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DEPARTMENT OF CHEMICAL ENGINEERING



**NOVEL GREEN SYNTHESIS OF TiO_2 PHOTOCATALYST
USING MATCHA JAPANESE GREEN TEA EXTRACT BY
SOL-GEL METHOD: INFLUENCE OF SURFACE
MORPHOLOGY ON PHOTOCATALYTIC PERFORMANCE**

MASTER OF SCIENCE, CHEMICAL ENGINEERING

RIYADH NAFEA ABDULLAH

THESIS SUPERVISOR

Assoc. Prof. Dr. Güler Bengüsu TEZEL TANRISEVER

SECOND THESIS SUPERVISOR

Dr. Mukheled A. AL-SAMERAIY

BOLU, 1/3/2025

ACCEPTANCE AND APPROVAL PAGE

The thesis entitled “NOVEL GREEN SYNTHESIS OF TiO_2 PHOTOCATALYST USING MATCHA JAPANESE GREEN TEA EXTRACT BY SOL-GEL METHOD: INFLUENCE OF SURFACE MORPHOLOGY ON PHOTOCATALYTIC PERFORMANCE” prepared and submitted by **RIYADH NAFEA ABDULLAH** in partial fulfillment of the requirements for the degree of **Master of Science** in Department of **CHEMICAL ENGINEERING** with unanimity vote is hereby approved.
1/3/2025

Jury Members

Signature

Supervisor
Assoc. Prof. Dr. Güler Bengüsu TEZEL
TANRISEVER
Bolu Abant İzzet Baysal University

.....

Member
Asst. Prof. Dr. Özlem ATEŞ DURU
Bolu Abant İzzet Baysal University

.....

Member
Prof. Dr. Fatma ÖZTÜRK
Bogazici University

.....

Institute of Graduate Studies Approval

Prof. Dr. İbrahim KÜRTÜL
Director of Institute of Graduate Studies

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ABSTRACT

NOVEL GREEN SYNTHESIS OF TiO₂ PHOTOCATALYST USING MATCHA JAPANESE GREEN TEA EXTRACT BY SOL-GEL METHOD: INFLUENCE OF SURFACE MORPHOLOGY ON PHOTOCATALYTIC PERFORMANCE

MSC THESIS

RIYADH NAFEA ABDULLAH

BOLU ABANT IZZET BAYSAL UNIVERSITY

INSTITUTE OF GRADUATE STUDIES

DEPARTMENT OF CHEMICAL ENGINEERING

**(SUPERVISOR: ASSOC. PROF. DR. GÜLER BENGÜSU TEZEL
TANRISEVER)**

(CO-SUPERVISOR: DR. MUKHELED A. AL-SAMERAIY)

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A heterogenous photocatalyst such as commercial TiO₂ (Degussa, P-25) is successfully applied under artificial UV irradiation for oxidation of organic pollutants. However, it suffers from limited surface area, thus affecting its photocatalytic performance and restricting its feasibility for industrial applications. The current study aimed to address this limitation and therefore it investigated, for the first time, matcha Japanese green tea (MJGT) as novel extracted material to greenly synthesized TiO₂ photocatalyst from three weighted powders of first harvest (GF1, GF2, GF3) and second harvest (GS1, GS2, GS3) using sol-gel method (effective method in controlling surface morphology). To achieve this aim, a working protocol was adopted in three stages including chemical and green synthesis of TiO₂, characterization of synthesized photocatalysts using relevant analytical techniques, and evaluation of their photocatalytic performance with methylene blue using batch photoreactor.

Experimentally, surface morphology of greenly TiO₂ photocatalysts in terms of crystallite sizes, mean particle size, surface roughness, BET surface area (S_{BET}) and optical properties as found by analyses of EDX, FE-SEM, AFM, BET, and UV-vis, respectively, was significantly enhanced compared with chemically control TiO₂ (CP). The best characterization results of greenly TiO₂ photocatalysts were at GF2 and GS2. In particular, the S_{BET} results were 164.44 m²/g for GF2 and 217.66 m²/g for GS2 compared with 13.78 m²/g for CP. Photocatalytic degradation of MB was 90% for GF2 and 98% for GS2. Photocatalytic mineralization of MB was 88% for GF2 and 97% for GS2.

In conclusion, significantly, MJGT modified surface morphology of TiO₂ towards enhancing its photocatalytic performance.

KEYWORDS: Matcha Japanese green tea, TiO₂, Green sol-gel, Photocatalysis, Methylene blue

ÖZET

**SOL-GEL YÖNTEMİ İLE MATCHA JAPON YEŞİL ÇAY EKSTRAKTI
KULLANILARAK TiO₂ FOTOKATALİSTİN SENTEZİ
YÜKSEK LİSANS TEZİ
RIYADH NAFEA ABDULLAH
BOLU ABANT İZZET BAYSAL ÜNİVERSİTESİ
LİSANSÜSTÜ EĞİTİM ENSTİTÜSÜ
KİMYA MÜHENDİSLİĞİ ANA BİLİM DALI
(TEZ DANIŞMANI: ASSOC. PROF. DR. GÜLER BENGÜSU TEZEL
TANRISEVER)
(İKİNCİ DANIŞMAN: DR. MUKHELED A. AL-SAMERAIY)
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Ticari TiO₂ (Degussa, P-25) gibi heterojen bir fotokatalizör, organik kirleticilerin oksidasyonu için yapay UV ışınlaması altında başarıyla uygulanmaktadır. Ancak, sınırlı yüzey alanına sahip olması nedeniyle fotokatalitik performansı ve endüstriyel uygulamalar için uygulanabilirliği kısıtlıdır. Mevcut çalışma bu sınırlamayı ele almayı amaçlamıştır ve bu nedenle ilk kez, ilk hasattan (GF1, GF2, GF3) ve ikinci hasattan (GS1, GS2, GS3) üç ağırlıklı tozdan sol-jel yöntemi (yüzey morfolojisini kontrol etmede etkili yöntem) kullanılarak yeşil olarak sentezlenen TiO₂ fotokatalizörüyle yeni ekstrakte edilmiş malzeme olarak Japon yeşil çayını (MJGT) araştırmıştır. Bu amaca ulaşmak için, üç aşamada bir çalışma protokolü benimsenmiştir (TiO₂'nin kimyasal ve yeşil sentezi, sentezlenen fotokatalizörlerin ilgili analitik teknikler kullanılarak karakterizasyonu ve toplu fotoreaktör kullanılarak metilen mavisi ile fotokatalitik performanslarının değerlendirilmesi).

Deneyssel olarak, kristalit boyutları, ortalama parçacık boyutu, yüzey pürüzlülüğü, BET yüzey alanı (S_{BET}) ve EDX, FE-SEM, AFM, BET ve UV-vis analizleriyle bulunan optik özellikler açısından yeşil TiO₂ fotokatalizörlerinin yüzey morfolojisi, kimyasal olarak kontrol edilen TiO₂ (CP) ile karşılaştırıldığında önemli ölçüde geliştirilmektedir. Yeşil TiO₂ fotokatalizörlerinin en iyi karakterizasyon sonuçları GF2 ve GS2'de sergilemiştir. Özellikle, GF2 ve GS2 için sırasıyla 164.44 m²/g ve 217.66 m²/g olarak bulunan S_{BET} değerleri, CP için elde edilen 13.78 m²/g değerine kıyasla oldukça yüksektir. Metilen mavisinin (MB) fotokatalitik bozunumu GF2 için %90, GS2 için %98 iken, mineralizasyon oranları ise sırasıyla %88 ve %97 olarak belirlenmiştir.

Sonuç olarak, MJGT, TiO₂'nin fotokatalitik performansını artırma yönünde yüzey morfolojisini önemli ölçüde değiştirdi.

ANAHTAR KELİMELEER: Matcha Japon yeşil çayı, TiO₂, Yeşil sol-jel, Fotokataliz, Metilen mavisi

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	iv
ÖZET.....	v
TABLE OF CONTENTS.....	vi
LIST OF FIGURES	viii
LIST OF TABLES	x
LIST OF ABBREVIATIONS AND SYMBOLS	xi
ACKNOWLEDGEMENT.....	xiii
1. INTRODUCTION	1
1.1 Background.....	1
1.2 Problem statement	2
1.3 Dye industrial wastewater.....	4
1.4 Advanced oxidation processes (AOPs)	5
1.4.1 Photolysis process	5
1.4.2 Photocatalysis process	5
1.5 Matcha Japanese Green Tea (MJGT)	20
1.5.1 Manufacture of MJGT	22
1.5.2 Extraction of MJGT.....	23
1.6 Model compound.....	26
1.7 Implications of Literature	27
1.8 Aim and objectives	27
2. MATERIALS and METHOD	29
2.1 Materials	29
2.2 Instruments and Measurement.....	29
2.3 Chemical synthesis of TiO ₂	31
2.4 Green synthesis of TiO ₂	32
2.5 Experimental setup and procedure.....	33
2.5.1 Photoreactor setup	33
2.5.2 Calibration curve of MB.....	34
2.5.3 Photolysis experiments	35
2.5.4 Photocatalysis experiments	36
2.6 Characterization Analysis Techniques of TiO ₂ Photocatalyst.....	37
2.6.1 X-ray Diffraction (XRD)	37
2.6.2 Fourier Transform Infrared (FTIR)	38
2.6.3 Field Emission Scanning Electron Microscopy and EDX	39
2.6.4 Atomic Force Microscopy (AFM).....	40
2.6.5 Brunauer-Emmett-Teller (BET) surface area	41

