Faculty of Resource Science and Technology

Adsorption and Photocatalytic Performance of Ternary TiO_2/ZnS/GO Composite for the Removal of Dyes

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Adsorption and Photocatalytic Performance of Ternary TiO_2/ZnS/GO Composite for the Removal of Dyes

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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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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 TiO_2/ZnS/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 TiO_2/ZnS/GO composites. Due to its superior performance, 1.0 g of the TiO_2/ZnS/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 TiO_2/ZnS/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 •OH and $\bullet O_2^-$ radicals. TiO_2/ZnS/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 TiO_2/ZnS/GO-CaAlg beads compared to the TiO_2/ZnS/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 TiO_2/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 (TiO_2) sebagai komponen utama telah diiktiraf untuk prestasinya yang amat memberangsangkan dalam rawatan air. Zink sulfida (ZnS) dan oksida grafin (GO) mengalakkan pemisahan pembawa cas pada TiO_2 yang boleh meningkatkan reaksi pemindahan elektron dan seterusnya meningkatkan prestasinya sebagai bahan fotokatalisis dan penjerapan. Tujuan kajian ini adalah untuk mengkaji keberkesanan komposit TiO_2/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 TiO_2/ZnS/GO. Berdasarkan prestasi perbandingan di antara nisbah TiO_2/ZnS/GO yang dikaji, 1.0 g TiO_2/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 TiO_2/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 $\bullet OH$ and $\bullet O_2^-$. Keputusan menunjukkan bahawa TiO_2/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 TiO_2/ZnS/GO dan TiO_2/ZnS/GO-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*

TABLE OF CONTENTS

		Page
DECLARATION		**i**
ACKNOWLEDGEMENT		**ii**
ABSTRACT		**iii**
ABSTRAK		**iv**
TABLE OF CONTENTS		**vi**
LIST OF TABLES		**x**
LIST OF FIGURES		**xi**
LIST OF ABBREVIATIONS		**xiv**
CHAPTER 1	**INTRODUCTION**	**1**
1.1	General Introduction	1
1.2	Problem Statement	5
1.3	Research Question	7
1.4	Objectives	8
1.5	Significance of the study	9
CHAPTER 2	**LITERATURE REVIEW**	**10**
2.1	Titanium dioxide (TiO_2) semiconductor	10
2.2	Zinc sulphide (ZnS)	14
2.3	Graphene oxide (GO)	16

