh et al., 2021; Sun et al., 2020), and other processes are examples of removal techniques that have been applied for MB removal. Conventional methods face challenges in breaking down MB dye into smaller inorganic molecules due to its resilience to heat and light, as well as its non-biodegradable nature (Liu et al., 2019). Each of these treatment procedures has advantages and disadvantages in terms of cost, feasibility, efficiency, and environmental impact.

For example, advanced oxidation methods (AOPs) were developed to remove dangerous organic pollutants such as MB by leveraging effective redox reactions that generate specific radicals while avoiding the generation of any other harmful chemicals. Various AOPs have been utilized for the photodegradation of MB, including ozonation (Athikoh et al., 2020), UV/H₂O₂ oxidation (Mohammed et al., 2021), electrochemical oxidation/degradation (Jawad and Najim, 2018), catalytic oxidation (Guergueb et al., 2020), heterogeneous photo-Fenton (Choquehuanca et al., 2021), and photocatalytic degradation (Dzinun et al., 2020). Ozonation has a number of disadvantages, including ozone's low solubility in water, increased energy requirements, and the creation of toxic byproducts (Khan et al., 2020). H₂O₂ exhibits poor UV light absorption characteristics, resulting in inefficient utilization of the light input. In the Fenton process, a major drawback is the generation of sludge containing iron hydroxide as a byproduct (Krishnan et al., 2017). The high operational expenses of the electrochemical process stem from significant energy consumption, posing a limitation (Nidheesh et al., 2020). Among various AOP methods, photocatalytic degradation techniques are frequently utilized for the removal of MB. Innovative approaches in photocatalytic degradation include hybrids or

integration with processes like sonocatalysis (Balakumara & Saravanathamizhan, 2016), nanofiltration (Naresh Yadav et al., 2021), adsorption (Sandoval et al., 2017), and biodegradation (Xiong et al., 2020). These integrated methods have demonstrated greater efficiency compared to individual processes alone.

2.10.1.2 Rhodamine B

The textile industry typically uses Rho B dye, a water-soluble dye, to colour wool clothing. Moreover, Rho B is widely used in biomedical research across a variety of industries, including paper, plastic, printing, biomedical, and leather, as a colouring agent, photosensitizer, water tracer, fluorescent marker for microscopic structural investigation, and biological stain (Tuzen et al., 2018; Chen et al., 2012b; Merouani et al., 2010). Hence, it is frequently found in the effluents released by these sectors of the economy. Rho B, an amphoteric dye that is a member of the xanthene dye class, is notable for being one of the first synthetic dyes used in the food and textile sectors. It is also regarded as one of the least environmentally hazardous xanthene basic dyes (Al-Gheethi et al., 2022). Rho B is defined as N-[9-(ortho-carboxyphenyl)-6-(diethylamino)-3H-xanthen-3-ylidene] diethyl ammonium chloride in IUPAC nomenclature. At 554 nm, it exhibits the maximum absorbance and has a molecular weight of 479.02 g mol⁻¹ (Üner et al., 2017). It is a basic red dye that dissolves easily in water and can be extracted in a dissolved state using butanol or ethanol. Usually, xanthene molecules' amino groups are modified to create Rho B through a process that merges the units to create a glycosidic bond (Singh et al., 2020). The molecular formula for Rho B is typically C₂₈H₃₁ClN₂O₃. The open/fluorescent Rho B form and the closed/nonfluorescent spirolactam form are in equilibrium in a neutral state. Yet, in basic conditions, the preference is for the closed, colourless form, while under acidic conditions, the open form is favoured (Birtalan et al., 2011).

The fact that Rho B is widely used in enterprises that discharge inadequately treated wastewater into the environment implies its presence in aquatic ecosystems is predictable. The introduction of Rho B into water has been associated with a variety of environmental issues and presents potential health hazards to both humans and animals. Even at relatively low concentrations (about 1.0 mg L^{-1}), it imparts a significant colour to the water, rendering it unfit for home use and eating (Adegoke et al., 2022). The presence of Rho B in surface water has a substantial impact on aquatic species by reducing light penetration to algae and other plants in the water, hence impeding photosynthesis. According to Kooh et al. (2016), Rho B is poisonous to *Cyprinodon variegatus* at a lethal dosage of 84 mgL^{-1} . Furthermore, Rho B can induce ocular damage, inflammation, and severe oral noxiousness in people (Adegoke et al., 2022). The ingestion of Rho B exposes individuals to additional risks. According to scientific evidence, Rho B is both mutagenic and carcinogenic, causing developmental and reproductive harm in both animals and humans (Ajiboye et al., 2021).

To address the problem of water pollution caused by the presence of Rho B dye, several wastewater treatment technologies for decolorization and degradation of Rho B in water have been examined. Methods based on physical, biological, or chemical principles are among the treatment choices. The adsorption technique, which is both affordable and environmentally benign, is a prime example of one of these treatment possibilities. Despite its limits, research questions in this sector are continually increasing, and adsorbent selection is evolving. Recently, there has been a major focus on improving adsorption processes by utilising membrane separation technologies. Wang et al. (2021) studied the removal of Rho B via an adsorptive membrane composed of graphene oxide-polydopamine connected with a polyether sulfone-sulfonated polyether sulfone membrane.

Chemisorption was discovered to be the adsorption method, and the composite material had an exceptional adsorption capacity of 26.34 mg g⁻¹. Similarly, Gharbani and Mehrizad (2022) extracted Rho B using an adsorptive membrane in another study. A graphitic carbon nitride, chitosan, and polyvinylidene fluoride composite was employed. Rho B had a maximum adsorption capacity of 33.46 mg g⁻¹, equating to 72.74% dye elimination. However, due to the inherent limitations of the adsorption process, various wastewater treatment options are being investigated, particularly with better oxidation procedures.

2.10.1.3 Methyl orange

The IUPAC abbreviation Orange III dye is sodium 4-[(4-dimethylamino) phenyldiazenyl] benzenesulfonate. MO is a synthetic azo dye that is widely used as a colouring additive in the textile and leather industries (Znad et al., 2018). It is widely used in the printing, paper, pharmaceutical, and food processing industries, as well as research facilities (Bhowmik et al., 2015; Sejie & Nadiye, 2016). MO is also used as an indication in coulometric methods for measuring fenoterol in the presence of various anti-asthmatic medications and kinetic assay methods for cyproheptadine in pharmaceutical firms, according to Znad et al. (2018). MO is a carcinogenic water-soluble azo dye that can be acidic or anionic. It has the potential to produce nausea and diarrhoea. High levels of MO exposure can lead to death (Eljiedi & Kamari, 2017). Intestinal microbes also convert it to aromatic amines. MO poses challenges for removal from aqueous solutions using conventional water filtration or treatment methods, given its stability, limited biodegradability, and water solubility.

MO dye has the chemical formula C₁₄H₁₄N₃O₃SNa and a molecular weight of 327.33 g/mol. MO dye has an absorption spectrum with a typical wavelength of 465 nm. It decomposes into a non-biodegradable alkaline organic pollutant. MO exists in its basic

form when dissolved in an aqueous solution. Conversely, as the solution becomes more acidic, protonation occurs, causing a colour change from yellow (alkaline) to red (acidic) (Jalil et al., 2010). The presence of the azo group ($\text{N}=\text{N}$) and its low biodegradability raise environmental concerns. It was observed that extensive research on the adsorption of MO was chosen as the adsorbate in this investigation because of its usefulness as a dye and pH indicator.

CHAPTER 3

MATERIALS AND METHODS

3.1 Materials and reagents

2-Propanol (C_3H_8O), methanol (CH_3OH), and hydrochloric acid (HCl) (37%) of reagent grades were purchased from Merck. Alginic acid sodium salt powder (NaAlg), calcium chloride dihydrate $\geq 99.0\%$ ($CaCl_2 \cdot 2H_2O$), graphite powder, phosphoric acid ACS reagent $\geq 85\%$ in H_2O (H_3PO_4), potassium permanganate ACS reagent ($KMnO_4$), titanium (IV) butoxide reagent 97% ($Ti(OC_4H_9)_4$), zinc sulfide 95.0% (ZnS), and p-benzoquinone $\geq 98\%$ ($C_6H_4O_2$) were all acquired from Sigma-Aldrich (USA). Hydrogen peroxide 30% (H_2O_2) was purchased from HmbG Supplies while sulphuric acid ACS reagent (H_2SO_4) was supplied by JT Baker. Methylene blue (MB) (82%), Methyl orange (MO) (85%) and Rhodamine B (Rho B) (95%) dyes were purchased from Sigma-Aldrich (USA).

3.2 Synthesis of TiO_2 and GO composites

TiO_2 was synthesized using the sol-gel method following the procedure reported by Kanakaraju et al. (2017). Initially, a solution containing 15 mL of $Ti(OC_4H_9)_4$ and 30 mL of C_3H_8O was stirred continuously for 20 minutes. Subsequently, 100 mL of distilled water (DI) was added dropwise into the mixture, followed by an additional 2 hours of stirring. The resulting mixture was filtered and dried in an oven at $100^\circ C$ for 2 hours. Finally, the composite was left at room temperature and then calcined for 5 hours at $300^\circ C$ using a furnace.

GO was synthesized by adapting Hummer's technique with graphite powder (Zaaba al., 2017). Solutions of 27 mL of H_2SO_4 and 3 mL of H_3PO_4 with a volume ratio of 9:1 were continuously mixed and agitated for several minutes (~20 min). Then, 0.225 g of graphite powder was added to the mixture under stirring conditions followed by 1.32 g of KMnO_4 . The solution was stirred for 6 hours until it turned dark green. To remove the excess KMnO_4 , 0.675 mL of H_2O_2 was added dropwise and the solution was constantly agitated for 10 minutes. The addition of H_2O_2 caused an exothermic reaction and the solution was left to cool down at room temperature. Subsequently, 10 mL of HCl and 30 mL of deionized water (DIW) were added to the reaction mixture, and it was subsequently centrifuged at 5000 rpm for 7 min. The supernatant was then decanted, and the residue was taken out and rewashed three times with the same amount of HCl and DIW as previously mentioned. To generate GO, the cleaned GO solution was dried in an oven at 90°C for 24 hours.

3.3 Synthesis of $\text{TiO}_2/\text{ZnS}/\text{GO}$ composites

To synthesize the binary TiO_2/ZnS photocatalyst, 1 g of TiO_2 and 1 g of ZnS were sonicated in 100 mL of DI for 1 hour. However, in the case of TiO_2/GO and ZnS/GO binary composites, GO was first sonicated for 1 hour before being mixed into TiO_2 or ZnS in 100 mL of DI, respectively. Using a Teflon vessel, all binary composites were heat treated for 5 hours at 180°C in a furnace. Finally, the binary composite mixtures were filtered and dried in an oven at 100°C for 2 hours.

To synthesize the $\text{TiO}_2/\text{ZnS}/\text{GO}$ (1:1:1) composite, 1 g of GO and 100 mL of distilled water (DI) were first sonicated for 1 hour. Then, 1 g of TiO_2 and 1 g of ZnS were

added to the GO solution. The solution was sonicated for 1 hour and stirred continuously for another 1 hour. The mixture was then added to the Teflon vessel and subjected to heat treatment at 180 °C in the furnace for 5 hours. Finally, the mixture was filtered and dried in an oven at 100 °C for 2 hours. The procedures were repeated by varying the desired amounts needed to prepare the TiO₂/ZnS/GO (1:2:1) and TiO₂/ZnS/GO (2:1:1) composites. Figure 3.1 summarizes the synthesis of TiO₂/ZnS/GO via the hydrothermal method.

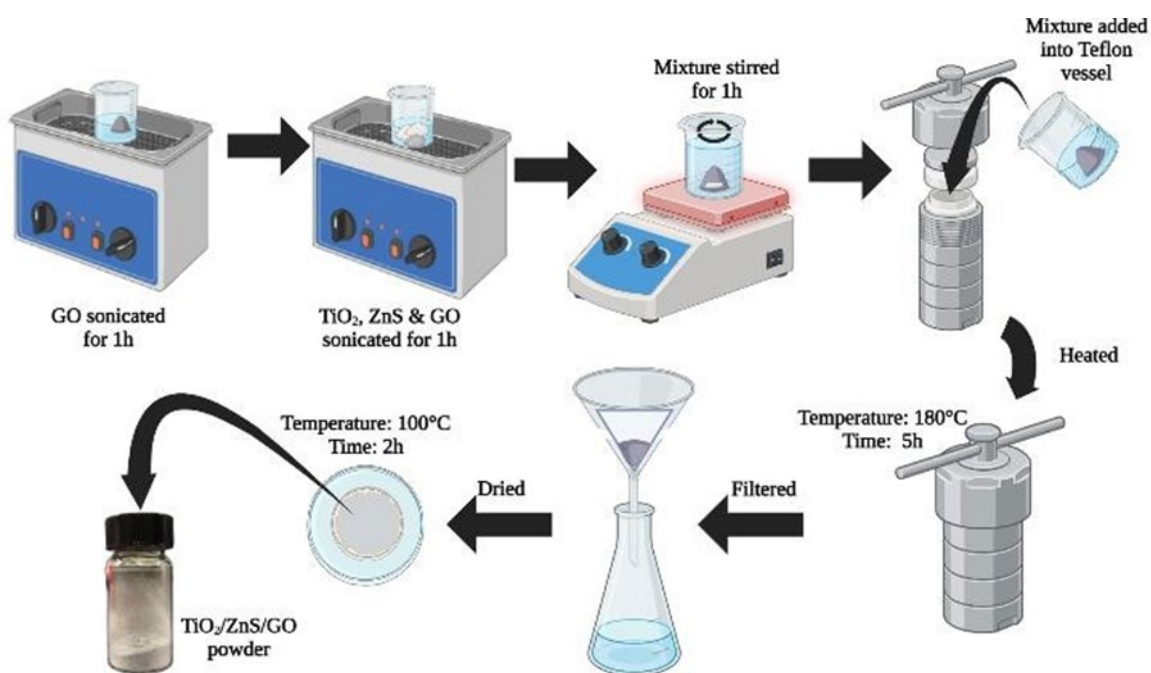


Figure 3.1: Schematic diagram of the synthesis of TiO₂/ZnS/GO via hydrothermal method.

3.4 Synthesis of TiO₂/ZnS/GO immobilized beads

The preparation method of immobilized beads was adapted from Kanakaraju et al. (2017). First, a 2% solution of sodium alginate (NaAlg) was constantly stirred overnight. Then, 50 mL of 2% NaAlg solution was mixed with TiO₂/ZnS/GO (1:1:1) solution while stirring continuously. The NaAlg and TiO₂/ZnS/GO composite mixture was continuously stirred for 2 hours. Using a peristaltic pump, the NaAlg and TiO₂/ZnS/GO mixture was

transferred to a beaker containing 50 mL of 20 g/L CaCl_2 solution. The resulting $\text{TiO}_2/\text{ZnS}/\text{GO}-\text{CaAlg}$ gel beads were left in the CaCl_2 solution overnight to fully form and solidify. The beads were then washed with DI and dried for 48 hours at room temperature before being used to compare the MB removal between powder and immobilized form.

3.5 Characterization of $\text{TiO}_2/\text{ZnS}/\text{GO}$ composite

The morphologies and structures of TiO_2 , ZnS , GO and $\text{TiO}_2/\text{ZnS}/\text{GO}$ were characterized using scanning electron microscopy (SEM) (Model JOEL JSM-6390LA) and Energy dispersive X-ray (EDX) spectroscopy (Model JOEL JSM-6390LA) with the help of Transmission Electron Microscopy (TEM) (Tecnai G2 20, FEI Company). The measurements were performed at an accelerating voltage of 10 kV under vacuum. Particle sizes were also identified from TEM images by Microstructure Measurement Software (ImageJ). Fourier- transform infrared spectroscopy (FT-IR) (Thermo Nicolet iS10 model) spectra for all samples were obtained using a standard KBr pellet in the wavenumber range of 400 to 4000 cm^{-1} . The powdered samples were observed using X-ray diffraction (XRD) (Model PANalytical X'pert Pro XRD) method using $\text{Cu K}\alpha$ radiation ($\lambda = 0.154 \text{ nm}$) in the scanning range of 2θ between 10° and 80° , with a rate of 0.04° per second. The accelerating voltage and applied current were 45 kV and 40 mA, respectively. For phase identification, an automatic Joint Committee on Powder Diffraction Standards (JCDPS) library search and the match were used. UV-Vis Diffuse Reflectance Spectroscopy (UV-Vis DRS Model Carry 5000) was applied to determine the band gap energy of the synthesized materials. The Brunauer-Emmett-Teller (BET) (Micromeritic/3Flex 3500), with an ideal temperature degassing of 150°C for 6 h was employed to determine the specific surface area and pore size of the $\text{TiO}_2/\text{ZnS}/\text{GO}$ and GO composites. Raman

technique was employed to detect carbon purity, bonding and hybridization were recorded by using a Raman-AFM (Raman Xplora Plus) (Nd: YAG laser 532 nm and Diode: 785 nm excitation). Electrochemical measurements were performed on a Autolab electrochemical workstation using a standard three-electrode cell with a working electrode, a platinum plate as the counter electrode, and a standard Ag/AgCl in saturated KCl as the reference electrode. For the working electrodes, 10 mg of photocatalysts were suspended in 5 mL ethanol and the mixtures were ultrasonically scattered for 30 min to form a homogeneous solution. Then, 0.1 mL solution was dropped onto a 1 cm x 1 cm fluorine-tin oxide (FTO) glass electrode with a sheet resistance of 8Ω . After the films were dried under ambient conditions, they were calcinated at 100°C for 1 h. The electrochemical impedance spectroscopies (EIS) were carried out at the open circuit potential in a 0.5 M Na_2SO_4 solution. The amplitude of the sinusoidal wave was 10 mV, and the frequency ranged from 10 kHz to 0.01 Hz. The electrolyte was purged with nitrogen prior to and during all measurements. The photoluminescence (PL) spectra of photocatalysts were measured using a fluorescence spectrophotometer (LS55) equipped with a xenon lamp at an excitation wavelength of 275 nm and 375 nm.