2.6.6 Transmission Electron Microscopy (TEM).....	41
2.6.7 Thermogravimetric Analyzer (TGA).....	42
2.6.8 Ultraviolet–visible spectroscopy (UV-vis).....	43
2.7 Evaluation Analysis Techniques.....	43
2.7.1 UV-vis spectroscopy	43
2.7.2 Total Organic Carbon (TOC)	44
3. RESULTS.....	46
3.1 Characterization of synthesized TiO ₂ (chemically vs. greenly)	46
3.1.1 XRD analysis.....	46
3.1.2 FTIR analysis.....	48
3.1.3 FE-SEM analysis	49
3.1.4 EDX analysis	52
3.1.5 AFM analysis.....	55
3.1.6 BET analysis.....	57
3.2 Further characterization of greenly synthesized TiO ₂ (GF2 vs. GS2).....	59
3.2.1 TEM analysis.....	59
3.2.2 TGA analysis	60
3.2.3 Optical analysis	61
3.3 Degradation of MB	62
3.3.1 Photolysis	62
3.3.2 Photocatalysis	63
4. DISCUSSION.....	70
4.1 Characterization of synthesized TiO ₂ (chemically vs. greenly)	70
4.1.1 XRD analysis.....	70
4.1.2 FTIR analysis.....	71
4.1.3 FE-SEM analysis	71
4.1.4 EDX analysis	72
4.1.5 AFM analysis.....	73
4.1.6 BET analysis.....	73
4.2 Further characterization of greenly synthesized TiO ₂ (GF2 vs. GS2).....	74
4.2.1 TEM analysis.....	74
4.2.2 TGA analysis	74
4.2.3 Optical analysis	75
4.3 Degradation of MB	76
4.3.1 Photolysis	76
4.3.2 Photocatalysis	76
5. CONCLUSION.....	80
5.1 Recommendations.....	84
REFERENCES.....	85
APPENDICES	101

LIST OF FIGURES

	<u>Page</u>
Figure 1.1. The crystal structures of anatase, rutile, and brookite formed from the octahedral complex (Yahaya et al., 2017).....	7
Figure 1.2. Diagram of mechanism of TiO ₂ photocatalysis (Dharma et al., 2022)8	8
Figure 1.3. Bottom-Up/Top-Down approaches for synthesis of nanoparticles (Yaseen Sharaf Zeebaree et al., 2022).....	15
Figure 1.4. Sketch of sol-gel steps (Ben Arbia et al., 2024)	17
Figure 1.5. Steps of manufacturing MJGT by the Jade Leaf brand	23
Figure 2.1. The instruments and measurements used in the study: (a) The electrical Balance FA1004, (b) Magnetic stirrer-heater SH-2, (c) The electric Centrifuge 80-1, (d) The annealing furnace Heraeus, (e) Dissolved Oxygen Kit, (f) pH Kit	31
Figure 2.2. Chemical synthesis of TiO ₂ via the sol –gel method.....	32
Figure 2.3. Green synthesis of TiO ₂ via the sol –gel method.....	33
Figure 2.4. A batch photoreactor setup	34
Figure 2.5. The calibration curve of methylene blue	35
Figure 2.6. X-ray diffraction XRD X' Pert Pr.....	38
Figure 2.7. Fourier Transform Infrared (FTIR) IRAffinity-1	39
Figure 2.8. Field Emission Scanning Electron Microscopy ZEISS SIGMA VP40	
Figure 2.9. Atomic Force Microscopy (AFM).....	40
Figure 2.10. The surface area analyzer (Gemini VII 2390t)	41
Figure 2.11. Transmission electron microscopy ZEISS LEO 912 AB	42
Figure 2.12. Thermogravimetric Analyzer (TGA) Mettler-Toledo	42
Figure 2.13. Ultraviolet–visible spectroscopy (UV-vis).....	43
Figure 2.14. Ultraviolet–visible spectroscopy UVVIS-1911DB	44
Figure 2.15. TOC-LCSN analyzer	45
Figure 3.1. XRD spectra of chemically and greenly synthesized TiO ₂ photocatalysts	47
Figure 3.2. FTIR spectra of synthesized TiO ₂ photocatalysts: (a) CP, GF1, GF2, GF3 and (b) GS1, GS2, GS3.....	49
Figure 3.3. FE-SEM spectra of synthesized TiO ₂ photocatalysts: (a) CP, (b) GF1, (c) GF2, (d) GF3, (e) GS1, (f) GS2 and (g) GS3	50
Figure 3.4. FE-SEM distribution histograms of synthesized TiO ₂ photocatalysts: (a) CP, (b) GF1, (c) GF2, (d) GF3, (e) GS1, (f) GS2 and (g) GS3	52
Figure 3.5. EDX spectra of synthesized TiO ₂ photocatalysts: (a) CP, (b) GF1, (c) GF2, (d) GF3, (e) GS1, (f) GS2 and (g) GS3.....	54
Figure 3.6. AFM spectra of synthesized TiO ₂ photocatalysts: (a) CP, (b) GF1, (c) GF2, (d) GF3, (e) GS1, (f) GS2 and (g) GS3.....	56
Figure 3.7. BET analysis of synthesized TiO ₂ photocatalysts	58
Figure 3.8. TEM images of greenly synthesized TiO ₂ photocatalysts: (a) GF2, (b) GS2 and TEM distribution histograms of the average particle sizes: (c) GF2, (d) GS2	60
Figure 3.9. TGA analysis of greenly synthesized TiO ₂ photocatalysts: (a) GF2 and (b) GS2	61

Figure 3.10. Optical analysis of greenly synthesized TiO ₂ photocatalysts: (a) GF2 and (b) GS2	62
Figure 3.11. Effect of various doses of the synthesized CP photocatalyst on the D	63
Figure 3.12. Effect of various doses of the synthesized GF2 photocatalyst on the D (%) of MB	64
Figure 3.13. Effect of various doses of the synthesized GS2 photocatalyst on the D (%) of MB	64
Figure 3.14. Effect of synthesized TiO ₂ photocatalysts at their optimum photocatalytic doses on the D% of MB and TOC removal (%) with respect to photocatalytic time, and pH and DO monitoring parameters of CP.....	65
Figure 3.15. Effect of synthesized TiO ₂ photocatalysts at their optimum photocatalytic doses on the D% of MB and TOC removal (%) with respect to photocatalytic time, and pH and DO monitoring parameters of GF2	66
Figure 3.16. Effect of synthesized TiO ₂ photocatalysts at their optimum photocatalytic doses on the D% of MB and TOC removal (%) with respect to photocatalytic time, and pH and DO monitoring parameters of GS2	66
Figure 3.17. Change in color of MB aqueous solution using synthesized TiO ₂ photocatalysts at their optimum photocatalytic doses: (a) CP, (b) GF2 and (c) GS2.....	67
Figure 3.18. A commercial photocatalyst TiO ₂ (BM): investigation of the optimum dose.....	68
Figure 3.19. Commercial photocatalyst TiO ₂ (BM): TOC removal (%) of MB, pH and DO monitoring.....	68
Figure 3.20. Commercial photocatalyst TiO ₂ (BM) color change monitoring	69
Figure 4.1. The D% of MB and the S _{BET} for the synthesized TiO ₂ photocatalysts (CP, GF2 and GS2)	77

LIST OF TABLES

	<u>Page</u>
Table 1.1. Advantages and disadvantages of synthesis methods (Ismael et al., 2024; Yaseen et al., 2024; Zain et al., 2024).....	19
Table 1.2. Surface morphology of greenly synthesized TiO ₂ (Abdulrazaq & Alwared, 2024; Chawraba et al., 2024; Helmy et al., 2021; Muraro et al., 2023; Nabi et al., 2021; Saikumari et al., 2019).....	20
Table 1.3. MJGT products in this study including manufacturer, origin, and cost (in USD per g of tea) (Meyer et al., 2023).....	21
Table 1.4. The relationship between extraction with TPC and TFC (Jakubczyk et al., 2020; Komes et al., 2010; Sielicka-Różyńska & Szulc, 2020; Zielinski et al., 2015).....	25
Table 1.5. Catechin concentration ($\pm$ standard error; all reported in mg/g tea) (Meyer et al., 2023; Zhao et al., 2024).....	26
Table 1.6. Contents of selected minerals and trace elements in matcha evaluated by (ICP-MS) (Kolářková et al., 2020)	26
Table 2.1. Materials used in the study	29
Table 3.1. Average crystallite size of chemically and greenly synthesized TiO ₂ (anatase phase)	47
Table 3.2. EDX analysis for the chemical compositions of the MJGTF and MJGTS extracts	53
Table 3.3. The AFM analysis of surface topography and roughness	57
Table 3.4. The BET analysis of chemically and greenly synthesized TiO ₂ photocatalysts	59

LIST OF ABBREVIATIONS AND SYMBOLS

MB	: Methylene Blue
AOP	: Advanced Oxidation Process
UV	: Ultraviolet
CB	: Conduction Band
MJGT	: Matcha Japanese Green Tea
MJGTF	: Matcha Japanese Green Tea First harvest
MJGTS	: Matcha Japanese Green Tea Second harvest
DO	: Dissolved Oxygen
XRD	: X-ray Diffraction
FTIR	: Fourier Transform Infrared spectroscopy
FESEM	: Field Emission Scanning Electron Microscopy
EDX	: Energy-Dispersive X-ray
AFM	: Atomic Force Microscopy
BET	: Brunauer-Emmett-Teller
BJH	: Barrett, Joyner, and Halenda
TEM	: Transmission Electron Microscopy
TGA	: Thermogravimetric Analysis
UV-vis	: Ultraviolet–visible spectroscopy
VB	: Valence Band
HOMO	: Hight Occupied Molecoular Orbitals
LUMO	: Lowest Unoccupied Molecoular Orbitals
Eg	: Bandgap energy
TPC	: Total Polyphenol Content
TFC	: Total Flavonoid Content
EC	: Epicatechin
EGC	: Epigallocatechin
ECG	: Epicatechin-3-gallate
TTIP	: Titanium (IV) Tetra Isopropoxide
CP	: Chmiecally synthesized TiO ₂ photocatalyst (control photocatalyst)
BM	: Benchmark TiO ₂ photocatalyst (Degussa, P-25)
GF_x	: Greenly synthesized TiO ₂ photocatalyst with MJGTF
GS_x	: Greenly synthesized TiO ₂ photocatalyst with MJGTS
D_{XRD}	: Average crystallite size
D	: Mean particle size
σ_{sd}	: Standard deviation
α	: Ult optical absorption coefficient