2.4 Binary TiO_2/ZnS composites 18

2.4.1 Fabrication methods of TiO_2/ZnS composites 21

2.5 Binary of TiO_2/GO composites 30

2.5.1 Fabrication methods of TiO_2/GO composites 30

2.6 Photocatalytic Performance of TiO_2/ZnS-based ternary composites 39

2.7 Photocatalytic Performance of TiO_2/GO-based ternary composites 48

2.8 Immobilization of TiO_2-based materials on Alginate 52

2.9 Parameters affecting photocatalytic degradation 54

2.9.1 Dosage of photocatalyst 54

2.9.2 Concentration of dye 55

2.9.3 Solution pH 56

2.9.4 Presence of radical scavengers 57

2.10 Model Pollutants 59

2.10.1 Dyes 59

CHAPTER 3 MATERIALS AND METHODS 66

3.1 Materials and reagents 66

3.2 Synthesis of TiO_2 and GO composites 66

3.3 Synthesis of TiO_2/ZnS/GO composites 67

3.4 Synthesis of TiO_2/ZnS/GO immobilized beads 68

3.5 Characterization of TiO_2/ZnS/GO composite 69

3.6 Dye solutions concentration 70

3.7 Photocatalytic experiments 71

3.8 Efficiency comparisons and recycling study 73

CHAPTER 4 RESULTS AND DISCUSSION 74

4.1 Characterization of TiO_2/ZnS/GO 74

4.1.1 Raman Spectroscopy 74

4.1.2 FTIR spectra 75

4.1.3 XRD analysis 78

4.1.4 SEM-EDX analysis 79

4.1.5 BET surface area analysis 83

4.1.6 TEM analysis 85

4.1.7 Spectral analysis of UV-Vis DRS 86

4.1.8 Electrochemistry analysis 88

4.2 TiO_2/ZnS/GO performance on MB removal 90

4.2.1 Control experiments 90

4.2.2 Parameters that affect the removal of MB 94

4.3 Recyclability potential of TiO_2/ZnS/GO 108

4.4 Elucidating MB, MO, and Rho B removal by TiO_2/ZnS/GO 112

CHAPTER 5 CONCLUSION AND RECOMMENDATION 116

5.1 Conclusion 116

5.2 Recommendations 117

REFERENCES **119**

APPENDICES **157**

LIST OF TABLES

		Page
Table 2.1:	Effect of synthesis methods of binary TiO_2/ZnS composites on their properties and performance	26
Table 2.2:	Effect of synthesis methods applied for the synthesis of binary TiO_2/GO composites on their properties and performance	34
Table 4.1:	Elemental compositions of the prepared samples	82
Table 4.2:	Result of BET surface area analysis of TiO_2/ZnS/GO	83
Table 4.3:	Comparison of elemental compositions between TiO_2/ZnS/GO powder and TiO_2/ZnS/GO-CaAlg before and after 150 min UVA irradiation	110

LIST OF FIGURES

Page

Figure 2.1:	Crystalline structures of TiO_2: (a) rutile, (b) anatase, and (c) brookite (Source: Baranowska-Wójcik, 2020).	10
Figure 2.2:	Principle of TiO_2 photocatalysis in the presence of pollutant (Source: Sujatha et al., 2020).	14
Figure 2.3:	The (a) sphalerite and (b) wurtzite crystal structures of ZnS (Source: Jamal et al., 2020).	16
Figure 2.4:	Graphene sheet oxidation to form GO (Source: Yu et al., 2022).	17
Figure 2.5:	Schematic illustration of the photodegradation process using a binary TiO_2/ZnS (Source: Priya et al., 2021).	20
Figure 2.6:	(a) Photocatalytic rate constant of binary TiO_2/ZnS on MB (b) BG (Source: Prasannalakshmi and Shanmugam, 2017).	22
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).	25
Figure 2.8:	(a) Proposed photodegradation mechanism of TiO_2/Ag3PO4@GO and (b) TEM micrograph of the recycled TiO_2/Ag3PO4@GO composite (Source: Al-Kausor and Chakrabortty, 2020).	48
Figure 2.9:	Mechanism of the TiO_2/Cr2S3/GO photocatalyst to degrade OPs (MB, Rho B, and MO) (Source: Hasan et al., 2020).	51
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).	52
Figure 2.11:	Chemical structures of (a) Methylene blue, (b) Rhodamine b, (c) Methyl orange.	59
Figure 3.1:	Schematic diagram of the synthesis of TiO_2/ZnS/GO via hydrothermal method.	67
Figure 4.1:	Figure 4.1: Raman spectra of (a) TiO_2/ZnS/GO (1:1:1, 1:2:1, 2:1:1) and (b) GO.	74
Figure 4.2:	FTIR spectra of (a) TiO_2, (b)TiO_2/ZnS/GO (1:1:1), (c) GO, (d) ZnS.	76

Figure 4.3: XRD spectra of (a) GO, (b) TiO_2/ZnS/GO (2:1:1) (c) TiO_2/ZnS/GO (1:2:1), and (d) TiO_2/ZnS/GO (1:1:1). 78

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) TiO_2/ZnS/GO (1:1:1). 80

Figure 4.5: EDX (a) analysis and (b) mapping of TiO_2/ZnS/GO (1:1:1). 81

Figure 4.6: BET nitrogen adsorption isotherm plot for (a) GO, (b) TiO_2/ZnS/GO (1:1:1, 1:2:1, and 2:1:1). 84

Figure 4.7: TEM images of TiO_2/ZnS/GO (1:1:1) at (a) 3000× magnifications and (b) 10,000× magnification, and (c) particle size distribution histogram of TiO_2/ZnS/GO (1:1:1). 85

Figure 4.8: (a) UV-Vis DRS of TiO_2/ZnS/GO (1:1:1, 1:2:1, 2:1:1) and GO and (b) Kubelka Munk plot of the diffuse reflectance spectra for TiO_2/ZnS/GO (1:1:1, 1:2:1, and 2:1:1), TiO_2, and ZnS. 86

Figure 4.9: (a) The EIS and (b) photoluminescence spectra of TiO_2, ZnS and TiO_2/ZnS/GO (1:1:1 and 2:1:1). 89

Figure 4.10: Blank experiments using TiO_2, ZnS, GO, TiO_2/ZnS (1:1), TiO_2/ZnS/GO (1:1:1, 1:2:1, and 2:1:1). 90