3.6 Dye solutions concentration

Individual stock solutions (1000 ppm) of MB, MO and Rho B were prepared by dissolving 1.2195 g, 1.1765 g, and 1.0526 g of powder, respectively in DI. Each stock solution was subsequently diluted to achieve the desired concentrations within the range of 20 ppm to 35 ppm. These intervals were established using the reported ranges found in pertinent literature, typically spanning from 20 ppm to 50 ppm (Liu et al., 2016; Talebi et al., 2017; Kale et al., 2020; Mou et al., 2013; Ramadhani and Helmiyati, 2020). For the

preparation of the mixed dye solution, the concentration of each dye solution (MB, MO, and Rho B) was fixed 20 ppm and diluted in 100 mL of a volumetric flask.

3.7 Photocatalytic experiments

Photocatalytic experiments were conducted with different dosages (0.1 to 1.0 g) and different MB concentrations (20 ppm – 35 ppm) to determine the ideal dosage of TiO₂/ZnS/GO composite for MB removal. The photocatalytic experiment was carried out with constant stirring and consisted of two phases after the addition of the composite. First, an equilibrium phase in the absence of light was maintained for 90 min, followed by a 3 h irradiation phase under UVA light ($\lambda = 365$ nm; OSRAM). Throughout all experiments, the UVA lamp was kept 18 cm away from the reactor. Prior to UV-Vis spectrophotometer examination, a 15 mL amount of the MB solution was removed and centrifuged (Agilent Cary 60 UV-Vis Spectrophotometer). The wavelength of 664 nm represents the maximum absorption peak, λ_{max} , from the MB chromophore group. The removal percentage of the MB solution was calculated according to Eq. (3.1):

$$\text{Percentage removal (\%)} = \frac{C_i - C_f}{C_i} \times 100 \quad (\text{Equation 3.1})$$

where C_i is the concentration of MB in the initial aqueous solution (ppm) after the equilibrium and C_f is the concentration of MB in the aqueous solution at specified intervals (ppm).

The pH studies were conducted at pH values of 3.00, 5.00, 7.00, and 10.00. The pH of the solution was adjusted using either dilute 0.1 M HCl or 0.1 M NaOH solutions, with the initial pH representing the starting point. The final pH was recorded after the photocatalytic treatment. The point zero charge (pHpzc) of TiO₂/ZnS/GO (1:1:1) was determined by adding 50 mL of 0.01 M NaCl into six separate Erlenmeyer flasks

(Kosmulski, 2018). In each flask, the pH was adjusted to 3.00, 5.00, 7.00, and 10.00 using either 0.1 M HCl or 0.1 M NaOH, where the solution's pH in each flask represented the initial pH. Subsequently, 1.0 g of TiO₂/ZnS/GO (1:1:1) was added to each flask and stirred continuously for 24 h before measuring the final pH of the solution. The pH_{pzc} of the optimized TiO₂/ZnS/GO (1:1:1) is the point where the pH_{final} = pH_{initial} meets. The pH readings were recorded using the Milwaukee pH 55 Pocket Digital pH Meter.

The radical scavengers study was conducted to determine their roles in the photocatalytic degradation of MB. The scavengers investigated include hole (methanol), hydroxyl radical, •OH (isopropyl alcohol, hydrogen peroxide), and superoxide anion radical, O₂^{-•} (benzoquinone). Concentrations of methanol, isopropyl alcohol, hydrogen peroxide and benzoquinone were fixed as 0.2 mmol/L, 1 mmol/L, 0.1 mmol/L, and 0.2 mmol/L, respectively. These concentrations were modified based on the findings reported by Mittal et al. (2019).

Two additional dyes, namely MO and Rho B, were also investigated in the photocatalytic experiments using 1.0 g/L of TiO₂/ZnS/GO (1:1:1) composite. These dyes were studied individually at a concentration of 20 ppm, as well as in a mixture (MB, MO, and Rho B) using the same concentration. The experimental procedures for photocatalysis were identical to those described earlier. To determine the degradation percentage of individual dyes in the mixture condition, the wavelengths of 464 nm, 568 nm, and 664 nm corresponding to the highest absorption peaks (λ_{max}) of MO, Rho B and MB chromophore groups, respectively, were monitored.

3.8 Efficiency comparisons and recycling study

Control experiments were conducted to compare the efficiencies of TiO_2 , ZnS, GO, TiO_2/ZnS , with $\text{TiO}_2/\text{ZnS}/\text{GO}$ (1:1:1). To establish adsorption equilibrium, dark adsorption studies were carried out using blank and composite samples with constant stirring without light irradiation for 3 hours. A 15 mL of MB solution was withdrawn and centrifuged (Agilent Cary 60 UV-Vis Spectrophotometer) prior to UV-Vis spectrophotometer examination. The removal percentage of the MB solution was calculated according to Equation 3.1. In addition, the recycling study of the best performing $\text{TiO}_2/\text{ZnS}/\text{GO}$ photocatalysts in the form of powder was evaluated for constant use for up to four cycles. The $\text{TiO}_2/\text{ZnS}/\text{GO}$ (1:1:1) beads were also evaluated for recycling studies. The samples (powder or beads) retrieved from the first treatment cycle using MB solution (20 ppm) were separated from the treated solutions by gravity filtration and subsequently washed three times with DI. DI was used for washing as ethanol might affect the composites' structure, thus affecting the degradation process (Ramadhani & Helmiyati, 2020). The powder $\text{TiO}_2/\text{ZnS}/\text{GO}$ was dried for two hours at 100°C in an oven, while the beads were left to dry overnight at room temperature. Using newly made MB solutions for every cycle, both samples that were recovered from the first cycle were used again for future cycles conducted under similar experimental conditions.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Characterization of TiO₂/ZnS/GO

4.1.1 Raman Spectroscopy

Raman spectroscopy is commonly utilized for the analysis of the organized or disorganized crystal structures of carbonaceous materials, examining alterations in both structure and vibrations that encompass entire molecules or significant molecular structures (Ferrugiarì et al., 2015). According to Leyva-Porras et al. (2015), the anatase phase of TiO₂ is expected to exhibit a distinct set of six primary modes, which are located at 144 cm⁻¹, 197 cm⁻¹, 399 cm⁻¹, 515 cm⁻¹, and 639 cm⁻¹. It can be observed that the band absorption values at 639 cm⁻¹ and 199 cm⁻¹ indicated the symmetric stretching vibration of O-Ti-O and anatase band (Figure 4.1(a)) in TiO₂/ZnS/GO (1:1:1), TiO₂/ZnS/GO (1:2:1), and TiO₂/ZnS/GO (2:1:1) spectra. These findings directly confirm the presence of the pure anatase phase. However, TiO₂/ZnS/GO (1:1:1) exhibited a higher intensity of anatase TiO₂ compared to TiO₂/ZnS/GO (2:1:1), attributed to the balanced composition of TiO₂, ZnS, and GO. This balanced composition likely promotes the formation of a greater proportion of anatase TiO₂, resulting in a higher intensity of the corresponding Raman spectra band. The longitudinal optical (LO) phonon is responsible for the vibration and structure spectra recorded at 644 cm⁻¹ (Kashinath et al., 2017).

The Raman spectra of TiO₂/ZnS/GO composites (1:1:1, 1:2:1, and 2:1:1) exhibited characteristic D bands at 1354 cm⁻¹, 1362 cm⁻¹, and 1364 cm⁻¹, as well as G bands at 1595 cm⁻¹, 1598 cm⁻¹, and 1609 cm⁻¹. These bands provided evidence of the presence of GO within the composites. This was further supported by the identification of D and G bands

in the Raman spectra of GO (as shown in Figure 4.1(b)). The D and G bands of all TiO₂/ZnS/GO ratios shifted to higher wavenumbers as compared to GO. This movement of D and G bands shows that there is an interaction between the TiO₂, ZnS, and graphene. The intensity ratio of the D to G bands (I_D/I_G) can be used to calculate the disorder degree composites. The ratio of TiO₂/ZnS/GO (1:1:1) is lower than other ratios (Figure 4.1(a)). The I_D/I_G ratio proves the graphene is a multilayer due to the integration of TiO₂/ZnS/GO. The involvement of TiO₂ and ZnS in decorating the GO surface in the formation of TiO₂/ZnS/GO composites was substantiated by the appearance of Raman peaks at 645 cm⁻¹ and 639 cm⁻¹, which corresponded to the respective D and G bands of carbon in GO. This correlation was also noted by Indhumathy and Prakasam in 2020.

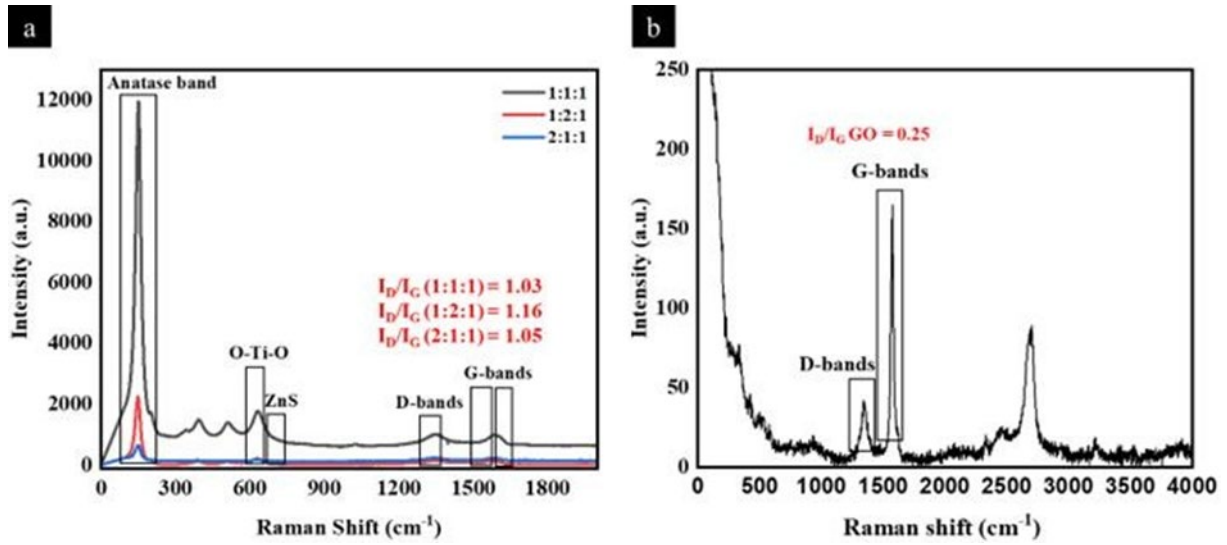


Figure 4.1: Raman spectra of (a) TiO₂/ZnS/GO (1:1:1, 1:2:1, 2:1:1) and (b) GO.

4.1.2 FTIR spectra

Figure 4.2(a)-(d) shows the infrared (IR) spectra of TiO₂, ZnS, GO, and TiO₂/ZnS/GO (1:1:1) in the range of 400 cm⁻¹ – 4000 cm⁻¹. The other TiO₂/ZnS/GO ratios (1:2:1 and 2:1:1) were not characterized, as TiO₂/ZnS/GO (1:1:1) was considered the ideal

composite for other parameters such as dosage, dye concentration, mixed dye solutions, solution pH, and the presence of radical scavengers. The spectrum for all materials showed a similar broad absorption band from 3400 cm^{-1} to 3700 cm^{-1} as well as from 1600 cm^{-1} to 1700 cm^{-1} , which could be attributed to surface-adsorbed water and hydroxyl groups that could function as photoexcited traps on the catalytic surface and produce hydroxyl radicals for the oxidation of organics (Guo et al., 2018). The absorption peak found at 2375 cm^{-1} can be attributed to the stretching of O-H bonding and O=C=O adsorption bands. The existence of hydroxyl groups can impact the elimination of dye by facilitating interactions such as hydrogen bonding, thereby promoting the adsorption of dye molecules onto surfaces and assisting in their removal whereas the presence of O=C=O could potentially influence the pH of the system, affecting dye adsorption or precipitation processes (Zhuang et al., 2020). The absorption bands between 640 cm^{-1} and 420 cm^{-1} correspond to the vibration mode of the O–Ti–O band in the anatase crystalline phase (Figure 4.2(a)-(d)). The presence of Zn–S symmetric bending is also detected in Figs 4.2(b) and (d) at 635 cm^{-1} . According to Shahriary and Athawale (2014), the absorption peaks at 1635 cm^{-1} and 732 cm^{-1} are attributed to the stretching vibrations of C-C and C=O of the carboxylic acid and carbonyl group, proving its presence at the edges of GO (Figure 4.2(c)).

The presence of symmetric and asymmetric stretching vibrations of CH_2 can be observed in Figure 4.2(a) and (d) at 2920 cm^{-1} and 2854 cm^{-1} , respectively. The existence of CH_2 groups present in adsorbent materials can serve as active sites for dye molecules to adsorb onto surfaces. The CH_2 groups in adsorbent materials act as active sites for dye molecules to adhere to surfaces due to their hydrophobic nature, forming Van der Waals interactions (Zhang et al., 2020). The stretching vibrations can affect the accessibility and affinity of these sites for dye molecules. Moreover, the symmetric and asymmetric

stretching vibrations can contribute to the binding sites within the composite (Shehap & Akil, 2016). The interactions between CH₂ groups and other components with ZnS and GO can enhance the binding forces, leading to improved structural integrity and performance of the ternary composite. The stretching vibration of carboxylic acid (C-O) in the GO composites is correlated with the absorption peaks at 1385 cm⁻¹ and 1110 cm⁻¹ (Figure 4.2(c) and (d)). The carboxylic acid groups on GO provide abundant sites for chemical reactions and interactions with other substances. The C-O stretching vibration is indicative of the presence of these functional groups on the GO surface (Kumar & Jiang, 2016). The TiO₂/ZnS/GO composite was validated by the associated chemical bonds and peaks observed in the TiO₂, ZnS, and GO spectra.

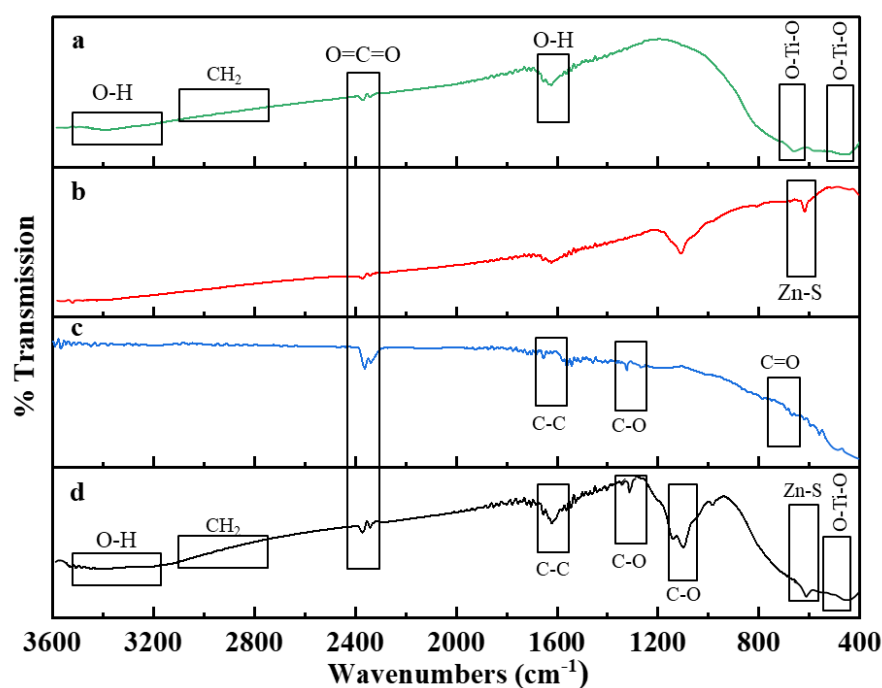


Figure 4.2: FTIR spectra of (a) TiO₂, (b) ZnS, (c) GO, (d) TiO₂/ZnS/GO (1:1:1).

4.1.3 XRD analysis

The XRD patterns of GO and TiO₂/ZnS/GO composites were depicted in Figure 4.3. The XRD patterns revealed the distinctive peaks at $2\theta = 25.4^\circ$ that are associated with TiO₂ anatase (JCPDS21-1272) (Figure 4.3(b)-(d)). Additionally, the characteristic ZnS peaks around $2\theta = 28.6, 33.1, 47.6, 56.4, 69.5, 76.9,$ and 88.6 degrees were also found, supporting the formation of ZnS deposited on the GO sheets (based on JCPDS 03-065-0309). The intensity of the ZnS peak at $2\theta = 28.6^\circ$ also increased significantly for TiO₂/ZnS/GO (1:2:1), as ZnS has a higher content than TiO₂ and GO. The combination of TiO₂, ZnS, and GO may result in better dispersion of ZnS within the composite. Improved dispersion can lead to a more uniform distribution of ZnS crystals, contributing to higher XRD peak intensities (Qin et al., 2019).

According to JCPDS 012 – 0212, diffraction peaks at $2\theta = 26.4, 42.3, 44.4, 54.5,$ and 77.4 were related to GO. However, none of the composites contained the GO diffraction peaks. This indicates that during the synthesis process, the GO sheets were completely exfoliated and coated with TiO₂ and ZnS composites (Ramos et al., 2020). Furthermore, a broad peak at $2\theta = 54.5^\circ$ corresponding to GO was observed with the enlargement of diffraction patterns (Figure 4.3(a)). The broadening of the diffraction patterns could be associated with the stacking of individual graphene oxide layers. The presence of oxygen functional groups causes disorder in the layer arrangement by preventing graphene sheets from stacking optimally (Lin et al., 2023). This is further supported by the ID/IG ratios from the Raman analysis of TiO₂/ZnS/GO (Figure 4.1). Given that the composites are covered in TiO₂ and ZnS, the diffraction may be caused by low content and, as a result, low diffraction intensities (Zhang et al., 2013).