B	: Constant depending on the transition probability
TOC	: Total Organic Carbon
D (%)	: Photocatalytic degradation percentage of MB
TOC (%)	: Total Organic Carbon removal percentage
C₀	: Initial Concentration of MB
C_t	: Concentration of MB during reaction time
TOC₀	: Initial concentration of TOC in MB solution
TOC_t	: Concentration of TOC during reaction time
FWHM	: Full Width at Half Maximum
Rwp	: Weighted Profile R-factor
FoM	: Figure of Merit
Sq	: Root-mean square roughness coefficient
Ssk	: Surface skewness
Sku	: Surface kurtosis
Sa	: Surface arithmetic height
Sz	: Surface maximum height
S_{BET}	: Specific surface area by Brunauer-Emmett-Teller
d_p	: Average pore size
V_p	: Pore volume

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1. INTRODUCTION

1.1 Background

The textile industry is one of the largest industrial activities, producing significant amounts of pollutants such as dyes (Kumari et al., 2023; Rajput et al., 2022). A common textile dye is methylene blue (MB), which is a blue cationic thiazine. The nature of this dye is highly toxic and carcinogenic (Giovannetti et al., 2015; Mohamadpour & Amani, 2024). The presence of MB in industrial wastewater effluent can cause serious environmental problems such as an increase in toxicity, a decrease in the solubility of dissolved oxygen and a decline in light penetration, thus significantly affecting aquatic ecosystems (Dabwan et al., 2015; Giovannetti et al., 2015). Consequently, environmental concern regarding its impact on the environment has been raised (Kumari et al., 2023).

Many conventional (physical, chemical and biological) processes are used to treat dye industrial wastewater (i.e., MB) (Solayman et al., 2023). For example, adsorption as a physical process and coagulation-flocculation-sedimentation process as a chemical process are effective in removing dye. However, these processes remove the dye pollutant from one phase to another, generating secondary waste associated with various environmental problems (Crini & Lichtfouse, 2019; Feng et al., 2023; Mondol et al., 2021; Solayman et al., 2023; Thambiliyagodage & Mirihana, 2021). A biological process is widely applied for biodegrading (i.e., breaking down) a wide range of synthetic dyes via utilizing the metabolic activities of microorganisms. This process is considered environmentally friendly and cost-effective. However, the rate of biodegradation is generally slow when dealing with higher concentrations of dye. This leads to limiting their real applications. In order to mitigate the drawbacks of traditional processes, Advanced Oxidation Processes (AOPs) present a compelling alternative (Hashem et al., 2020; Solayman et al., 2023).

AOPs can generate free hydroxyl radicals ($\text{HO}^\bullet$) as a strong and powerful oxidizing agent (Solayman et al., 2023). These radicals can effectively degrade a broad range of dye types (Ismail & Sakai, 2022). Photocatalysis, one of the AOPs, has recently attracted much attention and become a promising technology for the oxidation of dye pollutants such as MB. This process uses a nanostructured semiconductor metal oxide as a heterogenous photocatalyst in the presence of

ultraviolet (UV) irradiation from solar or artificial light sources to form the HO[•] by the redox reactions (R. Kumar et al., 2020; Meijide et al., 2022). These highly reactive radicals can oxidize (i.e., degrade into mineralize) an organic pollutant (i.e., MB) either partially into intermediate compounds, which are amenable to the biological treatment or totally into CO₂, H₂O and final products (anion compounds) (Khalf et al., 2024; Mohtar et al., 2021).

Among a variety of heterogenous photocatalysts, titanium oxide (TiO₂) is one of the most popular photocatalyst applied due to its several interesting characteristics such as inexpensive, insoluble in water, easy availability, high photostability and high photocatalytic performance (Friedmann, 2022; Serpone, 2018). The TiO₂ photocatalyst has been conventionally synthesized by various methods such as hydrothermal (Tian, 2022), co-precipitation (A. Kaur & Sud, 2023) and sol-gel method (Mahyar & Amani-Ghadim, 2011). The sol-gel method is efficient to control the surface properties, cost-effective, and does not require a complex and expensive equipment (Zain et al., 2024).

1.2 Problem statement

TiO₂ is facing two main limitations that restrict its feasibility for industrial applications. The first limitation is that TiO₂ has a relatively low surface area, resulting in decreasing the total number of active sites available and then lowering captured photons (Hosseini et al., 2022; Venkatachalam et al., 2007). Consequently, the efficiency of TiO₂ as a photocatalyst is significantly impacted. Additionally, TiO₂ possesses a wide bandgap energy (3.2 eV for anatase and 3.0 eV for rutile), limiting its photocatalytic activity to the UV light region (Chaudhary et al., 2023; Ouerghi et al., 2023).

To address these limitations, traditional chemical synthesis methods for TiO₂ were modified, either through chemical or environmentally friendly approaches. Chemical synthesis using metals such as (Cu, Co, Ni, Cr, Mn, Nb, V, Fe and Ag), non-metals such as (N, S, C, B, P, I and F) and noble metals such as (Pt, Pd and Au) is applied to replace Ti atoms and occupy them effectively. This replacement changes the conduction band (CB) of the TiO₂ photocatalyst due to the change of Ti (d) orbital of the photocatalyst by the replaced metal (d) atoms, thus modifying its electrical and optical properties in terms of narrowing its bandgap energy as well as structural properties. This chemical synthesis has shown a

significant mitigation in the limitations that faces TiO₂ synthesis (C. H. Nguyen et al., 2018; Zaleska, 2008). However, some of these chemical elements are toxic and have harmful and hazardous effects on human health and the environment (Chaudhary et al., 2023; Ouerghi et al., 2023). Due to environmental concerns associated with the chemical synthesis of TiO₂ (Budi et al., 2010), research has shifted towards environmentally friendly synthesis methods as a more sustainable alternative. Green synthesis or biosynthesis uses biological hosts such as bacteria, actinomycetes, algae, fungi and yeast, and plant extracts from edible fruit pulp and non-edible parts (leaves, stems, roots and seeds) to assist the production of nanostructured heterogeneous photocatalysts (Benassai et al., 2021; Patra et al., 2018). The plant extracts have been extensively applied in the synthesis of these photocatalysts because they are readily available, inexpensive, easy to handle and eco-friendly and rich in phytochemical (secondary metabolite) compounds such as polyphenols (C. H. Nguyen et al., 2018; Zaleska, 2008). These compounds, in particular flavonoids, can act as chelating, stabilizing, capping and reducing agents of metal ions. Flavonoids possess an ability to donate electrons due to their ability to capture oxygen molecules. The hydroxyl group may act as a reductant for metal ions (Eddy et al., 2024; Tejashwini et al., 2023). One example of these plant extracts is the regular green tea from the leaves of *Camellia sinensis* (*C. sinensis*). It is rich in high content of catechins (a sub-class of flavonoids) and other small amounts of phytochemicals such as caffeine, phenolic acids and other sub-classes of flavonoids (mainly quercetin, kaempferol, myricetin and rutin). As a result, green tea leaf extract was used as an attractive material for modifying the surface morphology of nanostructured photocatalysts such as ZnO (MalligArjuna Rao et al., 2021; Vieira et al., 2023) and TiO₂ (Saikumari et al., 2019; Verma et al., 2016). Another type of green tea is matcha. Matcha is a traditional Japanese tea. It is a powdered form from the leaves of *Camellia sinensis* (*C. sinensis*). Matcha has generally a similar chemical composition profile compared to a regular green tea. However, it possesses ten times polyphenols than that of regular green tea. Therefore, matcha green tea is one of the richest antioxidants from natural sources (Cardoso et al., 2020; Musial et al., 2020). The high concentration of polyphenols in matcha Japanese green tea (MJGT) extract makes it a particularly intriguing candidate for the green synthesis of heterogeneous photocatalysts. These polyphenols are expected to significantly modify the surface morphology of the photocatalyst. To

the best of our knowledge, no reported literature is available on the application of MJGT extract for green synthesis of heterogenous photocatalysts. Therefore, this Master's study aims to fill this gap.

1.3 Dye industrial wastewater

Textile industry is one of the biggest sectors in our modern life. This industry is a major contributor to environmental pollution, generating vast quantities of dye-laden wastewater (Lellis et al., 2019; Semeraro et al., 2015). Dyes are colored materials and classified into two types (natural and synthetic). Natural dyes are from animals, plants and minerals without chemical processing (Haleem et al., 2024). Synthetic dyes are manufactured in factories or laboratories. These dyes are categorized into three main types with respect to the surface charge of the dye molecule: cationic (basic dyes), anionic (direct, acid and reactive dyes) and nonionic (disperse dyes) (Yadav & Shukla, 2024). These dyes are toxic, carcinogenic, mutagenic and stable (Chan et al., 2024). Therefore, discharging untreated dye-laden wastewater poses a significant threat to human health, the environment, and aquatic life. Even at very low concentrations (e.g., 1 mg/L), it is considered a serious pollutant (Haleem et al., 2024).