Figure 4.11: Pseudo-first-order kinetics of (a) TiO_2, (b) ZnS, (c) GO, and (d) TiO_2/ZnS/GO (1:1:1). 92

Figure 4.12: The effect of adsorbent dosage (0.1 – 1.0 g) of TiO_2/ZnS/GO (1:1:1) on the removal of 20 ppm of MB. 94

Figure 4.13: Removal efficiency of 1.0 g of TiO_2/ZnS/GO at different initial MB concentrations (20 – 35 ppm) after 150 min of UVA irradiation. 96

Figure 4.14: Removal efficiency of 1.0 g of TiO_2/ZnS/GO at different initial MB pH (3 – 10) after 150 min of UVA irradiation. 98

Figure 4.15: Point of zero charge (pHpzc) of TiO_2/ZnS/GO (1:1:1). 99

Figure 4.16: TiO_2/ZnS/GO (1:1:1) on the removal of MB in the presence of different scavengers. 101

Figure 4.17: Removal efficiency of TiO_2/ZnS/GO (1:1:1) for (a) individual MB, MO and Rho B and (b) mixed dyes solution. 103

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 TiO_2/ZnS/GO (1:1:1). 105

Figure 4.19: TiO_2/ZnS/GO-CaAlg beads in mixed dyes solution after 3 h of treatment under UVA. 106

Figure 4.20: Recycling performance of (a) TiO_2/ZnS/GO powder and (b) TiO_2/ZnS/GO-CaAlg beads in removing MB (20 ppm) after 4 cycles. 107

Figure 4.21: (a) and (c) SEM images TiO_2/ZnS/GO powder and TiO_2/ZnS/GO-CaAlg, respectively before irradiation, (b) and (s) TiO_2/ZnS/GO powder and TiO_2/ZnS/GO-CaAlg after irradiation (4 cycles). 109

Figure 4.22: Schematic illustration of the adsorption and photocatalytic degradation of TiO_2/ZnS/GO on dyes (MB, Rho B and MO). 114

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
hv	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 m^3 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 TiO_2 alone, combining TiO_2 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 TiO_2-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 TiO_2-based ternary composites (Hong et al., 2020). For example, the ZnS-graphene/TiO_2 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/TiO_2, 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 TiO_2 nanoparticles (Kale et al., 2020).

As such, this study embarked on producing TiO_2-based ternary photocatalysts with improved charge separation by combining TiO_2, 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 TiO_2/ZnS/GO composite was synthesized using the hydrothermal method, a cost-effective and versatile approach for materials synthesis. The hydrothermally synthesized TiO_2/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 TiO_2/ZnS/GO on alginate (Alg). Immobilization of TiO_2/ZnS/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) TiO_2/ZnS/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 TiO_2/ZnS/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 TiO_2 introduces a variety of potential solutions. The presence of ZnS or GO into TiO_2 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 TiO_2, 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, TiO_2/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) TiO_2/ZnS/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 TiO_2/ZnS/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 TiO_2/ZnS/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 TiO_2/ZnS/GO with its photocatalytic activity?
b. How do the adsorption capacities of TiO_2, ZnS, GO, TiO_2/ZnS (1:1), and TiO_2/ZnS/GO (1:1:1, 1:2:1, and 2:1:1) differ between each other?
c. How is the photocatalytic performance of TiO_2/ZnS/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 TiO_2/ZnS/GO composite powder and TiO_2/ZnS/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 TiO_2/ZnS/GO composite powder and TiO_2/ZnS/GO-CaAlg beads?

1.4 Objectives

The main objective of this study was to fabricate multifunctional TiO_2/ZnS/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 TiO_2/ZnS/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 TiO_2/ZnS/GO (1:1:1, 1:2:1, and 2:1:1),

c. To evaluate the parameters that affect the photocatalytic performance of TiO_2/ZnS/GO composite namely dosage, concentration of dye, mixed dyes solution, solution pH, and presence of radical scavengers,

d. To compare the photocatalytic efficiency of TiO_2/ZnS/GO powder and TiO_2/ZnS/GO-CaAlg beads for the degradation of MB, MO, Rho B and mixed dyes solution, and

e. To investigate the reusability of TiO_2/ZnS/GO powder and TiO_2/ZnS/GO-CaAlg beads for up to four cycles.