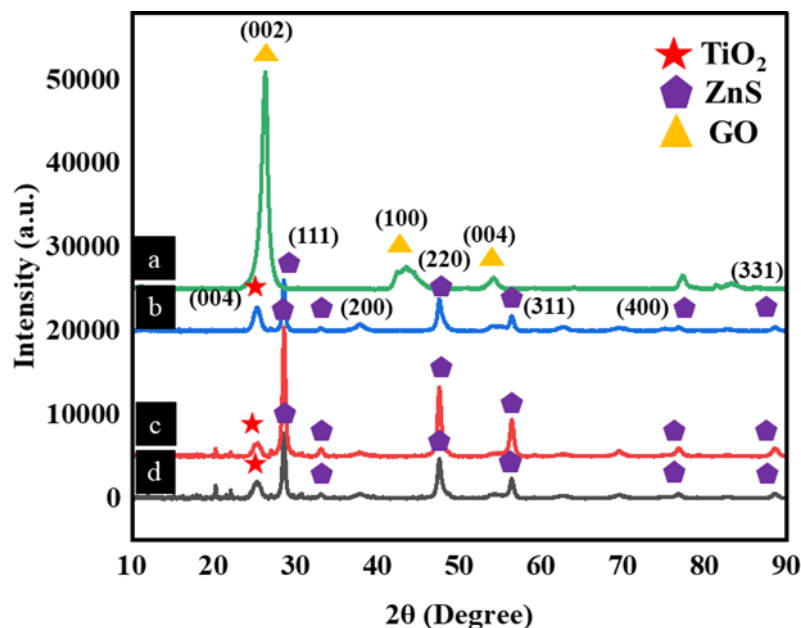


Figure 4.3: XRD spectra of (a) GO, (b) TiO₂/ZnS/GO (2:1:1) (c) TiO₂/ZnS/GO (1:2:1), and (d) TiO₂/ZnS/GO (1:1:1).

4.1.4 SEM-EDX analysis

SEM analysis was employed to examine the surface morphology of the prepared samples (Figure 4.4). The surface of TiO₂ morphology synthesized by the sol-gel method is shown to be agglomerated with smooth spherically shaped TiO₂ (Figure 4.4(a)). As a result of attractive forces such as van der Waals forces or electrostatic interactions, TiO₂ particles may agglomerate. The surface energy of the particles and the presence of functional groups can influence aggregation tendencies (Krzosa et al., 2023). Commercial ZnS can also be seen to have an agglomerated rice-like appearance (Figure 4.4(b)). The GO sheet's surface emerges to be somewhat smooth and crinkled (Figure 4.4(c)). The spherically shaped TiO₂ can be observed to be attached and agglomerated on the surfaces of both ZnS and GO (Figures 4.4d and 4.4(e)). TiO₂ nanoparticles may adsorb onto the surfaces of ZnS and GO through physical adsorption or chemical bonding. This adsorption can lead to the attachment and subsequent agglomeration of TiO₂ on the surfaces of ZnS and GO

(Kordouli et al., 2015). Figure 4.4(f)) shows the agglomerated ZnS attached to the surface of GO. Based on the SEM images of TiO₂/ZnS/GO (1:1:1) composite, the wrinkled sheets of GO are believed to facilitate the uniform growth and dispersion of ZnS and TiO₂ (Figure 4.4(g)). The irregularities in the GO structure, including wrinkles and folds, create a textured surface. This textured surface enhances the interaction between GO and ZnS/TiO₂, allowing for better adhesion and distribution of the nanoparticles (Bai et al., 2013). It can be observed that both TiO₂ and ZnS have homogenously adhered to the GO sheets. Park et al. (2014) stated that good particle dispersion would result in high photocatalytic activity. These observations were well supported by the EDX analysis of the composites, as shown in Figure 4.4 and Table 4.1.

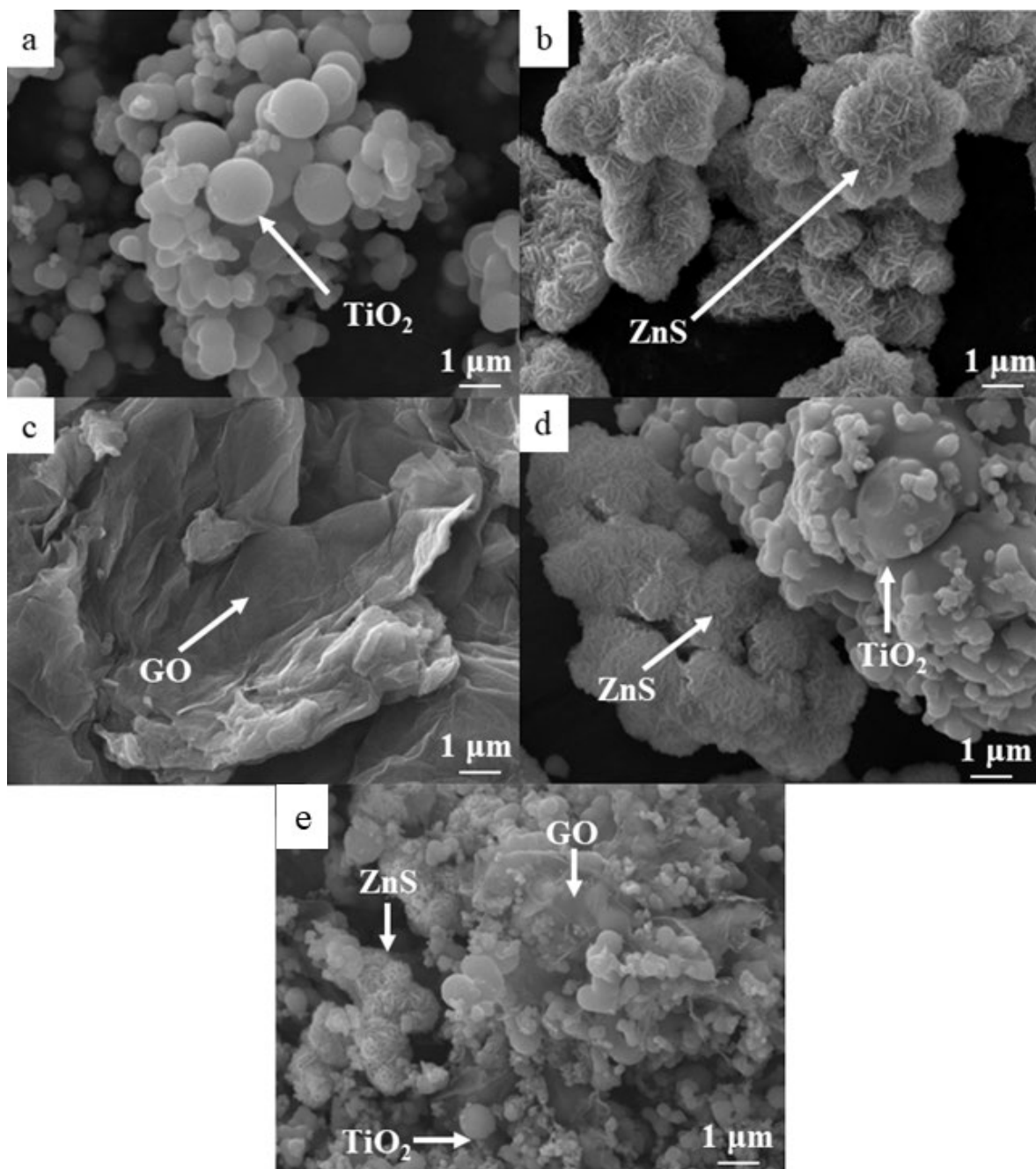


Figure 4.4: SEM images of (a) TiO_2 , (b) ZnS , (c) GO , (d) TiO_2/ZnS , (e) TiO_2/GO , (f) ZnS/GO , and (g) $\text{TiO}_2/\text{ZnS}/\text{GO}$ (1:1:1).

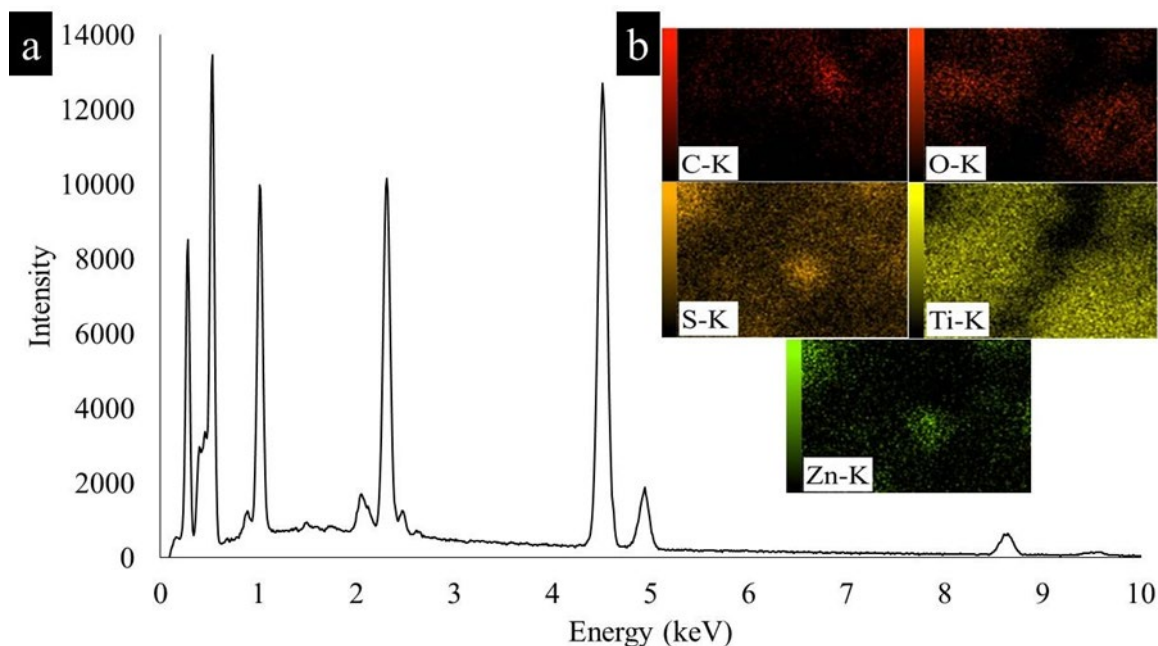


Figure 4.5: EDX (a) analysis and (b) mapping of $\text{TiO}_2/\text{ZnS}/\text{GO}$ (1:1:1).

The elemental compositions and EDX analysis results for the prepared samples are shown in Figure 4.5 and Table 4.1. All major elements (Ti, O, Zn, S, and C) were consistently identified in all ratios of $\text{TiO}_2/\text{ZnS}/\text{GO}$ composites, affirming the successful synthesis without the presence of other elemental impurities. The higher weight percentages of Ti in TiO_2/GO and $\text{TiO}_2/\text{ZnS}/\text{GO}$, compared to other composites, indicate the successful synthesis of these composites (Figure 4.5, Table 4.1). When comparing $\text{TiO}_2/\text{ZnS}/\text{GO}$ (2:1:1) with samples at ratios of 1:1:1 and 1:2:1, a noticeable decrease in the composition of C was observed, likely attributed to the doubled amount of TiO_2 on the surface, leading to a reduction in the C element composition. TiO_2 has a significantly higher atomic mass than carbon. Therefore, the addition of TiO_2 , even in a relatively small amount, can contribute significantly to the overall mass of the material. This increased mass of TiO_2 , when compared to carbon, results in a lower percentage of carbon in the overall composition (Table 4.1). However, the weight percentage of zinc (Zn) element is almost similar between 1:1:1 and 1:2:1 because although the 1:2:1 theoretically doubles the

amount of Zn, the overall composition and distribution of elements in the composite may not directly translate to a proportional increase in the weight percentage of Zn. This could be due to factors such as particle size distribution, surface coverage, and homogeneity of the composite (Gui et al., 2023).

Table 4.1: Elemental compositions of the prepared samples.

Samples	Weight % of elements				
	Ti	O	Zn	S	C
TiO₂/ZnS	24.67	13.73	24.70	10.89	26.01
TiO₂/ZnS/GO (1:1:1)	29.27	18.53	26.68	13.02	10.50
TiO₂/ZnS/GO (1:2:1)	20.17	12.19	27.98	18.84	20.82
TiO₂/ZnS/GO (2:1:1)	41.91	27.27	19.76	8.15	2.91

*Nd-not detected

4.1.5 BET surface area analysis

A larger surface area of a photocatalyst material would result in higher photoactivity (Shi & Vakoc, 2014). Based on Table 4.2, GO has the highest surface area compared to the ternary composites. Although GO is expected to have a higher adsorption capacity due to its larger surface area, attributed to its 2D structure and numerous functional groups (e.g., hydroxyl and carboxyl groups), its surface chemistry may not be optimized for effective dye adsorption (Figure 4.2 (d)). The BET surface area increased from 42.33 m²/g to 68.05 m²/g for TiO₂/ZnS/GO (1:1:1) and TiO₂/ZnS/GO (2:1:1), respectively, when the amount of TiO₂ was doubled.

Table 4.2: Result of BET surface area analysis of TiO₂/ZnS/GO

Samples	Surface area (m ² /g)	Pore size (nm)	Pore volume (cm ³ /g)
GO	266.68	60.28	6.4
TiO ₂ /ZnS/GO (1:1:1)	42.33	8.22	0.09
TiO ₂ /ZnS/GO (1:2:1)	40.57	8.02	0.08
TiO ₂ /ZnS/GO (2:1:1)	68.05	6.43	0.11

A larger surface area of a photocatalyst material would result in higher photoactivity (Shi, 2014). Based on Table 4.2, when the amount of TiO₂ was doubled, the BET surface area increased from 42.33 m²/g to 68.05 m²/g for TiO₂/ZnS/GO (1:1:1) and TiO₂/ZnS/GO (2:1:1), respectively (Figure 4.6(b)). The obtained BET results suggest that the higher amount of TiO₂ in the composite could have a direct effect on its photocatalytic performance (Oppong et al., 2019). The wide pore size of TiO₂/ZnS/GO (1:1:1) indicated the high amount of oxygen functionality, which aids in the separation of graphene layers and coating of TiO₂ particles during the composite preparation (Pérez-Molina et al., 2020). There was a large change in the pore size for TiO₂/ZnS/GO (1:1:1) composites as compared to TiO₂/ZnS/GO (1:2:1 and 2:1:1) (Table 4.2). The micropore and mesopore structures of graphene are thought to be permeable to ZnS and TiO₂, despite a decrease in surface area overall. According to Park et al. (2014), the blockage of graphene's surface micropores may be the cause of the decrease in the surface area and pore volumes of the 1:1:1 and 1:2:1 composite. The TiO₂/ZnS/GO sample (1:1:1) with larger mesopores and wide pore size distribution might exhibit better adsorption and photocatalytic activity

because the larger mesopores improve the accessibility of active sites and the smaller mesopores increase the number of active sites (He et al., 2015).

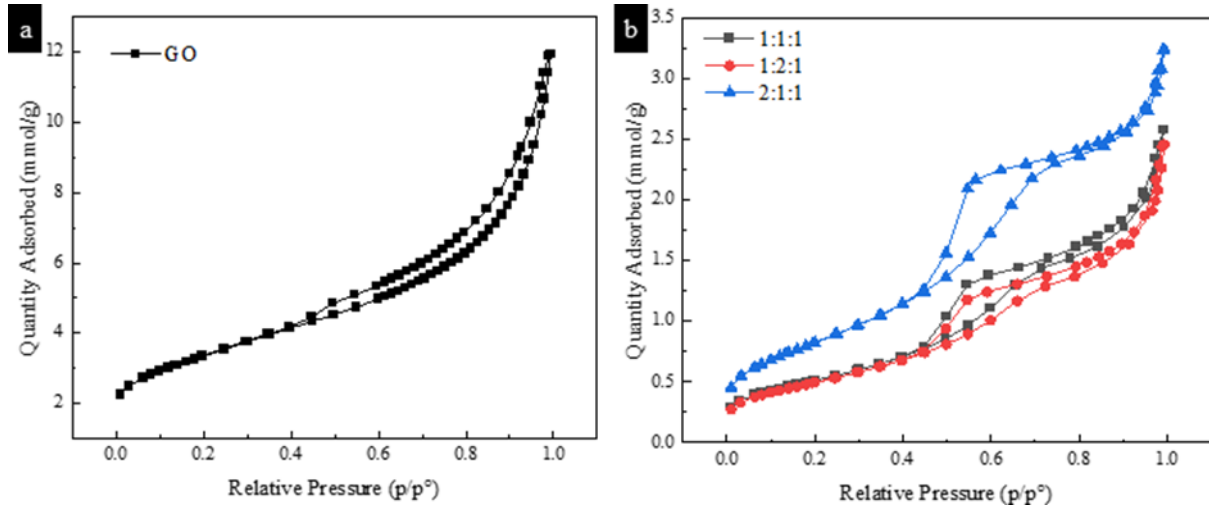


Figure 4.6: BET nitrogen adsorption isotherm plot for (a) GO, (b) TiO₂/ZnS/GO (1:1:1, 1:2:1, and 2:1:1).

4.1.6 TEM analysis

The TEM image of TiO₂/ZnS/GO shows that graphene appears as a homogeneous and smooth sheet (Figure 4.7(a)). The particle distribution of TiO₂ and ZnS particles ranged from 0.01 to 0.03 μm , as observed in the enlarged TEM image of TiO₂/ZnS/GO. Specifically, ZnS particles exhibited a rice-like shape with an average size of 0.0217 μm , while TiO₂ particles appeared spherical with an average size of 0.0157 μm , confirming the presence of both components (Figure 4.7(b)). The size and presence of TiO₂ and ZnS can be further determined through comparative analysis with reference data from the literature. For example, Dubey et al. (2019) determined that TiO₂ nanoparticles exhibit a spherical shape with an average size of 0.0134 μm , whereas Qin et al. (2017) demonstrated that the nanocomposite of ZnS has an average size ranging from 0.02 to 0.5 μm . The particle size histogram estimated the average particle size of 28.9 nm for TiO₂/ZnS/GO (1:1:1) (Figure

4.7(c)). Furthermore, Qin et al. (2019) observed that there is a dispersion of ZnS and TiO₂ on the GO sheet surface, which results in interfacial contact between the ZnS and TiO₂ particles. Since the interfacial interaction between TiO₂, ZnS, and GO is closely linked to the charge carrier transfer process in GO, it is reasonable to anticipate that the photocatalysis process would result in good charge carrier transfer (Zhuang et al., 2020).