Dyes like MB are conventionally treated by physical, chemical and biological processes. Other side, the physiochemical processes such as coagulation-flocculation-sedimentation, membrane separation and adsorption are highly efficient in treating (i.e., removing) dyes from their aqueous solutions. However, the principal limitation of using them is the transfer of dye as a pollutant from the liquid phase (i.e., aqueous solution) to another phase (i.e., solid phase) (Aragaw & Bogale, 2023) like precipitated sludge by coagulation-flocculation-sedimentation process (Zaharia et al., 2024), fouling by membrane separation (Solaiman et al., 2024) and adsorbed molecules of dye onto a solid surface of the used adsorbent (Al-Tohamy et al., 2022). Therefore, secondary disposal problems appear and are then needed for further treatment. This leads to increase the cost of operation and time-consuming unit operations (Iwuzor et al., 2021). On the other side, the biological process faces a challenge to easily degrade dyes since the nature of these dyes is refractory and resistant to biodegradation. Its biodegradation performance is slow and takes a long reaction time (Hashem et al., 2020; Olatunde et al., 2020; Uddin et al., 2023; Wu et al., 2021).

To protect the environment and public health from the dye pollution, dye industrial wastewater effluents must be treated to meet the natural water quality, new technologies and processes are required to achieve this target. Advanced oxidation processes (AOPs) have been found to be a better solution for treating dyes.

1.4 Advanced oxidation processes (AOPs)

AOPs are able to generate free hydroxyl radicals ($\text{HO}^\bullet$) as highly reactive powerful oxidizing agents (Khader et al., 2024). These AOPs via these radicals are capable of degrading (i.e., oxidizing or removing) an extent range of dyes successfully (Z. U. H. Khan et al., 2023). There are many different types of AOPs found in the literature (Khader et al., 2024; S. Khan et al., 2024; Mukherjee et al., 2023). In the current M.Sc. study, two relevant AOPs associated with the nature of this study are discussed below.

1.4.1 Photolysis process

Photolysis is one of the AOPs that uses sufficient photon energy from the source of ultraviolet (UV) irradiation (solar or artificial lights) to photolytically degrade (i.e., break down) the covalent bonds of organic pollutants such as dyes either directly or indirectly through production of the $\text{HO}^\bullet$ (S. Dong et al., 2022; Im et al., 2012; Wang et al., 2023). Their photolytic performance depends on the ability of these pollutants to absorb this energy (Aljeboree et al., 2021). Ahmed et al., (Y. Ahmed et al., 2016) reported that the photolysis had a limited photolytic degradation percentage ($< 1\%$) in the treatment of 20 mg/L MB after the photolytic time of 60 min. Generally, the performance of photolysis in the photolytic degradation of pollutants is limited (Baleh et al., 2024; Santos et al., 2023). As known in the literature, the degradation of dyes by the photolysis process is less than that of other AOPs such as photocatalysis (Le et al., 2024). Given the focus of this Master's thesis on photocatalysis rather than photolysis, the influence of photolysis as a degradation mechanism during the photocatalytic reactions mediated by the synthesized TiO_2 photocatalysts is expected to be minimal.

1.4.2 Photocatalysis process

Photocatalysis is one of the AOPs that uses UV irradiation in the presence of a nanostructured semiconductor metal oxide as a photocatalyst to initiate the

chemical photoreactions at mild conditions (Ameta et al., 2018; Mohamadpour & Amani, 2024). The photocatalyst can be applied in this process either homogeneous when its phase is similar to the phase of reactant or heterogenous when its phase is different from the phase of reactant (Mohamadpour & Amani, 2024; Olatunde et al., 2020).

Heterogenous photocatalysis using heterogenous photocatalysts such as TiO_2 , ZnO , CdO , CdS , Fe_2O_3 , SnO_2 and ZnS (S. K. Chang et al., 2024; Nurhidayah et al., 2024; Prabhu et al., 2024; Pritha et al., 2024; Shakoor et al., 2024). Among these photocatalysts, TiO_2 is predominantly applied for the treatment of a wide range of organic pollutants like dyes due to its availability, cost-effectiveness, high photocatalytic activity and high stability. (Bayan et al., 2021; Patterson & Patterson, 2011; Yang et al., 2024).

TiO_2 is found in three distinct crystalline structures: anatase, rutile and brookite. Figure 1.1 illustrates that anatase and rutile structures are tetragonal and brookite is orthorhombic. Rutile is a stable form of TiO_2 , while anatase and brookite are unstable. In terms of synthesis, brookite is hard to synthesize in the laboratory when compared with other forms (Sangeeta et al., 2024; Thakur et al., 2024).

The anatase phase is favored by calcination temperatures between 400 and 600 °C, while temperatures ranging from 600 to 800 °C promote the formation of the rutile phase. Given that the anatase phase exhibits higher photocatalytic activity, it is the preferred phase for practical applications (Napruszewska et al., 2024; Patterson & Patterson, 2011).

Anatase and rutile TiO_2 , with bandgap energies of 3.2 and 3.0 eV, respectively, require photons in the UV range (254-388 nm) for activation. However, only a small fraction (6%) of solar radiation reaches Earth in this UV range, significantly limiting their photocatalytic activity (Patterson & Patterson, 2011).

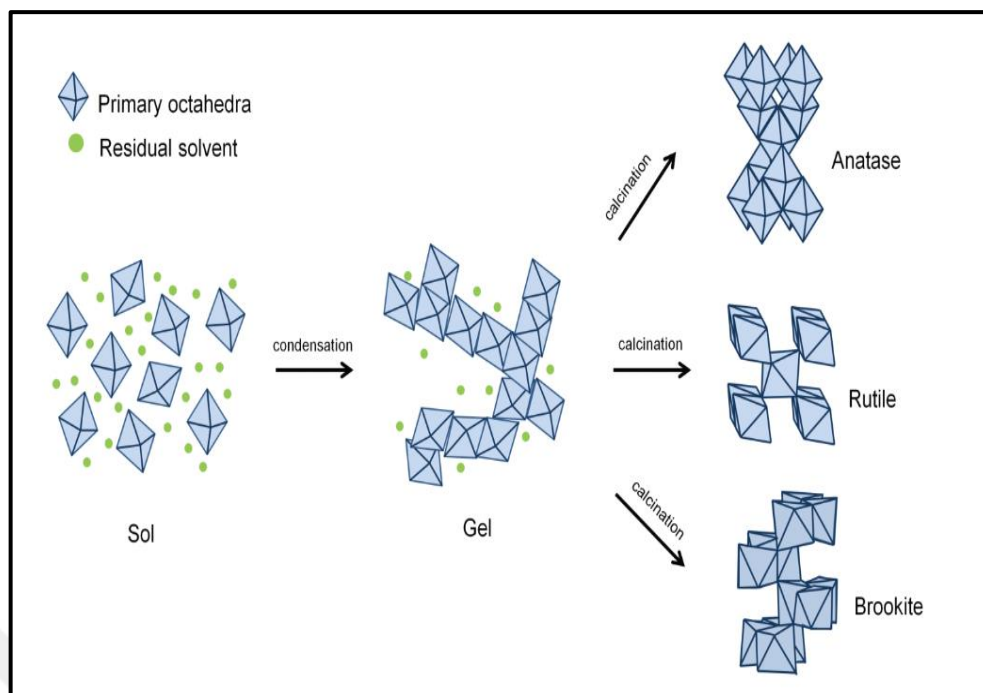


Figure 1.1. The crystal structures of anatase, rutile, and brookite formed from the octahedral complex (Yahaya et al., 2017)

1.4.2.1 Reaction mechanism of TiO₂ photocatalyst

From the electronic band structure point of view, the solid semiconductor photocatalyst consists of two molecular orbital bands. The first one is the valence band (VB), which is located at the highest occupied molecular orbitals (HOMO) with a higher energy level and the conduction band (CB), which is located at the lowest unoccupied molecular orbitals (LUMO) with a lower energy level. The difference in these energies is known as a bandgap energy of the photocatalyst (E_g) (H, 1997; Madkhali, Prasad, Malkappa, Yeol, & Govinda, 2023).

The reaction mechanism of photocatalysis using heterogenous photocatalyst, for example TiO₂, is shown in Figure 1.2 (Dharma et al., 2022). The pollutant molecules are transported from the reactant solution into the surface of the photocatalyst followed by their adsorption onto the active sites of the photocatalyst surface. After attaching these molecules, the photocatalysis mechanism starts with the absorption of sufficient photon energy $\geq E_g$ of the TiO₂ photocatalyst, leading to activation of the valence band (VB). As a result of this activation, the photoinduced formation of charge carriers, holes (h_{VB}^+) and electrons (e_{CB}^-), in the valence band (VB) and conduction band (CB), respectively occurs. On one side, the formed h_{VB}^+ can act either as a conventional oxidant to oxidize (i.e.,

degrade) the dye molecules or react with water molecules to form free hydroxyl radicals ($\text{HO}^\bullet$), which is a conventional oxidant. On the other side, the formed e_{CB}^- can react with adsorbed oxygen molecules on the surface of the photocatalyst to generate the superoxide radical ions ($\text{O}_2^{\bullet-}$). After these redox reactions, several chemical reactions occur to form perhydroxyl radicals ($\text{HO}_2^\bullet$), which is a conventional oxidant. The generated radicals in terms of $\text{HO}^\bullet$, $\text{O}_2^{\bullet-}$ and $\text{HO}_2^\bullet$ plays a significant role in effectively degrading the pollutants (i.e., dyes) into CO_2 , H_2O and final products (anions) at a complete mineralization (Arun et al., 2023; Luo et al., 2024; Popoola et al., 2024).