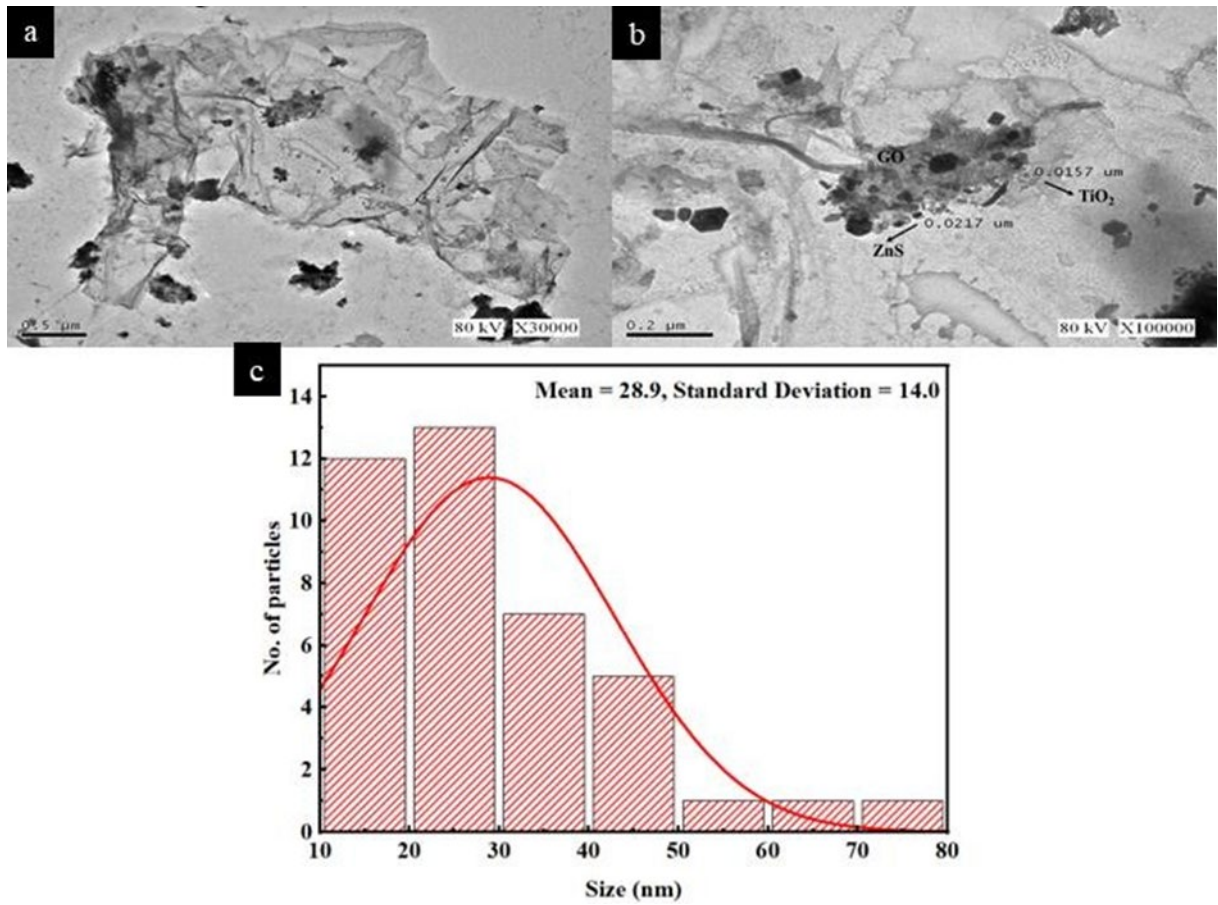


Figure 4.7: TEM images of TiO₂/ZnS/GO (1:1:1) at (a) 3000× magnifications and (b) 10,000× magnification, and (c) particle size distribution histogram of TiO₂/ZnS/GO (1:1:1).

4.1.7 Spectral analysis of UV-Vis DRS

The UV-Vis DRS spectra of the synthesized TiO₂/ZnS/GO (1:1:1, 1:2:1, 2:1:1) composites are shown in Figure 4.8. According to the findings in Figure 4.8, all the

produced composites exhibit a sharp edge at around 350 nm with $E_g = 3.45$ eV. Although there is no significant change in absorption in the visible range, the UV-Vis DRS of the 1:1:1 composite showed the highest UV absorption compared to the other composites (1:2:1 and 2:1:1). The calculated band gaps for 1:1:1, 1:2:1, and 2:1:1 composite were 3.40 eV, 3.44 eV, and 3.43 eV, respectively. The $\text{TiO}_2/\text{ZnS}/\text{GO}$ composite here is recognized for its significant band gap, which restricts its absorption to the UV spectrum. In contrast to the ZnS band gap, which is around 3.70 eV and corresponds to a wavelength of roughly 335 nm, the TiO_2 bandgap is 3.2 eV. By raising the photocatalyst's specific surface area, improving the dispersion of TiO_2/ZnS nanoparticles on the GO sheet, and lowering the recombination charge rate, the addition of GO to the TiO_2/ZnS composite can enhance its photocatalytic activity. However, because GO is a wide-bandgap semiconductor with a band gap of 3.90 eV, or a wavelength of about 318 nm, it has little impact on the band gap of the composite (Lin et al., 2017).

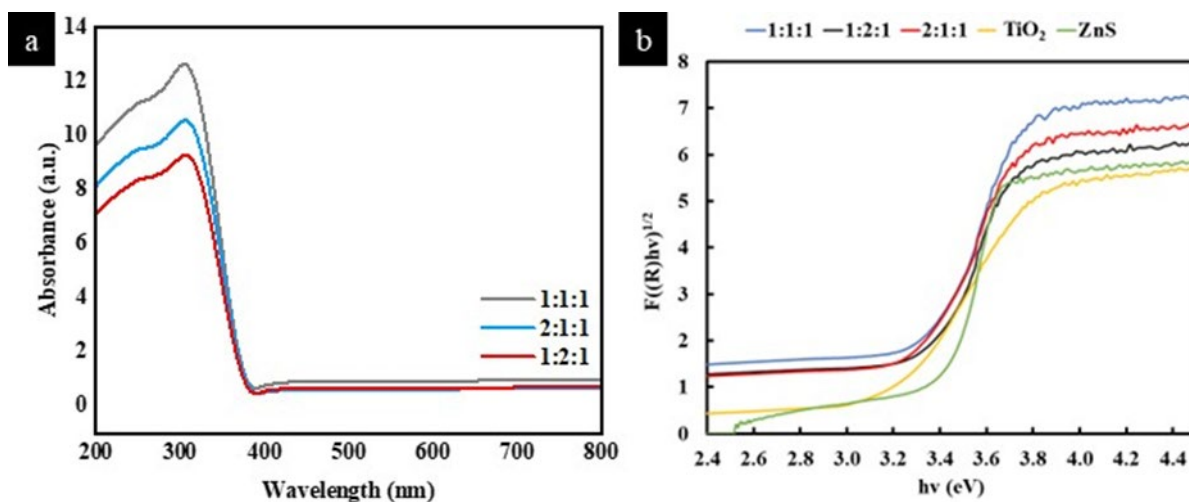


Figure 4.8: (a) UV-Vis DRS of $\text{TiO}_2/\text{ZnS}/\text{GO}$ (1:1:1, 1:2:1, 2:1:1) and GO and (b) Kubelka Munk plot of the diffuse reflectance spectra for $\text{TiO}_2/\text{ZnS}/\text{GO}$ (1:1:1, 1:2:1, and 2:1:1), TiO_2 , and ZnS.

Figure 4.8(b) shows the Kubelka Munk plot of the composites and blank samples, TiO₂ and ZnS. All prepared composites displayed sharp adsorption edges at about ~ 350 nm with $E_g = 3.45$ eV. Although there is no significant change in absorption in the visible range, the UV- Vis DRS of the 1:1:1 composite showed the highest UV absorption compared to the other composites (1:2:1 and 2:1:1). The calculated band gaps for 1:1:1, 1:2:1, and 2:1:1 composite were 3.40 eV, 3.44 eV, and 3.43 eV, respectively. This research showed that there is no optical absorption in the visible area of the composites. However, ternary composites offer other several advantages such as enhanced surface area and lower recombination rate of charge carriers for better photocatalytic degradation.

4.1.8 Electrochemistry analysis

Figure 4.9(a) and (b) show the EIS and PL spectra for ZnS, TiO₂, TiO₂/ZnS/GO (1:1:1) and TiO₂/ZnS/GO (2:1:1). The Nyquist plots consist of a depressed imperfect semicircle, corresponding to the charge transfer resistance (R_{ct}) in the interface of the electrode with electrolyte (Figure 4.9(a)). The R_{ct} values for TiO₂, ZnS, TiO₂/ZnS/GO (1:1:1) and TiO₂/ZnS/GO (2:1:1) calculated from the equivalent circuit were 702 k Ω , 442 k Ω , 192 k Ω and 290 k Ω , respectively. The TiO₂/ZnS/GO (1:1:1) composite sample possesses the lowest R_{ct} compared to other samples, indicating the highest electron-hole separation efficiency and fast interfacial charge transfer. Moreover, the large surface area of graphene oxide provides ample active sites for the deposition and interaction of TiO₂ and ZnS nanoparticles. This increased surface area can promote a higher density of interfacial contact points, facilitating efficient charge transfer (Padmanabhan et al., 2021). The balanced ratio ensures that each component contributes effectively to the overall charge transfer properties of the composite. Thus, the presence of TiO₂ and ZnS in the

composite enhances light absorption and promotes the generation of electron-hole pairs. Although ZnS possesses a wide band gap, it still absorbs light energy, albeit in the UV range due to its band structure. This absorbed energy is subsequently transferred to TiO₂, which has a narrower band gap. As a result, more electron-hole pairs are generated across both TiO₂ and ZnS when exposed to light, thereby enhancing the photocatalytic activity of the composite material (Wu et al., 2023). The GO component facilitates the injection of these charge carriers into the conductive pathways, reducing the overall charge transfer resistance (Guguloth et al., 2021).

Figure 4.9 (b) displayed the PL spectra for ZnS, TiO₂, TiO₂/ZnS/GO (1:1:1) and TiO₂/ZnS/GO (2:1:1) composites were explored by excitation wavelength at 275 nm at ambient conditions (Figure 4.9(b)). The highest PL emission intensity was observed for pristine ZnS followed by TiO₂ representing the high electron-hole recombination rates in ZnS and TiO₂. Nevertheless, the PL emission intensities of TiO₂/ZnS/GO (1:1:1) and TiO₂/ZnS/GO (2:1:1) composites were reduced upon the introduction of GO. The electron-hole recombination rate was the lowest for the TiO₂/ZnS/GO (1:1:1) composite. It is well known that the slower recombination of photogenerated charge carriers proves beneficial for photocatalysis (Balsamo et al., 2021). The emission peak at 416 nm is typical for pure TiO₂ due to band-to-band recombination (Xiaodan et al., 2006; Balsamo et al., 2021) or self-trapped electron recombination in TiO₂ (Priya et al., 2021). Trapped electrons and trapped holes defects correspond with the other bands at 460 and 480 nm, respectively. The composites exhibit a reduction in band emission intensities. This observation could be explained by the presence of GO, which can remove electrons from the semiconductor surface, reducing charge recombination. By exploiting the distinctive attributes of GO, the photocatalytic capabilities of TiO₂ and ZnS, and a meticulously optimized composition, the

TiO₂/ZnS/GO (1:1:1) composite attains improved interfacial charge transfer and effectively hinders the recombination of photoinduced electron-hole pairs. The composite design promotes efficient charge transfer pathways, reduces charge recombination, and maximizes the utilization of photoinduced charge carriers for potential applications in photocatalysis.

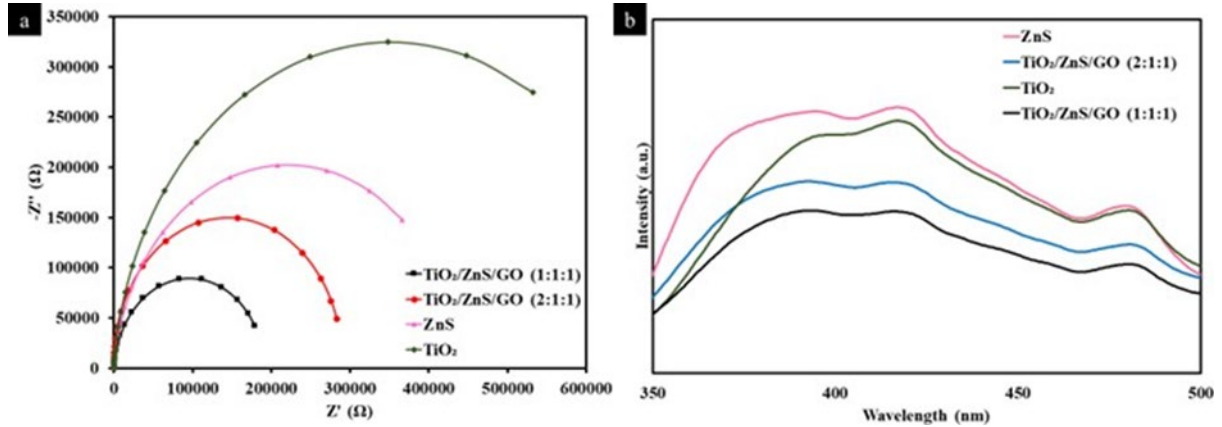


Figure 4.9: (a) The EIS and (b) photoluminescence spectra of TiO₂, ZnS and TiO₂/ZnS/GO (1:1:1 and 2:1:1).

4.2 TiO₂/ZnS/GO performance on MB removal

4.2.1 Control experiments

Dark experiments performed for all materials showed that equilibrium was achieved within 1 h (Appendix 2). Based on the results, TiO₂/ZnS/GO (1:1:1) showed the highest removal of MB after 180 min of adsorption compared to other composites. The presence of GO in the ternary composite can modify the surface properties such as surface charge and hydrophilicity, enhancing the adsorption of dye molecules (Paton-Carrero et al., 2022). Additionally, the incorporation of ZnS introduces additional active sites or functional groups on the composite surface, enhancing adsorption (Figure 4.2). While GO should theoretically exhibit higher adsorption capacity owing to its larger surface area

(Table 4.2) resulting from its 2D structure and abundance of functional groups (such as hydroxyl and carboxyl groups), its surface chemistry might not be optimized for efficient dye adsorption (Azizi et al., 2024). In contrast, ternary composites containing TiO_2 and ZnS could provide tailored surface chemistry with specific functional groups and active sites conducive to effective dye adsorption.

The reliability of $\text{TiO}_2/\text{ZnS}/\text{GO}$ as an excellent photocatalyst was established through a comparison of the MB removal performance of each material in the composites under UVA irradiation (Figure 4.10). The ability of TiO_2 , ZnS , GO , and TiO_2/ZnS composite to remove MB from the reaction medium was marginally low (Figure 4.10). The MB removal percentages were 6.7%, 12.3%, 26.6%, and 36.4%, respectively for TiO_2/ZnS (1:1), TiO_2 , ZnS , and GO , respectively.

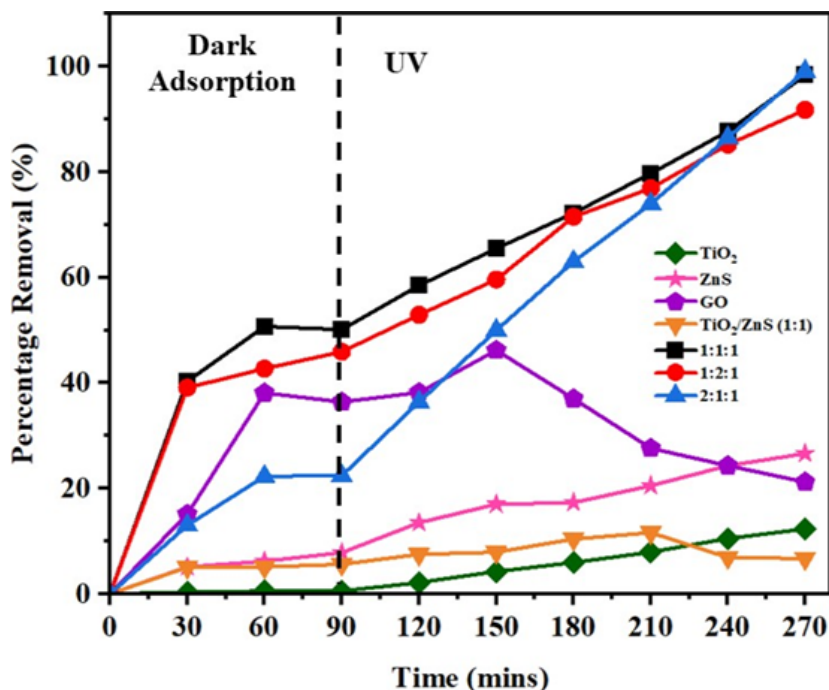


Figure 4.10: Blank experiments using TiO_2 , ZnS , GO , TiO_2/ZnS (1:1), $\text{TiO}_2/\text{ZnS}/\text{GO}$ (1:1:1, 1:2:1, and 2:1:1).

Even with an equal amount of TiO_2 and ZnS in the TiO_2/ZnS (1:1) composite, the removal of MB was not satisfactory, as compared to TiO_2 (12.3%), ZnS (26.6%), and GO

(36.4%), individually. However, a study revealed that a small amount of ZnS on the nanocomposite surface was sufficient to enhance the photoactivity of the catalysts (Chandrasekaran, 2020). A study conducted by Priya et al. (2021) corroborated this observation. According to their results, TiO₂ with a lower quantity of ZnS (0.25 M) showed excellent degradation, achieving a rate of 70.07%. On the contrary, when higher concentrations of ZnS (0.50 M and 0.75 M) were used in the synthesis of TiO₂/ZnS, the degradation rate was lower. A smaller crystallite size, reduced bandgap and larger surface area of TiO₂ with a lower amount of ZnS (0.25 M) improved the photocatalysts' performance. Indhumathy and Prakasam (2019) also noted that a rise in the amount of ZnS in the composites leads to a decline in their photocatalytic performance. This is due to the formation of a larger concentration of sulphur vacancies, which could serve as sites for the recombination of photogenerated electrons and holes, lowering the effectiveness of the catalysts. Additionally, Figure 4.10 demonstrates that the high rate of photogenerated electron-hole pair recombination prevents individual catalysts from achieving the necessary properties for photocatalytic treatment. However, GO has the highest removal of MB due to the large surface area. Consequently, the available adsorption sites also increased, which in turn enhanced the dye adsorption process (Naeem et al., 2018). Studies have reported that the extensive surface area of GO offers an increased number of surface adsorption sites for contaminants, leading to a significant enhancement of surface photocatalytic reactions and consequently boosting catalytic performance (Singh et al., 2020; Hong et al., 2022).