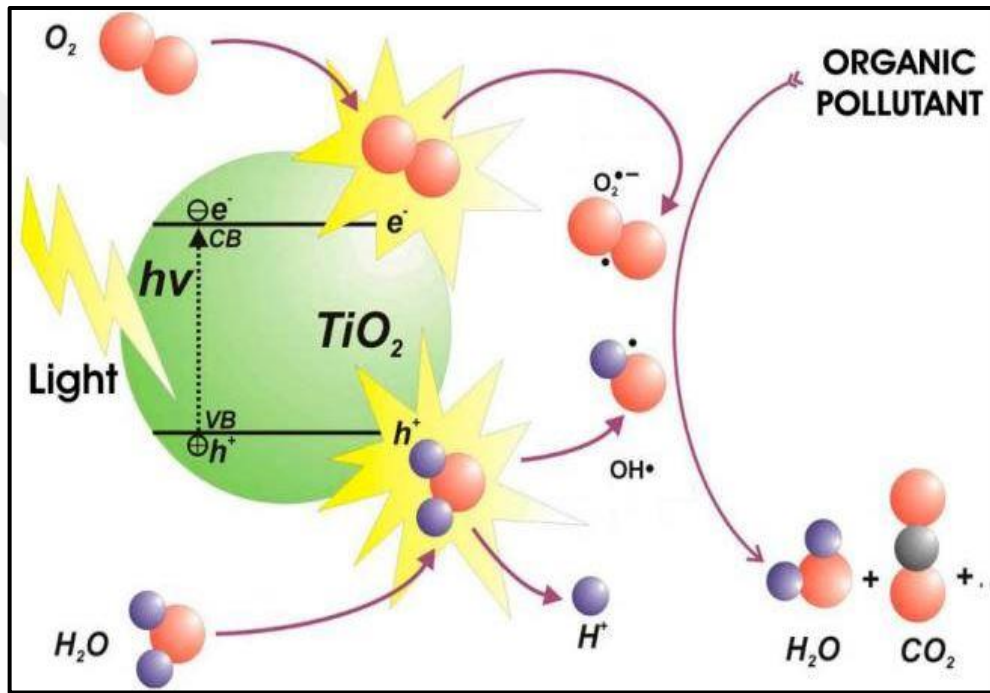
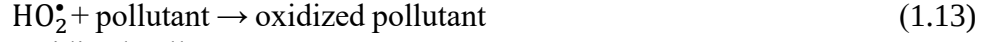
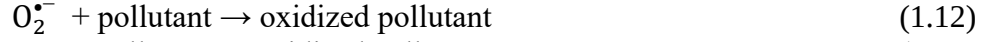
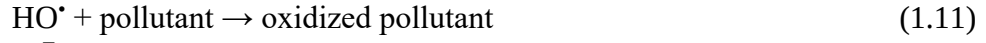
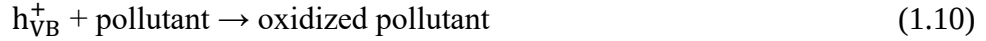


Figure 1.2. Diagram of mechanism of TiO_2 photocatalysis (Dharma et al., 2022)

The chemical reactions for representing the reaction mechanism of TiO_2 photocatalysis are shown in the following equations (1.1-1.14) (S. Ahmed et al., 2011; Madkhali, Prasad, Malkappa, Yeol, Govinda, et al., 2023; Pawar et al., 2018; Zangeneh et al., 2015).





1.4.2.2 Parameters affecting photocatalysis

The efficiency of photocatalysis is generally affected by several operational parameters. The most important relevant to the current M.Sc. study is shown below:

1.4.2.2.1 Types of photocatalyst

The photocatalysis process is essentially dependent on the type of heterogenous photocatalyst applied. A wide range of many types of photocatalysts based on their surface morphology and physiochemical characteristics are used in real applications such as TiO_2 , ZnO , CuO , Cu_2O , MgO and Fe_2O_3 (Ikram et al., 2021; X. Zhang et al., 2024). Among them, TiO_2 and ZnO photocatalysts, are widely applied in the treatment of dye industrial wastewater such as MB due to their effective efficiency in degrading MB as a refractory pollutant (AlMohamadi et al., 2024; Modi et al., 2022).

In real applications, there are two types of photocatalytic reactor configurations, which depend on the general state of the heterogenous photocatalyst applied. The first configuration is the slurry photocatalytic reactor (Fallahizadeh et al., 2024). In this type, the photocatalyst is used in the form of powder (i.e., slurry or suspended) and fed to the photocatalytic reactor. This type of photocatalytic reactor is highly efficient in terms of photocatalytic degradation performance due to the large effective surface area to be exposed to the UV irradiation. However, a significant drawback of this method is the requirement for separation and recycling of the photocatalyst, which can increase operational costs (Abd Rahman et al., 2023; Shukla et al., 2021; H. Zhang et al., 2023). The second configuration is the immobilized photocatalytic reactor. In this type, the photocatalyst is immobilized onto a support, such as a wall, plate, or beam. While this approach offers advantages like ease of separation and reuse, it often results in reduced photocatalytic performance compared to slurry photocatalytic reactors due to a significant decrease in the available active surface area (Sundar & Kanmani, 2020).

The slurry and immobilized photocatalytic reactors can be further categorized based on their flow configuration into batch and continuous modes (Shukla et al., 2021). For this Master's thesis, a batch mode operation using a suspended TiO_2 photocatalyst was selected due to its simplicity, high efficiency, low cost, and ease of operation.

1.4.2.2.2 Photocatalyst concentration

The concentration of the photocatalyst affects the photocatalytic degradation performance significantly. Generally, there is a direct proportional relation between the applied concentration of photocatalyst and the photocatalytic performance. This can be related to the increase in the photocatalytic active sites in the surface area of the photocatalyst. After a certain level of applied concentration of the photocatalyst, this performance decreases gradually with increasing the applied concentration of the photocatalyst due to a well-known phenomenon in terms of the light scattering (i.e., light is scattered by the increase in the concentration of the photocatalyst as suspended particles, leading to a decrease in exposing the effective surface area of the photocatalyst to the UV irradiation). At these conditions, the concentration of the photocatalyst applied is considered an optimum concentration (i.e., dosage or dose or loading) (AlMohamadi et al., 2024; Moeini et al., 2024).

1.4.2.2.3 pH of reactant solution

From the photocatalysis mechanism point of view, the initial pH of the reactant solution has a significant effect on the adsorption rate of pollutants onto the surface area of the applied photocatalyst. The pH of the surface of the applied photocatalyst can be qualitatively described by the charge of the surface area of the applied photocatalyst, which is known as a zero-point charge (ZPC). This ZPC is experimentally ranged between 5.8 and 6.4. If the pH of the reactant solution is less than pH_{ZPC} , this makes the surface of the photocatalyst positively charged. Thus, attracting the negatively charged (i.e., anionic) compounds. If the pH of the reactant solution is higher than pH_{ZPC} , this makes the surface of the photocatalyst negatively charged. Thus, repulsing the negatively charged (i.e., anionic) compounds. Vice versa for cationic compounds. Thus, the photocatalytic degradation performance is greatly affected by these conditions (Friedmann, 2023; Patterson & Patterson, 2011;

Xia et al., 2023). Generally, acidic conditions of pH play a significant role in improving the photocatalytic degradation performance when using HCl or H₂SO₄ as buffer solution. During the photocatalysis reactions, the chlorine ions or sulfate ions are converted into chlorine or sulfate radical forms. Both are conventional oxidizing agents and can further participate in degrading the organic pollutants (Minamoto et al., 2021). To avoid the influence of solution acidity (pH) on the photocatalytic degradation of Methylene Blue (MB), this Master's thesis will monitor the pH throughout the process. This will allow for a fairer comparison of the photocatalytic activity between the investigated photocatalysts (chemically synthesized vs. environmentally friendly options).

1.4.2.2.4Oxidant concentration

The use of conventional oxidant concentrations such as hydrogen peroxide (H₂O₂), dissolved oxygen (DO), persulfate anions (S₂O₈²⁻), hypochlorite (HClO) and ozone (O₃) can enhance the overall photocatalytic degradation and mineralization performance by increasing the generation rate of radicals (Massima Mouele et al., 2020; Shu et al., 2023). Further action of these conventional oxidants is their ability to work as scavengers in trapping the electrons (e_{CB}⁻) and then preventing them from recombining with the positive holes (h_{VB}⁺). For example, the DO can trap these electrons to form the superoxide radical ions (O₂^{•-}). These radicals can help in further degrading the organic pollutants (Y. Li et al., 2024).

To ensure a fair comparison between chemically and environmentally friendly photocatalysts, this study will monitor the oxidant concentration during the photocatalytic degradation of Methylene Blue (MB) under low-oxygen conditions. This means that the only source of oxygen for the reaction will be the oxygen dissolved in the MB solution, which is replenished through air diffusion.

1.4.2.2.5Reactant concentration

The reactant concentration can directly affect the photocatalytic performance. It is generally agreed in the literature that the higher the reactant concentration, the lower the photocatalytic performance (Srivastava et al., 2021). One example of reactant concentration is MB dye. Several authors reported that as the initial concentration of MB increases, the MB molecules are increased in their adsorption onto the surface of the photocatalyst. Consequently, the UV irradiation

is significantly adsorbed by these adsorbed molecules rather than the particles of TiO_2 photocatalyst. This leads to a decrease in the quantity of photons required to activate the active sites of applied photocatalyst. The overall photocatalytic performance decreases accordingly (AlMohamadi et al., 2024; Dadwal et al., 2024; Tawfik et al., 2022; Tayeb & Hussein, 2015).

1.4.2.2.6 Reaction temperature

For the chemical reactions, temperature plays a significant role in these reactions (Hemmatidoust & Samadi-Maybodi, 2024). While, for the photoreactions, generally the activation energy of these photoreactions is almost constant (i.e., it does not change significantly by the change of photoreaction temperature (Hussein, 2012). Several authors reported that the best temperature for the photocatalytic reactions ranges from 20 to 80 °C (AlMohamadi et al., 2024; S. Khan et al., 2024). Increasing the reaction temperature more than 80 °C leads to the recombination of the photoinduced charge carriers (holes (h_{VB}^+) and electrons (e_{CB}^-)). Thus, significantly decreasing the overall photocatalytic degradation performance (González-Burciaga et al., 2022). Also, higher reaction temperature can affect the solubility of dissolved oxygen in the reactant solution and as a result, the recombination of these charge carriers increases since the presence of dissolved oxygen is considered the conventional oxidant, having the ability to work as scavengers in trapping the electrons (e_{CB}^-) and then preventing them from recombining with the positive holes (h_{VB}^+) (González-Burciaga et al., 2022; Hou et al., 2018; S. Khan et al., 2024). Furthermore, the increase in the reaction temperature can affect the adsorption of pollutant molecules on the surface of the photocatalyst (Natarajan et al., 2014). In terms of the practical applications of photocatalysis process, the reaction temperature during the photocatalysis experiments increases because of the heat generation by the impact of the UV lamp. This point should be considered. In the current study, the reaction temperature will be monitored during photocatalysis experiments.

1.4.2.2.7 Light wavelength and intensity

The photocatalysis process uses UV irradiation as a source for sufficient quantities of photons and energy level to activate the mechanism of photoreactions of the photocatalyst. The source of UV irradiation can be used naturally from

sunlight or artificially from various types of mercury lamps, fluorescent lamps, light-emitting diodes (LEDs) lamps (Ibhadon & Fitzpatrick, 2013; Marcus et al., 2022).

Ultraviolet (UV) radiation is categorized into three primary spectral ranges: near-UV (UVA), far-UV (UVB), and extreme-UV (UVC). UVA radiation spans a wavelength range of 400-315 nm, corresponding to a photon energy range of 3.10-3.94 eV. UVB radiation, with a wavelength range of 315-280 nm, has a photon energy range of 3.94-4.43 eV. Lastly, UVC radiation, the most energetic of the three, covers a wavelength range of 280-100 nm and a photon energy range of 4.43-12.4 eV. It is well-established that longer wavelengths correspond to lower energy levels, and vice versa (Marcus et al., 2022).

Sunlight, with a wavelength exceeding 400 nm, possesses limited photon energy, accounting for only 4-5% of total sunlight. This inherent limitation hinders the practical application of heterogeneous photocatalysis in wastewater treatment (Gomes et al., 2019; Sendão et al., 2022). In contrast, artificial light within the UVC range, particularly a 254 nm wavelength generated by low-pressure mercury lamps, is widely employed for industrial wastewater treatment. This specific wavelength is favored due to its efficient utilization by TiO_2 photocatalysis, surpassing the efficiency of other wavelengths like 350 and 365 nm (Marcus et al., 2022). Consequently, a low-pressure UV lamp emitting 254 nm radiation will be utilized in this study.

The intensity of the light source significantly impacts photocatalytic reaction rates (Armaković et al., 2023; J. Li et al., 2024). Studies have shown a distinct relationship between light intensity and reaction order:

- **Low Light Intensity ($< 20 \text{ mW/cm}^2$):** At low intensities, the reaction rate increases linearly with increasing light intensity, suggesting a first-order reaction with respect to light (Al Miad et al., 2024).
- **Intermediate Light Intensity ($20\text{-}25 \text{ mW/cm}^2$):** In this range, the reaction rate exhibits a non-linear increase with light intensity, potentially indicating a second-order dependence (Reza et al., 2017).
- **High Light Intensity ($> 25 \text{ mW/cm}^2$):** At high intensities, the reaction rate becomes independent of light intensity, suggesting a zero-order dependence (Reza et al., 2017).

1.4.2.2.8Irradiation time

The photocatalytic degradation performance of pollutant increases directly with increasing the exposure of irradiation time. Typically, it was found that the irradiation time of 120 min was commonly used to ensure enough exposure period for activating the applied photocatalyst to keep the photocatalytic degradation of the target pollutant effective (Anil et al., 2019; I. Khan et al., 2022; Prasert et al., 2020). Therefore, in the current M.Sc. study, this exposure time will be selected.

1.4.2.3 Synthesis methods of TiO₂ photocatalyst

Two fundamental principles are used by nanotechnology for synthesizing nanomaterials: top-down and bottom-up sequential processes as illustrated in Figure 1.3 (Yaseen Sharaf Zeebaree et al., 2022). The methodology for synthesizing nanoparticles is divided into three approaches as follows:

- The first approach (physical methods): materials are broken down and reduced top-down to facilitate the creation of nano-sized structures. Popular physical methods include mechanical grinding and physical vapor deposition. The top-down method for synthesizing and constructing nanomaterials has several drawbacks, including its high cost, extended etching time, faults in the processed materials, and surface structural defects (Mathur et al., 2018).
- The second approach (chemical approach): several methods such as sol-gel (Nimmy et al., 2023), co-precipitation (Theka et al., 2024), and hydrothermal (Tian, 2022) are used.
- The third approach (biological method or green synthesis): all types of life sources in the green environment such as plants (Chaudhary et al., 2023), bacteria (Landage et al., 2020) and fungi (Chauhan et al., 2023) are used.

The chemical and biological methods are considered bottom-up steps; the bottom-up approach means building material from the ground up: molecule for molecule, atom for atom, or cluster for cluster (Abid et al., 2022). Bottom-up nanofabrication transcends the boundaries of miniaturization, offers practically boundless possibilities for the synthesis and design of functional nanostructured materials, and has the potential to be far more economical than top-down nanofabrication (Ijaz et al., 2020).

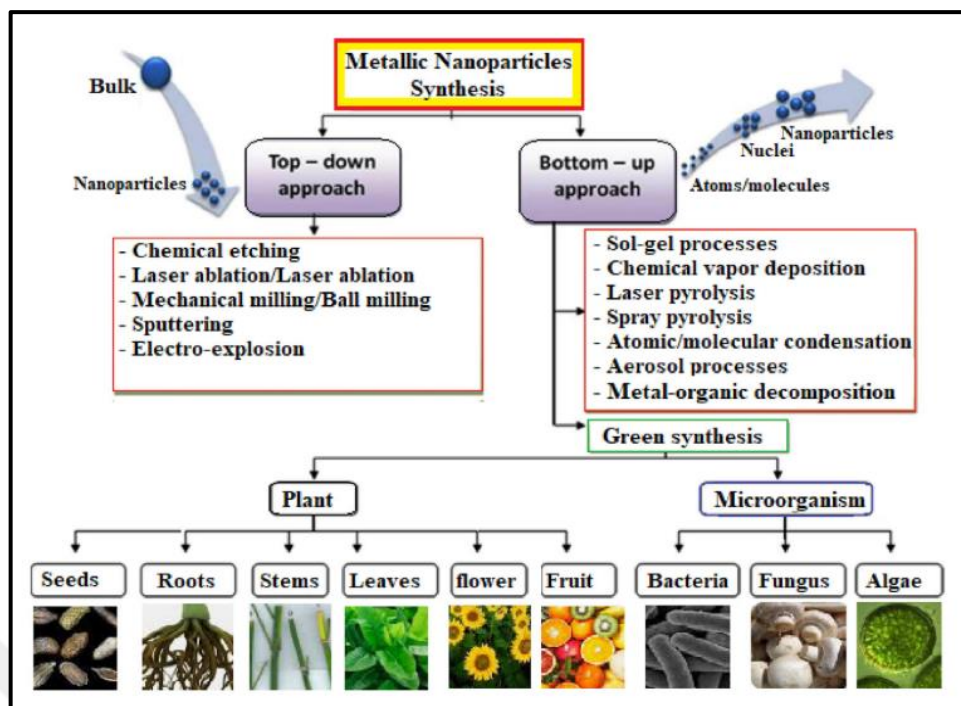


Figure 1.3. Bottom-Up/Top-Down approaches for synthesis of nanoparticles
(Yaseen Sharaf Zeebaree et al., 2022)

In the current M.Sc. study, the top-down approach was excluded due to its drawbacks. Thus, the bottom-up approach was chosen to synthesize TiO_2 photocatalyst. Further detail on the processes used in this approach is discussed below:

1.4.2.3.1 Hydrothermal method

The hydrothermal method is the reaction of solids with an aqueous solution as a solvent in a reaction vessel under high pressure and temperature conditions. The hydrothermal process occurs in a steel pressure vessel, commonly referred to as an autoclave. The processing parameters can be controlled by modification of temperatures and/or pressures (Abid et al., 2022). The advantages of this method are chemical homogeneity and significant efficiency (Mohadesi et al., 2024). Disadvantages of this method are high cost, equipment requirements, high temperature and pressure. Thus, these disadvantages limit its real application.

1.4.2.3.2 Co-precipitation method

Co-precipitation is a widely used technique for synthesizing both simple and complex oxides. It can be described by dissolving the precursor in a solvent and

then adding reagent chemicals to precipitate the active components. This allows the different positive ions to settle in a homogeneous mixture simultaneously. After that the formed impurities are removed by filtering and washing with distilled water. Drying and calcining at specific temperatures occur (Kumarage et al., 2023). In spite of its activity in the synthesis of TiO₂, this method suffers from the formation of impurities. This leads to effect on the surface morphology of the photocatalyst. Additionally, it uses reagent chemicals, generating significant amount of chemical sludge. The treatment of these sludges is required and thus making this treatment is not economic.