The ratios of TiO₂ to ZnS were varied while GO concentration was fixed. The TiO₂/ZnS/GO composites were prepared at three different ratios, 1:1:1, 1:2:1, and 2:1:1 and 1 g of each ratio was applied to determine their performance efficiency on MB

removal (Figure 4.10). Although removal of MB was high for all catalyst ratios (1:1:1, 1:2:1, and 2:1:1) with the exponential increase over time, the ratio of 1:1:1 was chosen for further study. The decision was made considering the materials' adsorption capacity under dark conditions and consistent improvement when exposed to UV light (Figure 4.10) and its highest absorption in the UV range based on the UV-DRS analysis (Figure 4.8(a)). Additionally, selecting these materials would result in decreased use of individual materials, which would otherwise increase the cost.

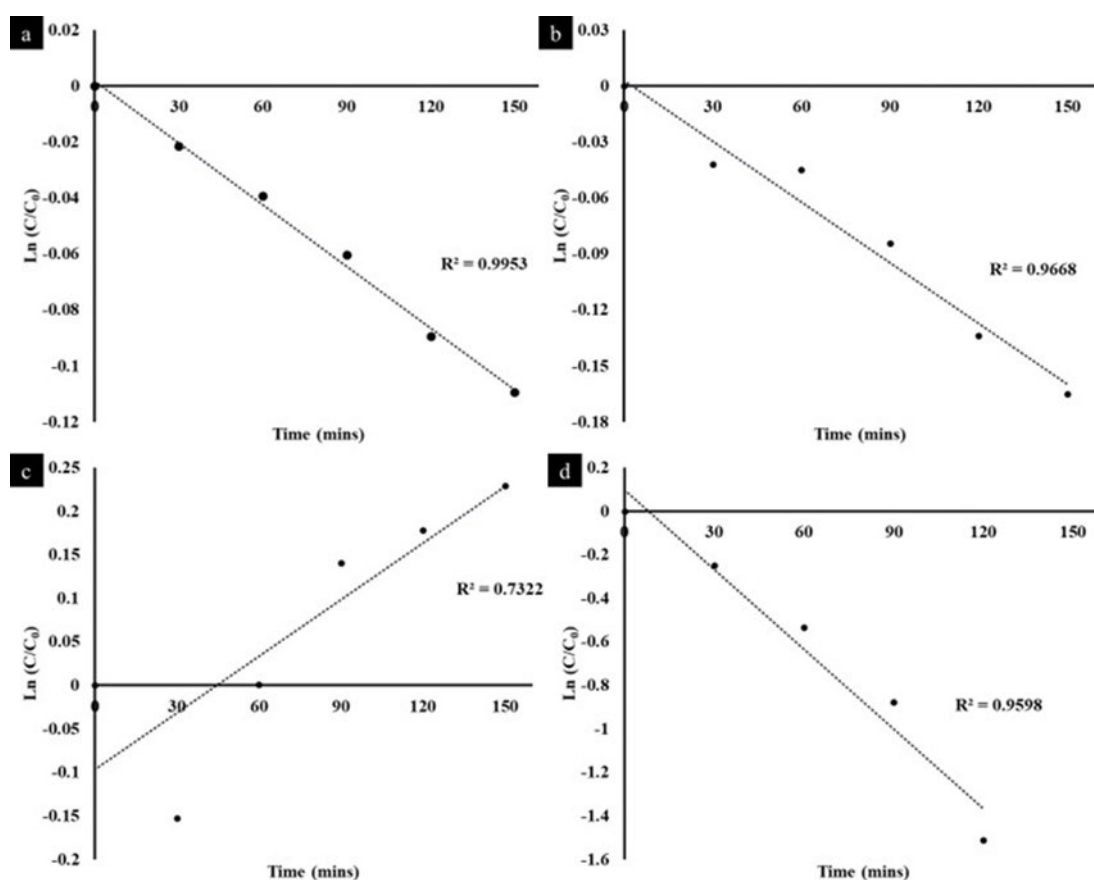


Figure 4.11: Pseudo-first-order kinetics of (a) TiO₂, (b) ZnS, (c) GO, and (d) TiO₂/ZnS/GO (1:1:1).

The catalyst followed pseudo-first order kinetic with a rate of 0.02 min^{-1} (Figure 4.11). The degradation rate of the 1:1:1 ratio composite was observed to be the highest compared to its counterparts, TiO₂, ZnS and GO (Figure 4.11) is likely a result of

synergistic effects, optimized composition, efficient charge transfer, and the utilization of a broader spectrum of light for photocatalysis. The combined photocatalytic activity of TiO₂, ZnS, and GO in the composite contributes to its superior performance in degrading pollutants compared to individual components. The chosen ratio of materials is considered adequate and aligns with the sustainable and practical idea of immobilization. GO in the composite can serve as an efficient electron shuttle due to its high electron conductivity. It can facilitate the rapid transfer of photoinduced electrons from TiO₂ and ZnS to the surface, reducing the recombination of electron-hole pairs and increasing the efficiency of ROS generation (Padmanabhan et al., 2021). As such, the TiO₂/ZnS/GO (1:1:1) composite was further investigated by varying other experimental conditions.

4.2.2 Parameters that affect the removal of MB

4.2.2.1 Effect of adsorbent dosage

To establish the ideal quantity of composite necessary to achieve maximal removal capability, various TiO₂/ZnS/GO (1:1:1) doses ranging from 0.1 to 1.0 g were applied to 20 ppm of MB (Figure 4.12). During the dark adsorption study, it was observed that for 60 min of equilibrium time, the removal of MB was about 5.9%, 16.1%, 38.2%, and 50.1% for 0.1 g, 0.3 g, 0.6 g, and 1.0 g of TiO₂/ZnS/GO, respectively which increased with the dosage of composite.

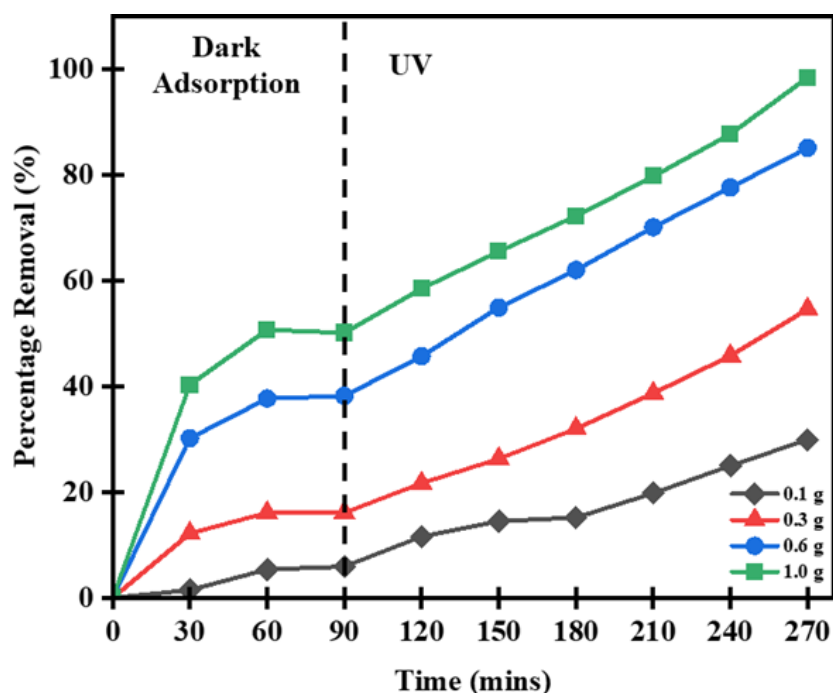


Figure 4.12: The effect of adsorbent dosage (0.1 – 1.0 g) of TiO₂/ZnS/GO (1:1:1) on the removal of 20 ppm of MB.

Based on Figure 4.12, the degradation of MB was found to increase from 29.9% – 98.4% as the amount of composite increased from 0.1 g to 1.0 g. This result aligns with the research conducted by Adly et al. (2019), which showed that increasing the dose increased the quantity of dye molecules adsorbed with the amount of photocatalyst as well as the number of photons adsorbed on active sites. On the other hand, the smallest amount of adsorbent dosage reduces the absorbance which results in lower photocatalytic activity (Jiang et al., 2013). Additionally, TiO₂/ZnS/GO's high specific surface area (42.33 m²/g) is credited with its exceptional photocatalytic properties, as it can offer an abundance of active sites for both adsorption and photocatalytic degradation processes (Table 4.2). Research conducted by de Moraes et al. (2018) found that the initial rise in adsorption could be linked to an augmented surface area and a greater abundance of available adsorption sites.

When a higher dosage (1.3 g) was applied to the removal of dyes, the difference in MB removal between 0.6 g and 1.0 g was greater than the removal difference observed at 1.3 g of TiO₂/ZnS/GO dosage (59.8%) (Appendix 4). This difference could be attributed to high agglomeration, which reduces the available surface area for interaction with MB molecules (Ziental et al., 2020). Consequently, this decrease in effective surface area can limit the number of active sites available for photocatalytic reactions, thereby reducing degradation efficiency over time. Overall, while increasing the amount of adsorbent can initially enhance photocatalytic activity by providing more active sites for reaction, there is a threshold beyond which further increases can lead to decreased efficiency due to agglomeration (Imran et al., 2019). Thus, the dosage of 1.0 g was fixed as the best-performing one under the investigated conditions.

4.2.2.2 Effect of initial concentrations

The effect of various concentrations of MB was investigated by keeping the dosage of TiO₂/ZnS/GO (1:1:1) constant at 1.0 g (Figure 4.13). The contribution of dark adsorption to MB removal ranged from 36.5% to 50.1% for the investigated MB concentrations. When exposed to UVA light, the maximal elimination of MB ranged from 76.4% to 98.4% (Figure 4.13). Although the removal trend appeared to be inconsistent with the increasing initial MB concentration, it can be observed that the removal decreases with increasing concentration. This could be ascribed to the fact that when dye concentrations increase, the amount of dye molecules adsorbed on the photocatalyst's surface increases, resulting in a decrease in the path length of photons entering the MB dye solution.

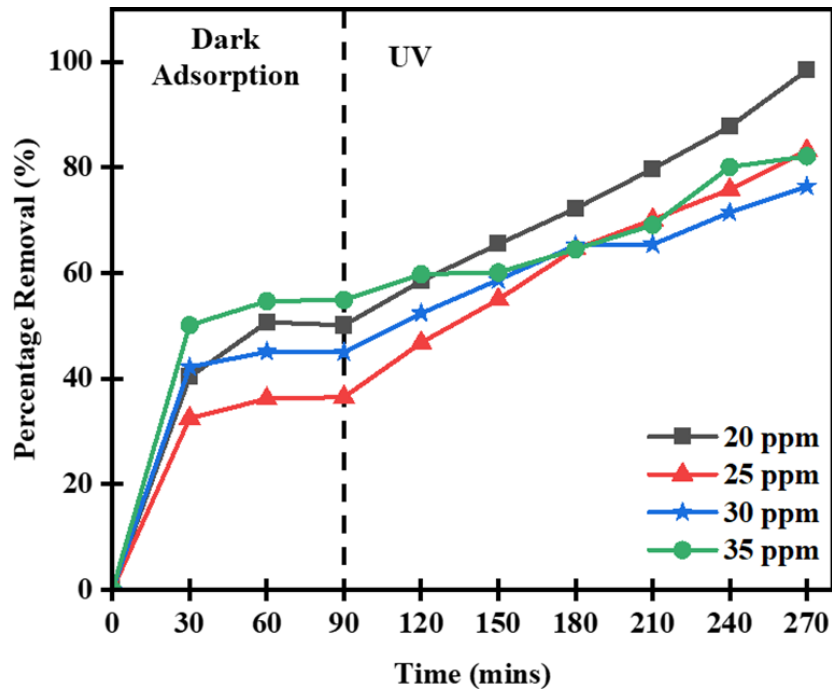


Figure 4.13: Removal efficiency of 1.0 g of $\text{TiO}_2/\text{ZnS}/\text{GO}$ at different initial MB concentrations (20 – 35 ppm) after 150 min of UVA irradiation.

According to Jabeen et al. (2017), the amount of catalyst surface area initially is available to aid by increasing the efficiency of degradation, however as dye concentration rose higher, the catalyst's active sites became completely occupied by dye molecules, resulting in no space for the generation of $\text{OH}^\bullet$ radicals. The incident light would have been filtered by the large concentration of dye, which eventually reduced degradation efficiency (Barjasteh- Moghaddam and Habibi-Yangjeh, 2011). Additionally, a significant quantity of UV energy may be absorbed by the dye molecules rather than the nanocomposite particles, reducing the photocatalytic activity's effectiveness (Wang et al., 2008). According to Gupta et al. (2012), an increasing number of dye molecules were adsorbed on the surface of the $\text{TiO}_2/\text{ZnS}/\text{GO}$ as the initial concentration of MB increased. The significant amount of dye that is adsorbed has an inhibiting impact on the reaction between dye molecules and photogenerated holes or hydroxyl radicals since there is no direct contact between them.

The results show that the irradiation period has a significant impact on the photodegradation of MB removal. According to Figure 4.13, the efficiency of MB removal and UV irradiation time exhibit a positive correlation for all initial dye concentrations, and the maximum removal of MB was attained after 150 min UVA irradiation.

4.2.2.3 Effect of pH and Determination of the Point of Zero Charge (pH_{pzc})

Another significant variable is the initial pH, which affects the photocatalyst's surface chemistry and controls how the dye molecules interact with one another. The effect of pH (3.00, 5.00, 7.00, and 10.00) was adjusted using 0.1 M HCl or 0.1 M NaOH, where each pH value represents the initial pH (Figure 4.14). Prior to radiation, the pH of the mixture was changed; it was not monitored during treatment. In comparison to pH 5 (60.5%), pH 7 (56.6%), and pH 10 (60.3%), the removal during dark adsorption was most effective at pH 3 (67.6%). Because the catalyst surface is negatively charged at lower pH values, cationic contaminants are more likely to adsorb on it. Because MB is a cationic dye, the negative charge in the feasible adsorption position competes with dye molecules, resulting in greater dye adsorption (Nayeri and Mousavi, 2020). Moreover, according to the $\text{pH}_{\text{pzc}} = 2.77$ (Figure 4.15), the catalyst carries a positive charge when the pH is below 2.77 and a negative charge when the pH is above this value. When the pH exceeds the pH_{pzc} , deprotonation occurs, resulting in an augmentation of negatively charged groups on the catalyst's active site. This enhancement improves the adsorption of MB ions on the TiO_2 surface via electrostatic interaction and photogenerated electrons.

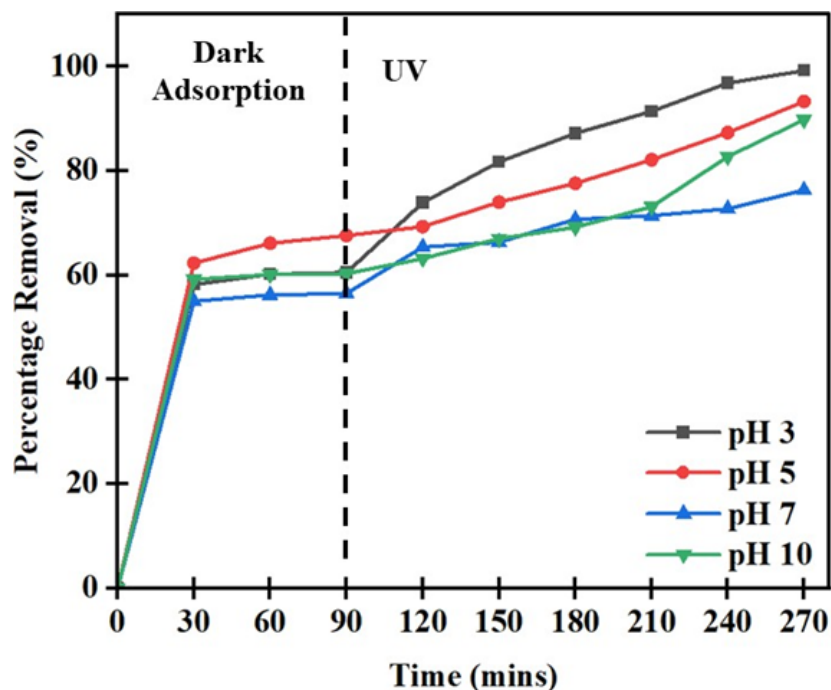


Figure 4.14: Removal efficiency of 1.0 g of TiO₂/ZnS/GO at different initial MB pH (3 – 10) after 150 min of UVA irradiation.

The highest removal MB removal was obtained at the acidic pH of 3 (99.2%), followed by pH 5 (93.3%), pH 10 (89.8%), and the lowest MB removal at the neutral pH of 7 (76.3%). The results showed the highest activity at pH 3 and almost complete removal of dye was obtained in 150 min as compared to its alkaline medium (pH 10). The results suggested that the de-ethylation process and chromophore cleavage occurred simultaneously in the solution of pH 3 more than pH 10, which enhanced the degradation efficiency. A large number of •OH radicals in an acidic system was also beneficial to hydroxylation on chromophores and then led to its cleavage.

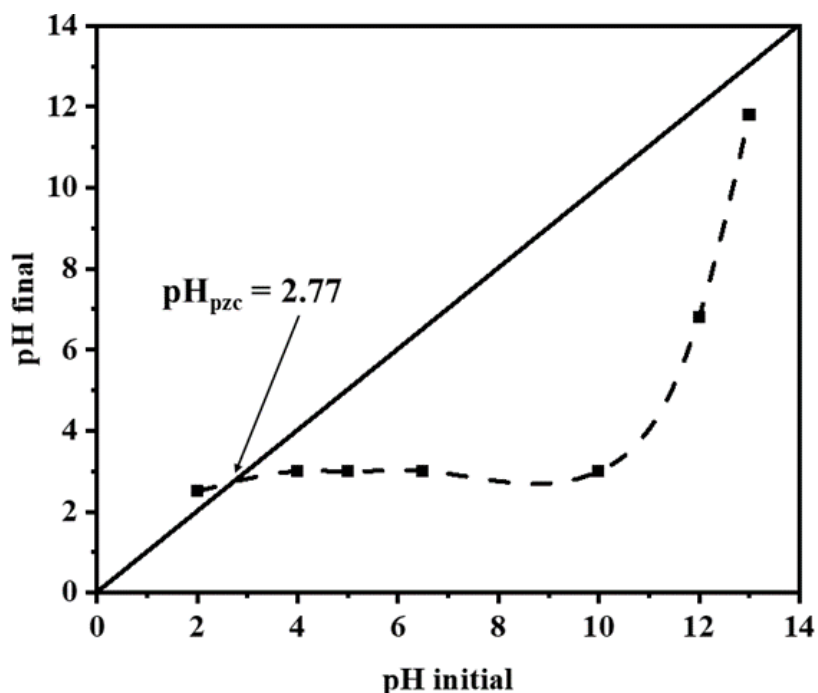


Figure 4.15: Point of zero charge (pH_{pzc}) of $\text{TiO}_2/\text{ZnS}/\text{GO}$ (1:1:1).