1.4.2.3.3 Sol-Gel method

Sol-gel is a bottom-up approach commonly used in synthesizing semiconductors such as TiO₂ and ZnO. It operates at ambient conditions and does not require complex and expensive equipment, facilitating the control over the size and shape of TiO₂. The sol-gel method refers to two terms (sol and gel). A sol is a colloidal suspension of solid nanoparticles dispersed in a monomer solution. The intermolecular interaction forces such as electrostatic repulsion and van der Waals are influencing factors on the stability of solid particles in the colloidal phase (sol) (Yadeta Gemachu & Fayisa Bogale, 2024). These intermediates are further linked to forming a 3D crosslinked network known as a gel. Afterward, this network is continuously increased via polycondensation reaction. As a result, a liquid phase inside this network is restricted. This leads to affecting the solid phase (i.e., expansion) and then the viscosity is increased accordingly. After the gelation stage, the stiffness of the gels is increased due to the phenomenon of aging. This phenomenon means that a condensation reaction of reactant in the gel forms a more cross-linked network, thus playing a significant role in strengthening this network and stiffening the gel (Arai et al., 2019). Figure 1.4 is a sketch of the sol-gel steps. The reaction steps are summarized in the following equations (1.15-1.17) (Yahaya et al., 2017):

Hydrolysis:



Condensation:



Where R in the equations (1.15 and 1.17) represents to ethyl, i-propyl, n-butyl.

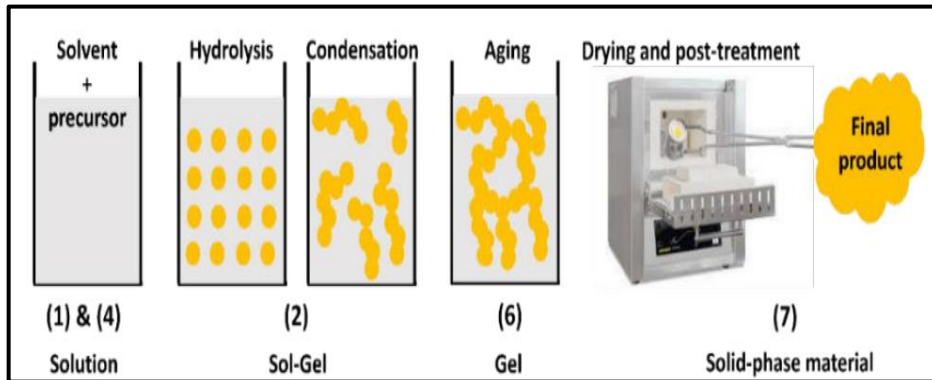


Figure 1.4. Sketch of sol-gel steps (Ben Arbia et al., 2024)

There are several basic strategies for successfully synthesizing TiO_2 using the sol-gel method. These strategies include control around the precursor chemistry, reaction conditions, and heat treatment. The key basic strategies in the sol-gel method (Ben Arbia et al., 2024):

In terms of choice of precursors: TiO_2 is primarily synthesized by hydrolysis using titanium tetrachloride (TiCl_4) and titanium trichloride (TiCl_3) as precursors because of its strong reactivity and ability to dissolve in organic solvents. The specific precursor type and dosage can influence the crystalline structure, surface area, and pore size of the TiO_2 that is generated by hydrolysis and condensation processes of alkoxides (Ben Arbia et al., 2024; C. Chang et al., 2023). In this study, titanium tetrachloride (TiCl_4) was chosen as a precursor because it is more reactive and soluble than titanium trichloride (TiCl_3) (Kakihana et al., 2010).

In terms of choice of solvent: the solvent selection is crucial in the sol-gel method to efficiently dissolve the precursors such as titanium tetrachloride (TiCl_4) and distribute the active components in the solution. This helps achieve a more homogeneous hydrolysis and prevents agglomeration of the end product (Kajitvichyanukul et al., 2005). Polar solvents, such as ethanol, methanol, and isopropanol, are commonly employed in the sol-gel method to speed up gel formation by their polar functional groups (Agafonov et al., 2017). Also, water or an alcohol is necessary for hydrolysis because it provides the oxygen needed to form the metal oxide (Parashar et al., 2020). Consequently, the solvent concentration directly affects the system's hydrolysis and condensation reaction rate, influencing

the characteristics of the resultant TiO_2 (C. Chang et al., 2023; Roevens et al., 2016). Therefore, low concentrations of solvents may prolong the crystallization time and lead to the formation of a high-viscosity gel. In contrast, high concentrations may reduce the solubility of the precursor and cause incomplete hydrolysis (Agafonov et al., 2017). The study conducted by Mahyar et al., (Mahyar & Amani-Ghadim, 2011) showed that the type of solvent significantly affects the crystal structure, particle size, shape, and textural properties of the prepared TiO_2 . They synthesized TiO_2 using different solvents such as isopropanol, methanol, and ethanol. The study further concluded that XRD results indicated that using isopropanol as a solvent resulted in TiO_2 with a pure anatase crystalline phase and smaller particle size. However, the TiO_2 prepared in methanol and ethanol contained a mixed anatase and rutile phase with larger crystal sizes. The nitrogen adsorption-desorption results showed that the TiO_2 prepared with isopropanol had the highest specific surface area compared with TiO_2 prepared in methanol and ethanol. Therefore, TiO_2 prepared in isopropanol may have higher photocatalytic performance than TiO_2 prepared in methanol and ethanol. As studied by Mahyar et al., the compatibility of isopropanol alcohol with the precursor (TiCl_4) gives the precursor more excellent surface morphology than methanol and ethanol. For these reasons, isopropanol was chosen as the solvent in this study.

In terms of heat treatment: drying and calcination are regarded as the most critical variables in the sol-gel method for synthesizing TiO_2 , owing to their direct influence on the surface morphology of TiO_2 . Alterations in the drying rate, whether by deceleration or acceleration, result in substantial modifications to the crystallinity, particle size, and surface area of nanoparticles (Ji et al., 2017). At the same time, the calcination temperature limits the phases of TiO_2 (i.e., anatase and rutile). Studies indicate that elevated calcination temperatures are associated with larger particle sizes, which decrease surface area and subsequently reduce photocatalytic activity (Kim et al., 2021; Lal et al., 2021; Velardi et al., 2020). In this study, a gradual drying rate at 80°C is recommended to prevent surface problems (i.e. cracking and deform), and the calcination temperature of 450°C is suggested to achieve anatase particles and enhance surface area, which is crucial for photocatalysis.

The advantages and disadvantages of the three presented methods used for synthesizing TiO_2 are summarized in Table 1.1.

Table 1.1. Advantages and disadvantages of synthesis methods (Ismael et al., 2024; Yaseen et al., 2024; Zain et al., 2024)

Synthesis method	Advantages	Disadvantages
Hydrothermal	Versatile morphology control	Requires optimization, sensitive to high temperature and pressure, waste generation
Co-precipitation	Size and morphology control, scalability, easy processing and functionalization	Requires optimization, poor crystallinity, time-consuming
Sol-Gel	Composition and morphology control, environmentally friendly	Time-consuming, particle agglomeration

1.4.2.3.4 Green synthesis of TiO₂

This method is principally utilized to overcome the restrictions of surface morphology and optical characteristics for the TiO₂ photocatalyst (Degussa, P-25) using the chemical sol-gel synthesis (H. Dong et al., 2015). As reported by the literature, the TiO₂ (Degussa, P-25) photocatalyst has a limited surface area of 50 m²/g and a large bandgap energy of 3.0 eV (Das et al., 2018). Successful attempts have been carried out to use the plant extracts as environmentally friendly materials in the green synthesis of TiO₂. For example, Helmy et al., (Helmy et al., 2021) used a Malva Parviflora plant extract for the green synthesis of TiO₂ photocatalyst using the sol-gel method. A significant enhancement in terms of surface area (135.5 m²/g) and bandgap energy (2.58 eV) was found. Another study carried out by Saikumari et al., (Saikumari et al., 2019) used conventional green tea extract for the green synthesis of TiO₂ photocatalyst using the sol-gel method. The resulting surface area and bandgap energy were found to be 87.4 m²/g and 2.86 eV, respectively. This green tea extract played a vital role in enhancing the surface area (i.e., increase) and optical characteristic (i.e., decrease) of TiO₂ due to the presence of polyphenols compounds, acting as reducing and stabilizing agents for the synthesis of TiO₂ photocatalyst. In addition to green tea extract, other types of plant extracts can be used in the literature as listed in Table 1.2.

Generally, the green sol-gel synthesis of TiO₂ is a safe, cost-effective, non-toxic and biocompatible process (Langa & Hintsho-Mbita, 2023).

Table 1.2. Surface morphology of greenly synthesized TiO₂ (Abdulrazaq & Alward, 2024; Chawraba et al., 2024; Helmy et al., 2021; Muraro et al., 2023; Nabi et al., 2021; Saikumari et al., 2019)

Type of plant extract	XRD (nm)	Particle size (nm)	BET surface area (m ² /g)	Pore size (nm)	Pore volume (m ³ /g)	Bandgap (eV)
Citrus Limetta	45	80-100	120.22	2.5	-	3.22
Malva parviflora	20.3	-	135.5	-	-	2.58
Aloe vera	32	287 ± 115	118	9.2	0.2	
Grape leaves	44.37	-	39.608	21.745	0.215	3.15
Cinnamon Bark	58 ± 0.5	101	13	27.9	0.05	1.47
Green tea	20.4		87.4	10.62	0.32	2.86

Another type of green tea is matcha, which is a traditional Japanese tea. Matcha Japanese green tea (MJGT) is higher rich in polyphenol compounds than that of regular green tea (Cardoso et al., 2020; Musial et al., 2020). The presence of these higher concentrations of polyphenols in MJGT extract is interesting to make it potentially a novel candidate for green synthesis of heterogeneous photocatalyst and will be expected to play a significant modification in its surface morphology. To the best of our knowledge, no reported literature is available on the application of MJGT extract for green synthesis of heterogenous photocatalysts.