The catalyst surface is negatively charged and capable of adsorbing cationic ions above the pH_{pzc} . Because of the positively charged $-\text{NR}_2$ group, the dye becomes positively charged at pH 3, even though the catalyst is negatively charged. The dye and catalyst surfaces are then attracted to each other by a strong electric force. The photodegradation process is significantly impacted by the physical adsorption of carboxyl acid groups onto the positively charged catalyst, which initiates the photosensitization process through charge injection (Verma et al., 2021). Therefore, a key factor in determining the degree of adsorption and, in turn, the rate of photodegradation is the ionic state of the substrate species.

4.2.2.4 Radical scavengers

MB removal using different radical scavengers such as methanol, isopropyl alcohol (IPA), hydrogen peroxide (H_2O_2), and benzoquinone (BQ) was investigated using 1.0 g of

TiO₂/ZnS/GO (1:1:1) and 20 ppm of MB solution (Figure 4.16). The MB removal trend is ranked as follows: absence of radical scavenger (98.4%) > H₂O₂ (94.4%) > methanol (93.6%) > IPA (89.9%) > BQ (89.3%). It can be observed that with the addition of IPA and BQ, there is a noticeable decline in MB removal which indicates that the •OH and O₂^{-•} radicals were dominating active species and played significant roles in the degradation process. The scavenging effect of IPA leads to a decrease in the generation of hydroxyl radicals, which are crucial for the degradation of OPs like MB whereas BQ quenches superoxide radicals, reducing their participation in the degradation process. However, the addition of methanol and H₂O₂ caused an insignificant decline in removal efficiency, demonstrating the minimal contribution of the photoinduced hole towards the degradation of MB dye. The H₂O₂ quench holes by accepting electrons, thereby interfering with the oxidation reactions that holes would otherwise participate in, ultimately preventing further oxidative processes from occurring. Methanol readily accepts electrons, counteracting the positive charge of the photoinduced holes. This scavenging effect reduces the availability of holes for participating in oxidation reactions, thus leading to an insignificant decline in the removal efficiency of MB. The aforementioned findings demonstrated that rather than holes, the reactive •OH and O₂^{-•} radical species were considered to be in charge of the photocatalytic degradation of dye.

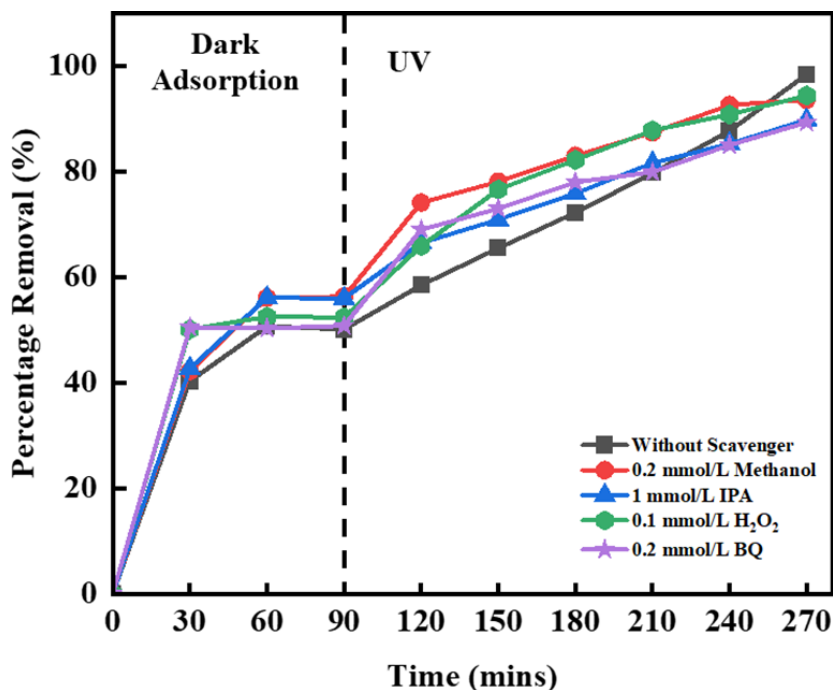


Figure 4.16: TiO₂/ZnS/GO (1:1:1) on the removal of MB in the presence of different scavengers.

4.2.2.5 Effect of mixed dyes solution

A mixed dye solution (MB, MO, and Rho B) was prepared to establish the ability of TiO₂/ZnS/GO (1:1:1) composite to remove multiple dyes as dye-laden effluents typically comprise a wide spectrum of dye candidates. These dyes are frequently employed in industrial operations that produce considerable amounts of dye-containing effluents, including textile, dyeing, paper, tannery, and paint (Nasar and Mashkoor, 2019). The cationic dyes MB and Rho B are commonly utilised in the dyeing of acrylic, wool, nylon, and silk. These dyes have distinct chemical structures based on the substituted aromatic group, which has one or more hydrogen atoms of a central structure that a replaced by functional or large substituent groups. Cationic dye molecules are positively charged, water-soluble, and generate coloured cations in solution. MO is a common water-soluble

azo dye that is also widely utilised in a variety of industries, including textile, paper, printing, and food, and is commonly discharged in industrial effluent (Ali et al., 2019).

For comparison purposes, the dyes were first investigated individually, where almost complete removal was achieved for MB (98.4%) followed by Rho B (95.7%) and MO (83.6%) at the end of 150 min of UVA irradiation (Figure 4.17 (a)). The removal of these individual dyes was substantially driven by the adsorption process. However, this trend was observed to decline when all the dyes were present in a mixture. MB retained its highest removal (99.1%). Rho B, which shares the same nature as MB was only removed by 62.1%, whereas MO became the least removed dye with 44.3% (Figure 4.17(b)).

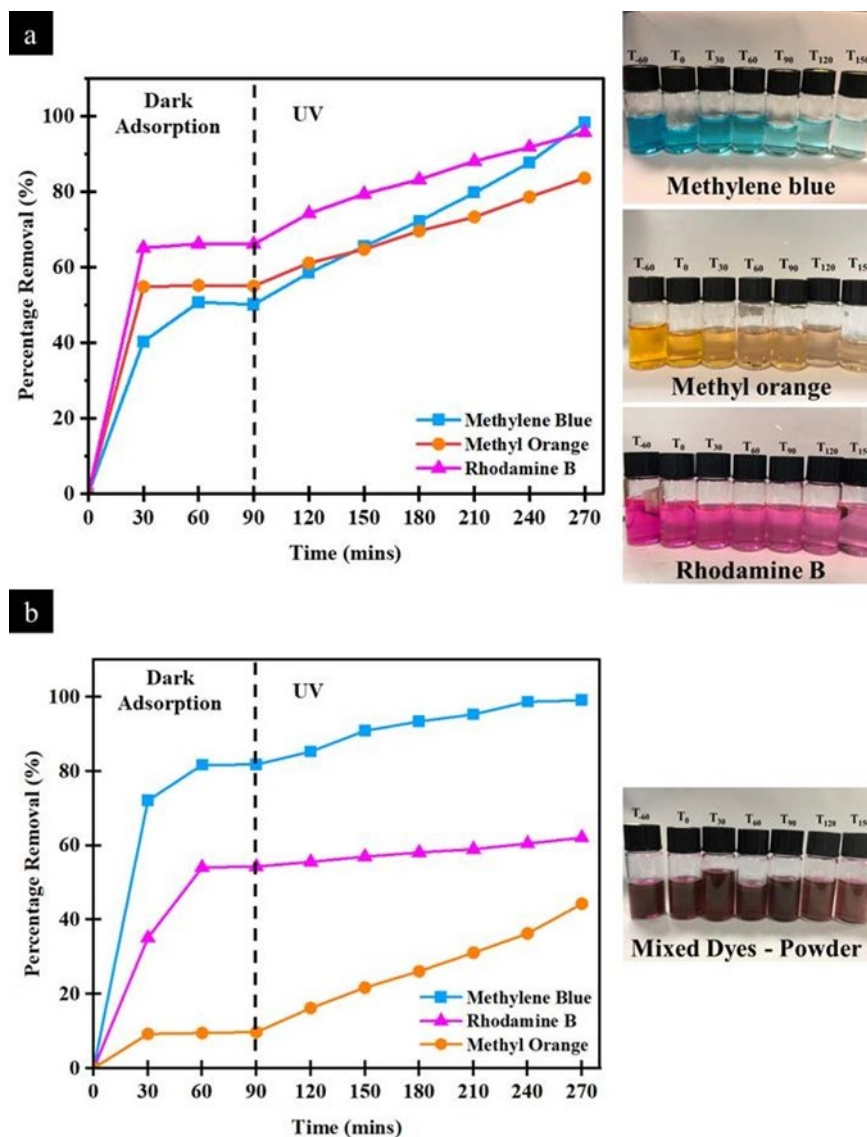


Figure 4.17: Removal efficiency of $\text{TiO}_2/\text{ZnS}/\text{GO}$ (1:1:1) for (a) individual MB, MO and Rho B and (b) mixed dyes solution.

The removal of individual cationic dyes MB and Rho B (Figure 4.17(a)) was higher than the mixed solution (Figure 4.17(b)), whereas MO appears as the least removed dye. The results in Figure 4.17(b)) suggest that when present together, the cationic dyes MB and Rho B exhibit comparatively better photocatalytic and adsorption properties than the anionic dye MO. The differing molecular structures of the dyes can account for their distinct behaviours during the photocatalytic degradation reaction. The composite's surface contains a high concentration of negative charges, which could selectively attract and bind

to the MB and Rho B molecules at specific active sites of the catalyst, leading to their faster degradation. As a result, the anionic MO dye may not undergo significant degradation due to its molecular properties (Figure 4.17(b)) (Reddy et al., 2015). MB has a simple molecular structure with N=N bond that can be easily degraded under light irradiation as compared to MO, which is relatively stable, symmetrical and has a conjugated molecular structure that is resilient to degradation (Yin, 2015).

Figure 4.18 illustrates the UV profile based on the time interval for both individual and mixed dyes. The intensity of the absorption peak of mixed dye solutions (Figure 4.18(a)), as well as individual dyes, MB (Figure 4.18 (b)), MO (Figure 4.18(c)), and Rho B (Figure 4.18(d)) decreases with irradiation time. The peak at 664 nm (MB) refers to the MB chromophore group, which includes the dimethylamine and thiazine groups (NH₂). These absorption bands surrounding the λ_{max} show loss of conjugation, specifically the breakage of organic molecules during UV irradiation adjacent to the azo link. Similar to this, the aromatic rings connected to the chromophore groups of dye molecules are responsible for the peaks at 294 and 256 nm (Figure 4.18(a) and (b)) (Tekin et al., 2018). The main absorption peaks at 664 nm decreased because of MB's N-demethylation and deamination, whereas the peaks at 294 and 256 nm decreased as a result of the degradation of the aromatic rings in the dye molecules (Tekin et al., 2018).

The mixed dye solutions (Figure 4.18(a)) do not exhibit MO peaks at 464 nm, unlike the individual dye samples (Figure 4.18(c)). MO typically generates absorption peaks at 464 nm and 270 nm, originating from its chromophoric groups. The absorption edge was found to be slightly shifted to a shorter wavelength. The peak at 464 nm becomes less intense with longer treatment times, indicating a degradation of the azo groups (-N=N-) in the MO molecules (Figure 4.19(c)). As time progresses, there is a noticeable increase

in strong absorption peaks associated with aromatic compounds within the 250 – 350 nm wavelength range. At 568 nm, the centre of the absorbance peak of Rho B, a chromophore with four N-ethyl groups on either side of the xanthene ring (Figure 4.19(a) and (d)), corresponds to the $n \rightarrow \pi^*$ transition of C=N and C=O groups. Rho B degrades directly through chromophore cleavage, which is followed by hydroxylation, aromatic ring opening, and mineralization (Thao et al., 2017).

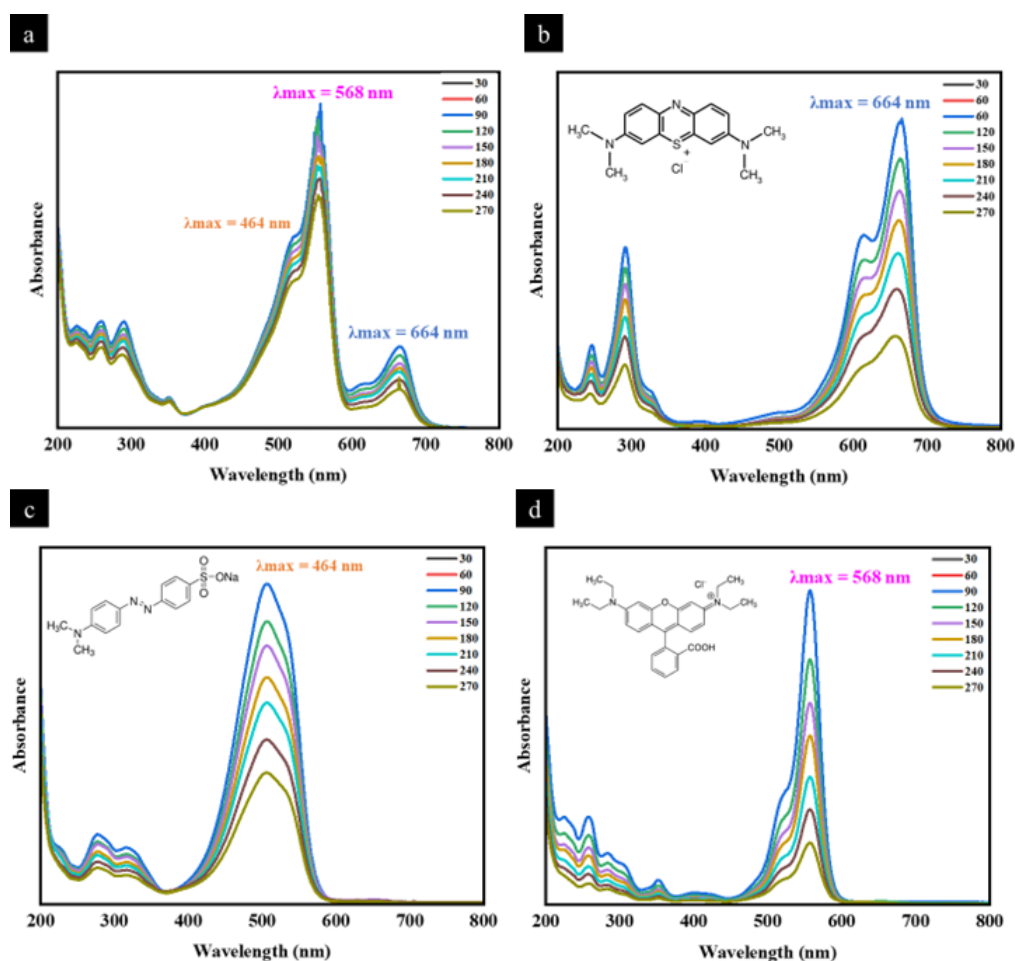


Figure 4.18: Absorption spectra of (a) mixed dye solutions (MB, MO and Rho B), individual dyes of (b) MB, (c) MO, and (d) Rho B degradation using $\text{TiO}_2/\text{ZnS}/\text{GO}$ (1:1:1).

Alg is a naturally occurring anionic polymer and various studies have applied this polymer for the removal of basic and dispersed dyes (Aljar et al., 2021). Figure 4.19 depicts the performance of $\text{TiO}_2/\text{ZnS}/\text{GO}-\text{CaAlg}$ beads in the mixed dye solution.

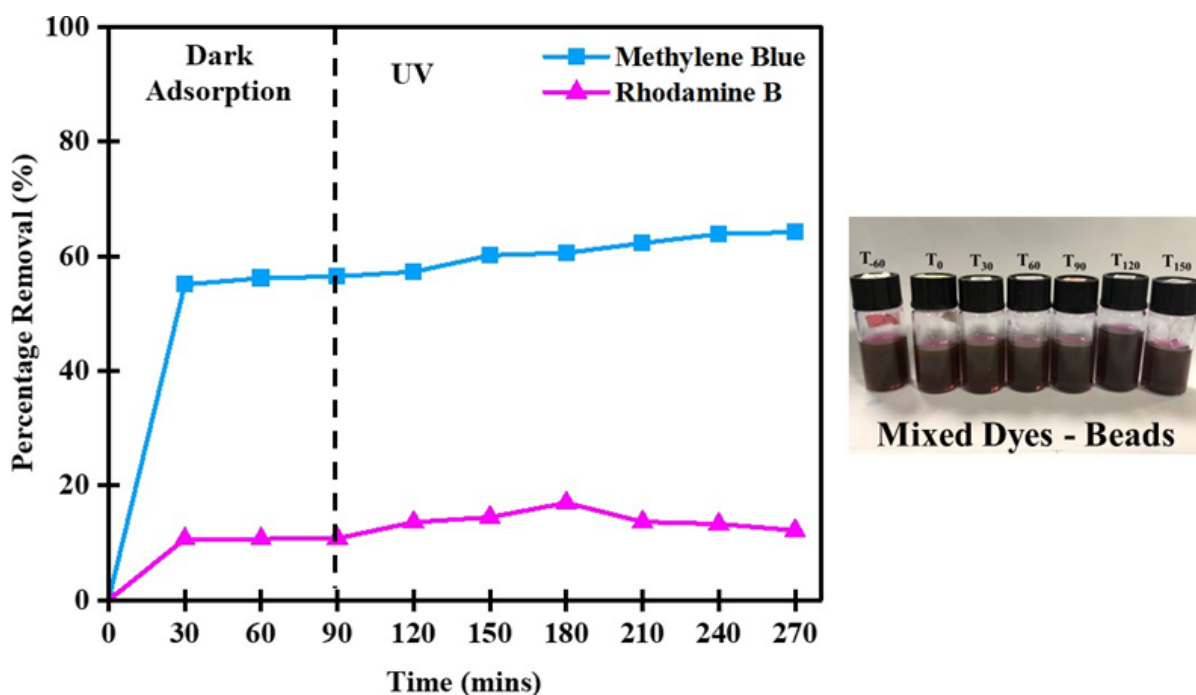


Figure 4.19: $\text{TiO}_2/\text{ZnS}/\text{GO}-\text{CaAlg}$ beads in mixed dyes solution after 3 h of treatment under UVA.

The adsorption capacity of the $\text{TiO}_2/\text{ZnS}/\text{GO}-\text{CaAlg}$ beads appears to be superior for the removal of MB and Rho B in the mixed dye's reaction system. However, no adsorption nor degradation of MO took place in the mixed dye solution. The binding of these cationic dyes to the anionic polymer can take place either by electrostatic or by other aggregation interactions, such as hydrogen bond and/or hydrophobic interaction. The additional strong interactions between the charge of the MB dye and the carboxylate group of alginates could also be responsible for the higher adsorption of MB (Tekin et al., 2018). Significant electrostatic forces occur between the positively charged groups of MB and Rho B and the negatively charged groups, like $-\text{COO}^-$ on alginate (Eldin et al., 2019). Due

to MB has simpler molecular structure with a N=N bond as compared to Rho B, MB can be easily degraded faster and easier under light irradiation.

4.3 Recyclability potential of TiO₂/ZnS/GO

The efficiency of TiO₂/ZnS/GO as a photocatalyst is influenced by several factors, such as particle size, surface area, and porosity. However, practical applications of TiO₂/ZnS/GO are restricted due to the difficulties in separating and recycling them after photocatalytic reactions. The immobilization of nanoparticles onto insoluble supports such as Ca-Alg has been attempted to overcome these drawbacks. Figure 4.20(a) shows the removal trend of MB after 4 cycles between TiO₂/ZnS/GO (1:1:1) powder and TiO₂/ZnS/GO-CaAlg beads. From the recycling study, there is a significant difference between each cycle for both powder and beads after 150 min UVA irradiation.

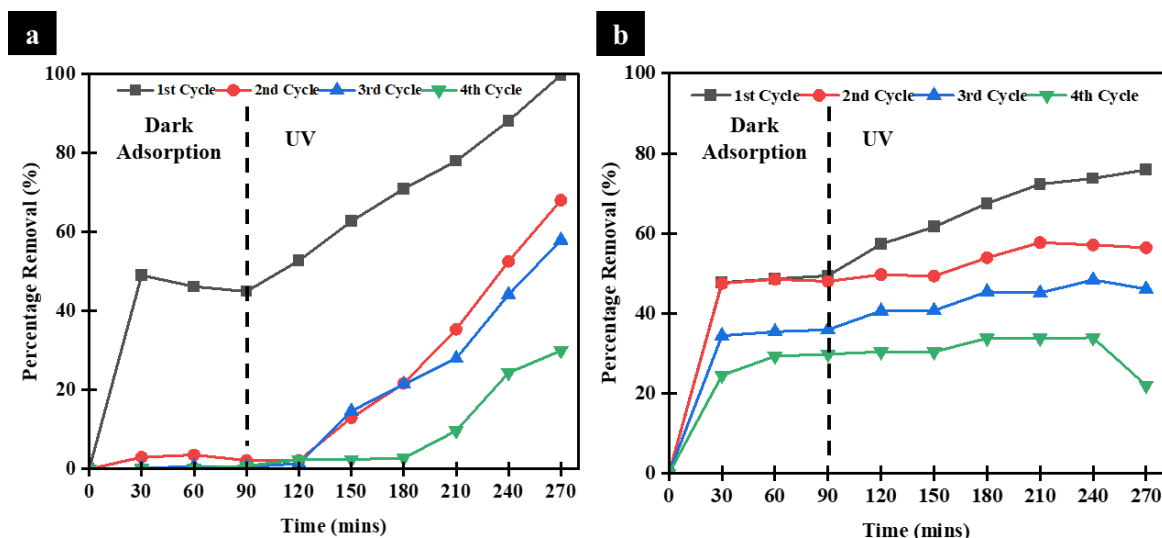


Figure 4.20: Recycling performance of (a) TiO₂/ZnS/GO powder and (b) TiO₂/ZnS/GO-CaAlg beads in removing MB (20 ppm) after 4 cycles.

Figure 4.20 illustrates the recyclability of TiO₂/ZnS/GO powder and TiO₂/ZnS/GO-CaAlg beads after being recovered and reused for the MB removal study. The powder

composite was recovered by filtering and regenerated with three DIW washes before drying in an oven at 100°C for 2 hours. Meanwhile, the TiO₂/ZnS/GO-CaAlg beads were also washed with DIW and dried at room temperature overnight after their treatment with MB. It was found that when the TiO₂/ZnS/GO-CaAlg beads were washed with 95% ethanol solution, the beads were not efficient enough to be reused as the removal of MB dye was ineffective. The efficiency of the TiO₂/ZnS/GO-CaAlg beads after washing with ethanol suggests that the washing process may have negatively impacted the structure of the beads, such as dissolution of the polymer matrix (CaAlg). This structural damage may hinder the immobilization or stability of the photocatalyst within the beads, resulting in efficiency upon reuse (Hermansson et al., 2016).

MB maintained a nearly constant removal trend over the investigated photocatalytic cycles (Figure 4.20(b)). The trend showed that the beads were more stable compared to the powder as CaCl₂ solution plays an important role in the crosslinking of alginate and Ca²⁺. Although the removal percentage using TiO₂/ZnS/GO powder was higher than the beads, the beads demonstrated higher stability regardless of a notable decrease in efficiency with the increasing number of cycle treatments. Mass monitoring before and after the application of the MB degradation has found that a weight reduction for TiO₂/ZnS/GO-CaAlg beads was 9% only (1.0 to 0.91 g) compared to TiO₂/ZnS/GO powder with 31% (1.0 to 0.69 g) after four cycles.

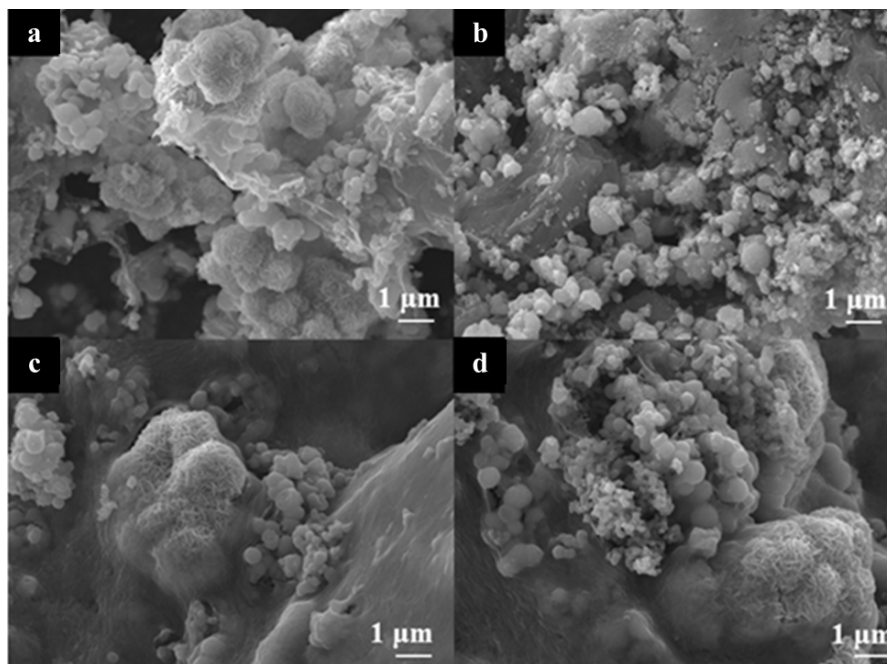


Figure 4.21: (a) and (c) SEM images $\text{TiO}_2/\text{ZnS}/\text{GO}$ powder and $\text{TiO}_2/\text{ZnS}/\text{GO}-\text{CaAlg}$, respectively before irradiation, (b) and (d) $\text{TiO}_2/\text{ZnS}/\text{GO}$ powder and $\text{TiO}_2/\text{ZnS}/\text{GO}-\text{CaAlg}$ after irradiation (4 cycles).

After irradiation, the morphologies on the beads are less severe compared to the powder form. The weight percentages of $\text{TiO}_2/\text{ZnS}/\text{GO}-\text{CaAlg}$ before and after 150 min UVA irradiation also showed less drastic loss of weight (Table 4.3). The CaCl_2 solution plays a crucial role in the crosslinking of Ca^{2+} and alginate. This cross-linking process strengthens the beads, allowing for their application in repeated cycles (Dallabona et al., 2012). The SEM images (Figure 4.21((a)-(b))) of the powder recovered showed that the surface morphology changed drastically compared to the beads (Figure 4.21 ((c)-(d))). Besides, there are less severe morphology changes on the beads after irradiation (Figure 4.21(d)). The beads exhibited high stability, although there was a noticeable decrease in efficiency as the number of treatment cycles increased, as compared to $\text{TiO}_2/\text{ZnS}/\text{GO}$ powder, which showed a higher removal percentage than the beads.

Table 4.3: Comparison of elemental compositions between TiO₂/ZnS/GO powder and TiO₂/ZnS/GO-CaAlg before and after 150 min UVA irradiation.

Samples	Weight % of elements							
	C	O	Na	S	Cl	Ca	Ti	Zn
TiO₂/ZnS/GO-CaAlg fresh beads	24.12	30.65	0.60	4.36	3.08	6.67	17.40	13.12
TiO₂/ZnS/GO-CaAlg after 150 min UVA irradiation	18.92	27.10	0.27	6.50	2.82	5.87	19.67	18.85
TiO₂/ZnS/GO (1:1:1) fresh powder	10.50	18.54	Nd	13.02	0.14	Nd	13.02	26.68
TiO₂/ZnS/GO (1:1:1) after 150 min UVA irradiation	9.44	17.50	Nd	12.67	0.13	Nd	12.43	13.69

*Nd: Not detected

EDX analysis of TiO₂/ZnS/GO powder and TiO₂/ZnS/GO-CaAlg beads showed only minimal differences in their intensities before and after 150 min UVA irradiation suggesting the stability of both materials under the experimental conditions (Appendix 3). Additionally, the weight percentages of the fresh TiO₂/ZnS/GO-CaAlg beads and after 150 min UVA irradiation also showed less drastic loss of weight (Table 4.3). Although TiO₂/ZnS/GO powder recycling exhibited better degradation, the beads might offer a cost-effective, readily recoverable, and recyclable hybrid photocatalyst for use in wastewater treatment systems.

4.4 Elucidating MB, MO, and Rho B removal by TiO₂/ZnS/GO

The results indicate that the TiO₂/ZnS/GO composite demonstrates great potential as a photocatalytic material for the degradation of dyes. The inclusion of TiO₂ and ZnS in the TiO₂/ZnS/GO composites enhances both the adsorption and photocatalytic degradation capabilities of the composite during the process of dye degradation (Figure 4.22). By providing additional adsorption sites for dye molecules, ZnS can improve the adsorption capability of the TiO₂/ZnS/GO composite. TiO₂ and ZnS heterojunction can also improve the transfer and separation of photo-generated electron-hole pairs, resulting in higher photocatalytic efficiency whereas GO acts as an adsorbent for contaminants, which can adsorb a wide range of contaminants (Figure 4.6(a)). GO in TiO₂/ZnS/GO composite provided a high surface area with sufficient functional groups (carboxyl, hydroxyl, and epoxy groups), improving the dispersibility and stability of the nanoparticles. Although the surface area of GO is larger than the 1:1:1 composite, the photocatalytic activity of TiO₂/ZnS/GO (1:1:1) showed notable improvement over GO due to the reduction of photogenerated charge carriers decrease upon the addition of TiO₂ and ZnS based on the recombination rate of TiO₂/ZnS/GO (1:1:1) (Figure 4.9 (b)) (Park et. al., 2014).

The following formulas are used to calculate the edge potential for the valence and conduction band of a semiconductor at the point of zero charge (Liu et al., 2015c).

$$E_{CB} = X - E^c - 0.5 E_g$$

$$E_{VB} = E_{CB} + E_g$$

Where X is the absolute electronegativity of the semiconductor, and the X values of TiO₂ and ZnS are 5.8 eV and 5.26 eV, respectively (Tonda et al., 2015). E^c is the energy of free electrons relative to the standard hydrogen electrode (E^c value is 4.5 eV) and E_g is the band

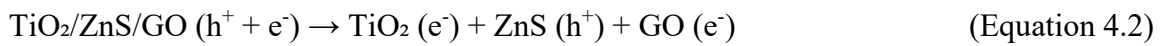
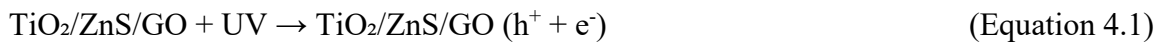
gap. The E_{VB} values of TiO_2 and ZnS were estimated to be 2.98 eV and 2.51 eV, respectively and the E_{CB} values calculated were -0.38 eV and -0.99 eV, respectively. The Fermi level of GO is -0.08 eV versus NHE. Due to its excellent electrical conduction, the 2D GO behaves as an electron transfer channel, which can transport the photo-induced electron quickly (Xu and Schoonen, 2000).

The potential of the valence band edge of TiO_2 (2.98 eV) and ZnS (2.51 eV) is greater than that of the oxidation potentials of $OH^-/\bullet OH$ (1.99 eV) and $H_2O/\bullet OH$ (2.34 eV), facilitating the oxidation of both OH^- and H_2O to generate $\bullet OH$ radicals. In addition, the potential of the conduction band for TiO_2 and ZnS is greater than that of the standard potential of $O_2/O_2^{\bullet -}$ (-0.33 eV) favouring the reduction of O_2 to $O_2^{\bullet -}$. Hence, both $\bullet OH$ and $O_2^{\bullet -}$ radicals are responsible for the degradation of MB in the presence of $TiO_2/ZnS/GO$.

The high surface area of GO ($266.86\text{ m}^2/\text{g}$) (Figure 4.6(a); Table 4.2) implies that it can also strongly adsorb the dye molecules. The anticipated processes involved in the dye removal are: (1) the dye molecules migrate to the outer surface of the composite, (2) the dyes enter the pores of adsorbent composite particles and (3) the adsorption takes place on the surface of the composite (Nagaraju et al., 2022). The chemisorption process involves electrostatic interactions and hydrogen bonds between the π electrons of GO and the cationic dyes (MB and Rho B). Rho B is a readily adsorbed planar molecule because of the interactions between the aromatic backbones of the dyes and the hexagonal skeleton of GO. Both MB and MO possess π -conjugated backbones, suggesting their potential to bind to GO through π - π bond interactions involving the aromatic rings of the dyes and the carbon basal plane of GO. MB and MO can interact with GO via hydrogen bonding with many hydroxyl groups in the GO structure. The $-OH$ group of GO and the N or S heteroatoms in the aromatic ring of MB can create hydrogen bonds. MO can also form H-

bonds with the -OH group of GO via the oxygen atoms in SO₃. GO can also adsorb MB via electrostatic interactions, which occur when species with opposite electrical charges attract one other.

Then, a series of chain reactions mediated by •OH and •O₂⁻ radicals will result in the photodegradation of dyes when electron-hole pairs develop at the semiconductor surface in response to light irradiation (Eq 4.1 – 4.5) (Kashinath et al., 2017; Yang et al., 2010). When UV light is irradiated on the TiO₂/ZnS/GO photocatalyst, electrons from the valence band are driven into the conduction band of ZnS, leaving holes in the valence band. The electrons are subsequently transferred to the conduction band of TiO₂. Due to the exceptionally high electron mobility of graphene, these electrons will be transferred from TiO₂ to graphene and then caught by O₂ to generate O₂⁻. In addition, photogenerated holes in ZnS-graphene's valence band migrate to the surface and oxidize hydroxyl to create •OH radical, which significantly aids in the oxidation of dyes. Overall, the adsorption and photocatalytic degradation processes work together to remove the dye molecules from the solution in the presence of TiO₂/ZnS/GO composite.



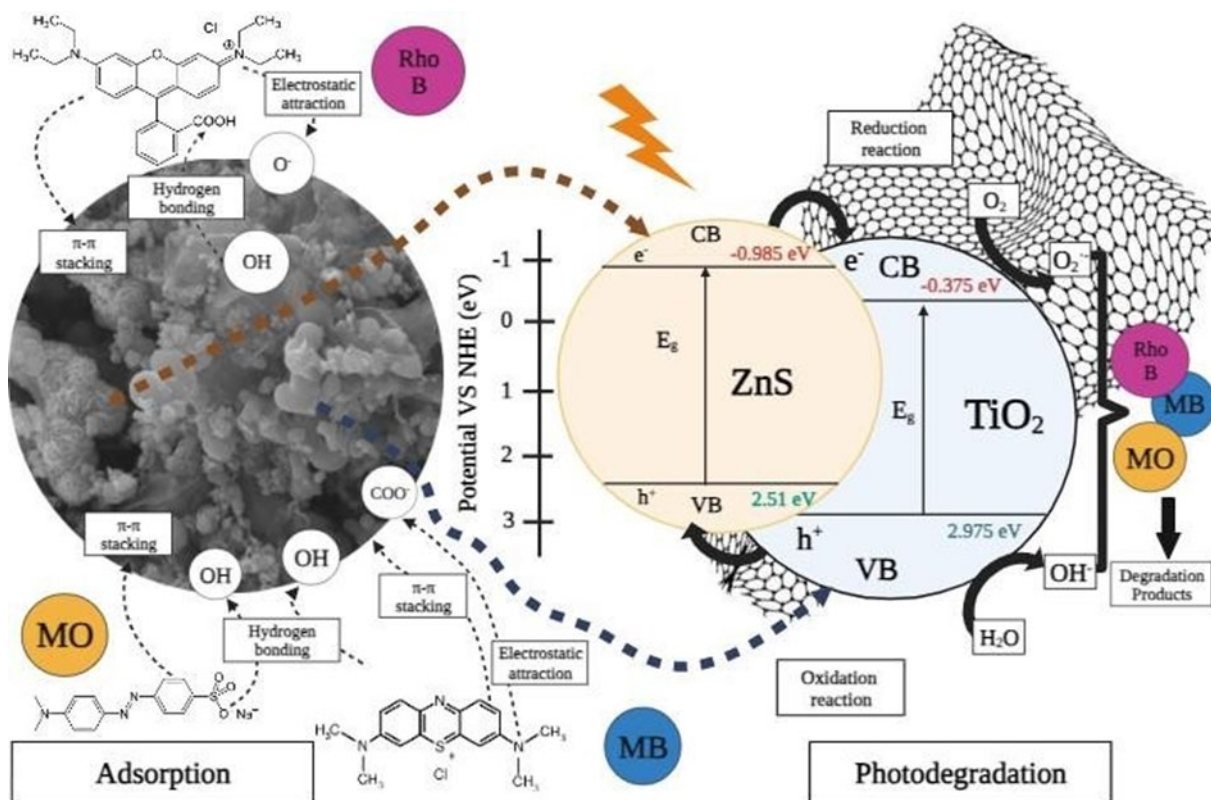


Figure 4.22: Schematic illustration of the adsorption and photocatalytic degradation of TiO₂/ZnS/GO on dyes (MB, Rho B and MO).

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The hydrothermal technique demonstrated its efficacy in the synthesis of $\text{TiO}_2/\text{ZnS}/\text{GO}$ composites, as confirmed through various characterization methods. The composite of $\text{TiO}_2/\text{ZnS}/\text{GO}$ with a ratio of 1:1:1 exhibits remarkable effectiveness in removing MB, achieving an impressive removal rate of 98.4%. The homogeneous distribution of TiO_2 on the surface and the vast surface area of the composite are responsible for its excellent performance. The incorporation of GO into the composite also significantly augmented its specific surface area, leading to enhanced adsorption of dyes and improved capabilities for charge transportation and separation based on the electrochemistry analysis. This can be further proven by the adsorption performance of $\text{TiO}_2/\text{ZnS}/\text{GO}$ with the highest removal of MB at 50.4%, as compared to its single and binary composites. The high performance of the $\text{TiO}_2/\text{ZnS}/\text{GO}$ (1:1:1) composite's photocatalytic efficiency is intricately influenced by the operational parameters. The $\text{TiO}_2/\text{ZnS}/\text{GO}$ ratio (1:1:1), dosage (1.0 g) and dye concentration (20 ppm) ensure sufficient active sites, while mixed dye solutions provide an understanding of interactions among different dyes whereas pH levels impact the surface charge and ionization, crucial for adsorption and photocatalysis. In the case of the radical scavengers study, the trend in MB removal is as follows: no radical scavenger (98.4%) > H_2O_2 (94.4%) > methanol (93.6%) > IPA (89.9%) > BQ (89.3%). In comparison, individual dye removal capacity order was found to be MB (98.4%) > Rho B (95.7%) > MO (83.6%) using $\text{TiO}_2/\text{ZnS}/\text{GO}$ powder whereas in mixed dye solutions, powder $\text{TiO}_2/\text{ZnS}/\text{GO}$ displayed better

performance than $\text{TiO}_2/\text{ZnS}/\text{GO}$ immobilized beads. Furthermore, compared to $\text{TiO}_2/\text{ZnS}/\text{GO}$ powder, the recycling study (four cycles) demonstrated the stability and sustainable performance of $\text{TiO}_2/\text{ZnS}/\text{GO}-\text{CaAlg}$ beads, making them more ecologically friendly and sustainable. Overall, this study emphasizes the multifunctional nature of the $\text{TiO}_2/\text{ZnS}/\text{GO}$ composite, which excels in both adsorption and photocatalysis. The $\text{TiO}_2/\text{ZnS}/\text{GO}$ composite and $\text{TiO}_2/\text{ZnS}/\text{GO}-\text{CaAlg}$ beads present a promising and cost-effective solution for wastewater treatment in industries that encounter complex dye mixtures.

5.2 Recommendations

The consideration of integrating new catalysts or different types of nanostructures (nanotubes or nanorods) into existing composite may enhance the photocatalytic capabilities of $\text{TiO}_2/\text{ZnS}/\text{GO}$ composite. This approach seeks to broaden the composite's range of active materials beyond TiO_2 , ZnS , and GO , aiming for synergistic effects that can significantly improve its overall performance in degrading pollutants under visible light exposure. By incorporating different catalysts or nanostructures, the composite may benefit from enhanced absorption spectra, more efficient charge separation and transfer processes, and a broader range of catalytic reactions. Ultimately, exploring additional catalysts opens up possibilities for creating advanced materials with superior photocatalytic efficiency for water treatment applications. Moreover, the utilization of Alg as a promising adsorbent in nanocomposite fabrication should be explored further, and subsequent investigations should focus on emerging degradation byproducts. Future studies can investigate the recyclability potential with different types of dyes, including mixed dyes, to evaluate the composite's effectiveness in adsorption and degradation properties. Additionally, it is

recommended to expand this study by enhancing the photocatalytic activity of $\text{TiO}_2/\text{ZnS}/\text{GO}-\text{CaAlg}$ through variations in the ratios of TiO_2 , ZnS , GO , and Alg for the removal of MB, MO, Rho B, and mixed dyes. Additionally, given the intended use of $\text{TiO}_2/\text{ZnS}/\text{GO}$ in water treatment, the assessment focuses on the potential leaching of substances from the composite into the treated water. This involves analyzing the water quality and ensuring that the treated water is safe for consumption and does not introduce harmful substances.

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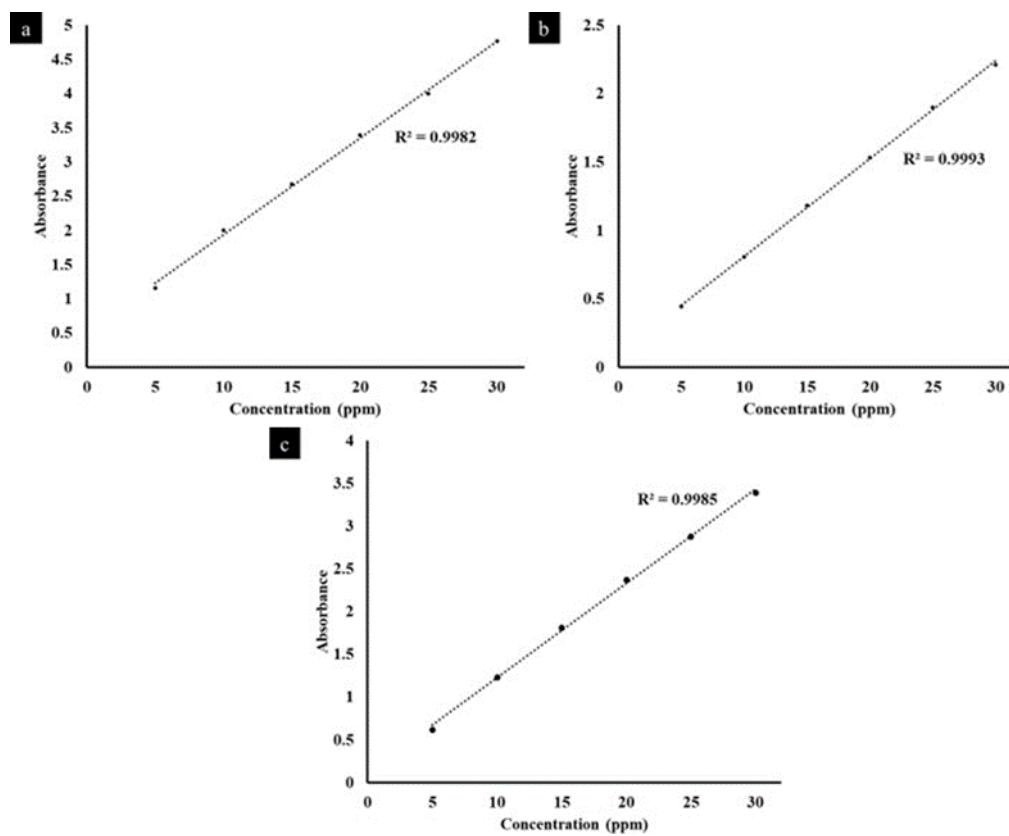
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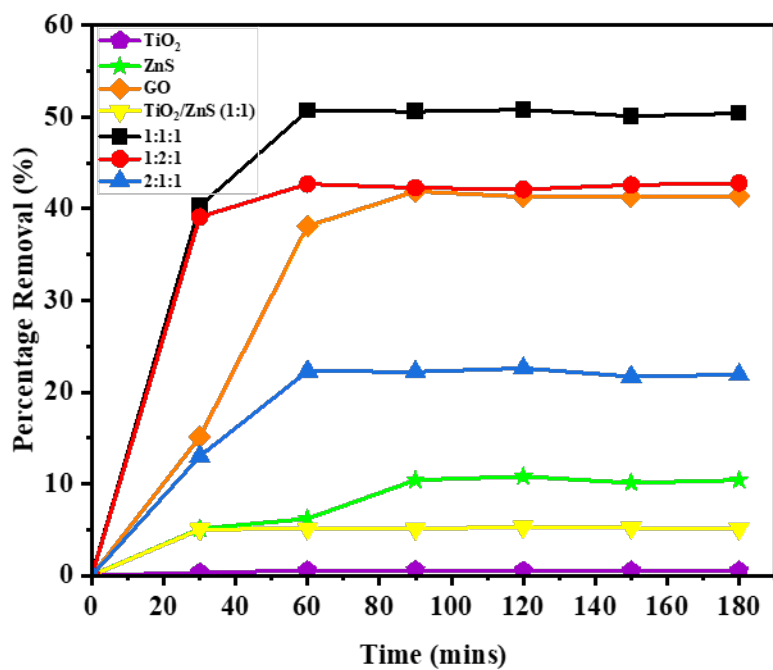
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APPENDICES

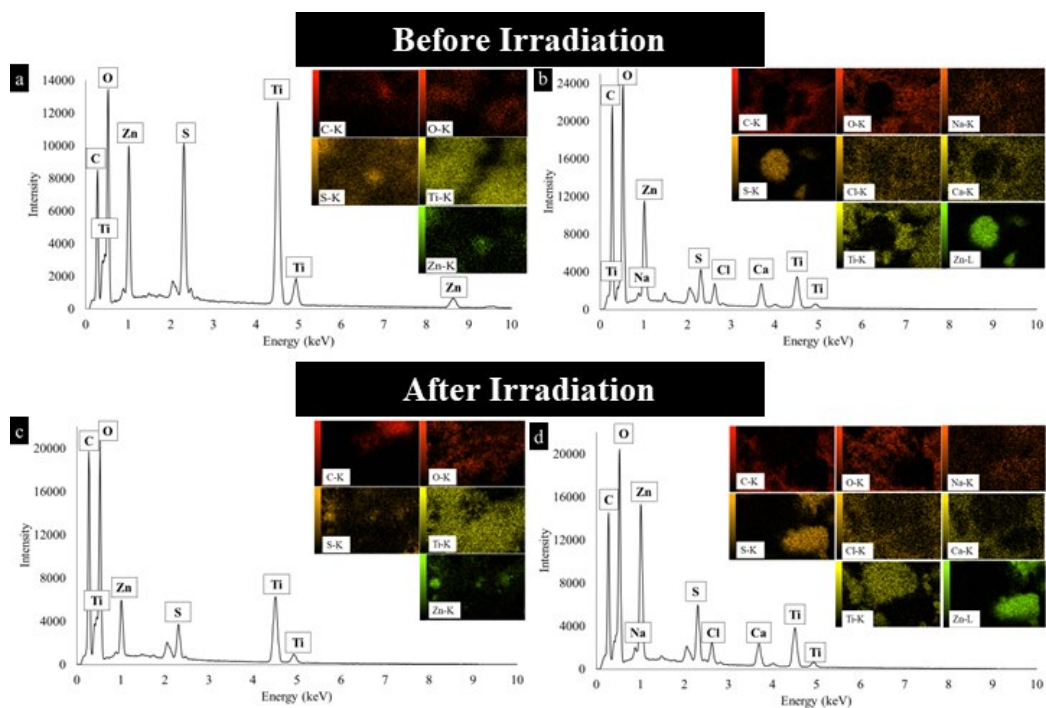
Appendix 1: Calibration curve of standard (a) MB, (b) Rho B, and (c) MO.



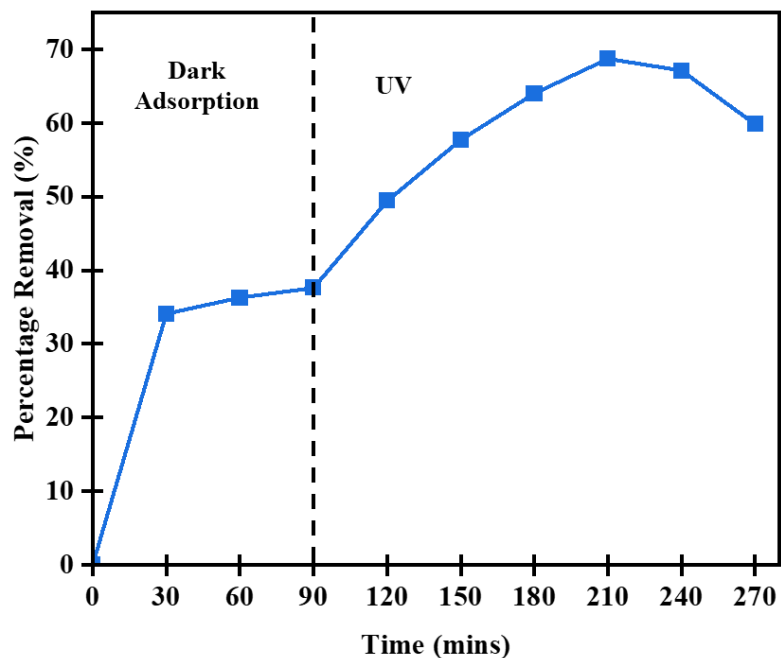
Appendix 2: Dark adsorption of TiO_2 , ZnS , GO , TiO_2/ZnS (1:1), $\text{TiO}_2/\text{ZnS}/\text{GO}$ (1:1:1), $\text{TiO}_2/\text{ZnS}/\text{GO}$ (1:2:1), and $\text{TiO}_2/\text{ZnS}/\text{GO}$ (2:1:1) after 150 min



Appendix 3: EDX mapping of a $\text{TiO}_2/\text{ZnS}/\text{GO}$ powder and b $\text{TiO}_2/\text{ZnS}/\text{GO}-\text{CaAlg}$, respectively before irradiation; c $\text{TiO}_2/\text{ZnS}/\text{GO}$ powder and d $\text{TiO}_2/\text{ZnS}/\text{GO}-\text{CaAlg}$, respectively after 150 min UVA irradiation.



Appendix 4: The effect of adsorbent dosage 1.3 g of TiO₂/ZnS/GO (1:1:1) on the removal of 20 ppm of MB.



Appendix 5: Photocatalytic experiments using various catalyst dosages (0.1 to 1.0 g) at 20 ppm MB solution.

Sample (g)	Time	Concentration (mg/L)	Removal Percentage (%)
0.1	90	18.8	5.9
	270	14.02	29.9
0.3	90	16.8	16.1
	270	9.1	54.6
0.6	90	12.4	38.2
	270	3	85.1
1.0	90	10	50.1
	270	0.32	98.4

Appendix 6: Photocatalytic experiments with various concentrations of MB solution (20 – 35 ppm) using 1.0 g of TiO₂/ZnS/GO (1:1:1)

Sample (ppm)	Time	Concentration (mg/L)	Removal Percentage (%)
20	90	10	50.1
	270	0.32	98.4
25	90	15.9	36.5
	270	4.2	83.2
30	90	16.5	45
	270	7.9	76.4
35	90	15.8	54.9
	270	6.3	82.1

Appendix 7: Photocatalytic experiments with different ratios of TiO₂/ZnS/GO (1:1:1, 1:2:1, and 2:1:1) with 1.0 g each in 20 ppm of MB

Sample (ratio)	Time	Concentration (mg/L)	Removal Percentage (%)
1:1:1	90	10	50.1
	270	0.32	98.4
1:2:1	90	10.8	45.9
	270	1.6	91.8
2:1:1	90	15.5	22.4
	270	0.17	99.1

Appendix 8: Photocatalytic experiments using various pH (3, 5, 7, and 10) with 1.0 g of TiO₂/ZnS/GO (1:1:1) in 20 ppm of MB

pH	Time	Concentration (mg/L)	Removal Percentage (%)
3	90	6.5	67.6

	270	0.65	96.8
5	90	7.9	60.5
	270	2.5	87.3
7	90	8.7	56.5
	270	4.7	76.3
10	90	5.4	60.3
	270	2.05	89.8

Appendix 9: Photocatalytic experiments using different dyes (MB, Rho B, and MO) individually with 1.0 g of TiO₂/ZnS/GO (1:1:1) powder

Sample (g)	Time	Concentration (mg/L)	Removal Percentage (%)
MB	90	10	50.1
	270	0.32	98.4
MO	90	8.7	55
	270	2.9	83.6
Rho B	90	6.8	66.1
	270	0.87	95.7

Appendix 10: Photocatalytic experiments using different dyes (MB, Rho B, and MO) in mixed solution with 1.0 g of TiO₂/ZnS/GO (1:1:1) powder

Sample (g)	Time	Concentration (mg/L)	Removal Percentage (%)
MB	90	0.91	81.8
	270	0.55	99.1
MO	90	18.06	9.7
	270	11.1	44.3
Rho B	90	0.74	54.3
	270	0.63	62.1

Appendix 11: Photocatalytic experiments using different dyes (MB and Rho B) in mixed solution with 1.0 g of TiO₂/ZnS/GO (1:1:1) beads

Sample (g)	Time	Concentration (mg/L)	Removal Percentage (%)
MB	90	8.7	56.5
	270	7.16	64.2
Rho B	90	17.8	10.8
	270	17.6	12.2

Appendix 12: Photocatalytic degradation of 20 ppm of MB solution by 1.0 g of TiO₂/ZnS/GO (1:1:1) powder and 1.0 g of TiO₂/ZnS/GO (1:1:1) beads through 4 cycles (recycle study)

Sample (g)	Time	Concentration (mg/L)		Removal Percentage (%)	
		Powder	Beads	Powder	Beads
1st	90	1.7	1.6	45	49.6
	270	0.54	1.03	99.8	75.9
2nd	90	2.6	1.6	0.9	48
	270	1.2	1.4	68.1	56.4
3rd	90	0.6	1.9	0.6	35.9
	270	1.4	1.7	57.9	46.1
4th	90	2.6	1.9	0.8	29.8
	270	1.9	2.2	30	22.2