1.5 Matcha Japanese Green Tea (MJGT)

Matcha tea is a powdered green tea produced from Tencha leaves that have been harvested, covered, and shaded. Because it is abundant in advantageous phytochemicals, matcha has become widely used in our daily lives as a nutritious beverage. Matcha has also been used in several pharmaceutical applications, primarily as a highly effective antibacterial and anti-cancer (Singh et al., 2024). The main raw material of green tea is the *Camellia sinensis* L. plant, which is extensively grown in Southeast Asia, Japan, China, and several other regions of the world. Nevertheless, the distinction between the many varieties of green tea and MJGT lies in the geographical regions, growing techniques, and processing techniques employed for MJGT. Hence, matcha possesses a phytochemical and bioactive

composition similar to green tea, albeit in different concentrations (Cardoso et al., 2020; Musial et al., 2020).

Matcha is classified according to the plant kingdom (Plantae), the vascular group (Tracheophyta), the tea family (Theaceae), and the genus (*Camellia*). It is cultivated in several regions of central and southern Japan, namely in the prefectures of Shizuoka, Kagoshima, Mie, Miyazaki, and Kyoto. Among these prefectures, Shizuoka and Kagoshima contribute to 70% of the total tea production in Japan. The outstanding quality of tea in these regions can be attributed to their temperate, misty atmosphere, fertile soil, and exceptionally balanced sunshine and rainfall, which are ideal circumstances for tea cultivation (Horie et al., 2017; Nakai, 2009).

Despite the growing global availability and popularity of matcha, further studies on its chemical and physical compositions are still required. Matcha is available from several brands worldwide, as seen in Table 1.3, which displays the cost of matcha at prominent international corporations. The cost of matcha is determined by its quality, specifically in relation to the timing of harvest and the technique of processing matcha. These factors result in variations in the physical and chemical compositions of the matcha (Meyer et al., 2023).

In this thesis, matcha Japanese green tea was obtained from the brand Jade Leaf, which is grown in Uji and Kagoshima, Japan.

Table 1.3. MJGT products in this study including manufacturer, origin, and cost (in USD per g of tea) (Meyer et al., 2023)

Brand	Manufacturer	Origin Green	Cost (USD/g)
First harvest			
Kenkō Tea Matcha Green	Kenkō Tea	Japan	\$0.93
Jade Leaf Matcha Green Tea Powder	Jade Leaf	Japan	\$0.83
Matcha Organics Japanese Matcha	Matcha Organics	Japan	\$0.87
Kiss Me Organics Matcha Green Tea Powde	Kiss Me Organics	Japan	\$0.95
Akira Matcha	Matcha Konomi	Japan	\$0.83
Second harvest			
Kenkō Tea Matcha Green	Kenkō Tea	Japan	\$0.37
Jade Leaf Matcha Green Tea Powder	Jade Leaf	Japan	\$0.33

Table 1.3. (continued). MJGT products in this study including manufacturer, origin, and cost (in USD per g of tea) (Meyer et al., 2023)

Brand	Manufacturer	Origin Green	Cost (USD/g)
Second harvest			
Zen Spirit Matcha Tea	Zen Spirit	Japan	\$0.30
Kiss Me Organics Matcha Green Tea Powde	Kiss Me Organics	Japan	\$0.22
Matcha Wellness Green Tea Powder	Matcha Wellness	Japan	\$0.33

1.5.1 Manufacture of MJGT

Matcha usually undergoes harvesting up to four rounds annually, often occurring between late April and early October. Commercially, matcha can be classified into four main categories: ceremonial grades from Ichibancha or (first harvest) leaves; it is the best quality matcha, which accounts for 40% of the total harvest of the four plucking rounds; culinary grades are from Nibancha or (second harvest or daily) matcha leaves; ingredient from Sanbancha (third harvest); and Yonbancha is fourth harvest. The third and fourth harvests are called late harvests (Anggraini, 2019; Hall, 2002).

Before the initial harvest, tea plants (*Camellia sinensis*) are shaded for approximately a month. This shading process, which varies in technique across different farms, serves two primary purposes: frost protection and nutrient enhancement. By limiting sunlight exposure, the tea leaves become thinner, darker, and richer in color. Moreover, suppressed photosynthesis prevents the conversion of amino acids into catechins, resulting in higher amino acid concentrations. Conversely, subsequent harvests conducted under full sunlight conditions yield tea leaves with elevated catechin levels (Phuah et al., 2023; Yamashita et al., 2020).

The stages of production of the MJGT are illustrated in Figure 1.5 After the harvest of plants, Aracha, or crude tea, is produced by steaming tea leaves, rolling, and drying them. Then, the stems and veins are removed to become Tencha by sorting using compressed air because the veins and stems are heavier than other leaf particles. Tencha is made up of small pieces of peeled leaves. Matcha is made by grinding Tencha with stone in a large granite mill called an Ish-Iusu. Finally, the matcha is packaged into specialized tins or pouches (Bonanno et al., 2019; Horie et al., 2017).



Figure 1.5. Steps of manufacturing MJGT by the Jade Leaf brand

1.5.2 Extraction of MJGT

Matcha Japanese green tea (MJGT) contains a high concentration of phytochemical components, including polyphenols such as catechins, flavonols, flavanols, and phenolic acids. These components comprise between 18% and 36% of the MJGT dry weight, and caffeine, chlorophylls, and amino acids comprise 4% of the MJGT dry weight. Polyphenols are thought to affect the synthesis of nanoparticles by acting as size-reducible and stabilizing agents, thereby increasing the surface area and photocatalytic activity (Koláčková et al., 2020; H. S. Nguyen et al., 2024; Saikumari et al., 2019). The polyphenol content of MJGT was examined by Karolina Jakubczyk et al., (Jakubczyk et al., 2024) who reported abundance levels of polyphenol acids, flavonoids, and caffeine. Also, the phytochemical content and antioxidant characteristics of MJGT are affected by the harvest timing, cultivation technique, and geographic origin.

The extraction of matcha is challenging due to several factors that influence the phytochemical content. These factors include the choice of solvent (hot or cold water and alcohol), temperature, time, and pH of MJGT infusion. In the same context, water is often used as a solvent for MJGT since it is environmentally benign and cost-effective (Phuah et al., 2023). Table 1.4 displays the total polyphenol content (TPC) and total flavonoid content (TFC) concentrations of

matcha compared to other water-extracted tea varieties, considering the influence of temperature and extraction time. The most abundant flavonoids found in matcha are flavanols, including anthocyanins, flavonols, flavonols, flavan-3-ols, flavanones, and isoflavones, which are the six groups of flavonoids (Koláčková et al., 2021; Manikharda et al., 2023; Phuah et al., 2023). Previous studies indicated a greater abundance of polyphenol compounds obtained from the second harvest of MJGT compared to the first, as shown in Table 1.4. In Table 1.4, the extraction temperature at 70 and 90°C found that the TPC of the second harvest was between 1736.31 and 1765.12 mg/L for 10 minutes, respectively, while its value decreased at 25°C to 1620.63 mg/L at 10 minutes. On the other hand, the TPC of the first harvest was 1499.88 and 1495.47 mg/L during the extraction time of 10 minutes at 70 and 90°C, respectively (Jakubczyk et al., 2020). The TFC of the second harvest was also higher than the first harvest under the same conditions (i.e., extraction time and temperature). Other researchers observed that the highest content of phytochemical compounds in tea infusion was at an extraction temperature of 80°C during a relatively short extract time (Jakubczyk et al., 2020). This is compatible with Table 1.4, which shows the optimum total polyphenol content (TPC), and total flavonoid content (TFC) was approximately 2230 and 1630 mg/L at 80 for 5 minutes, respectively (Komes et al., 2010). Meanwhile, the TPC of conventional green, white, and black tea was 1557.58, 1185.7, and 1369.70 mg/L at extraction temperatures of 80 and 90 °C and times 7.5 and 3 minutes, respectively. While the TFC of conventional green and black tea was 252.41 and 219.94 mg/L, respectively. Therefore, MJGT has higher TPC and TFC content than other teas.

Catechin is a type of polyphenol and consists of several compounds, including epigallocatechin-3-gallate (EGCG), which is predominant in MJGT, gallic acid (GA), epigallocatechin (EGC), epicatechin-3-gallate (ECG), and epicatechin (EC). The concentrations of catechin were studied in Table 1.5, which compares the catechin concentrations with different brands such as conventional green tea from 365, MJGTF and MJGTF from Jade Leaf, as well as black tea. According to Table 1.5, the MJGTS exhibits elevated levels of catechins compared to the MJGTF harvest, green tea (365), and black tea (Phuah et al., 2023; Zielinski et al., 2015).

On the other hand, the MJGT is abundant in minerals, which form 5% of the dry weight. However, the concentrations of minerals in matcha are influenced by

various environmental conditions, including the growth stage, soil composition, fertilization, and processing procedures (Koláčková et al., 2020; Phuah et al., 2023). The study by Teresa Kolakova et al., (Koláčková et al., 2020) aimed to quantify the mineral and trace element composition in matcha using inductively coupled plasma mass spectrometry (ICP-MS), as in Table 1.6, which includes data from several matcha brands. According to Table 1.6, potassium is the predominant element found in matcha, significantly contributing to the increase of the surface area for synthesis nanoparticles, which leads to increased photocatalytic activity (Kayani et al., 2023).

Finally, the MJGT can be described as a primary source of polyphenols (TPC) and Flavonoids (TFC) compared to the other types of tea. Based on the optimal extraction conditions shown in Table 1.4 . So, in this study, the extraction conditions will be carried out at 80 °C for 5 minutes.

Table 1.4. The relationship between extraction with TPC and TFC (Jakubczyk et al., 2020; Komes et al., 2010; Sielicka-Różyńska & Szulc, 2020; Zielinski et al., 2015)

Tea type	Time (min.)	Temperature (°C)	TPC (mg/L)		TFC (mg/L)	
			First harvest	Second harvest	First harvest	Second harvest
Matcha Japanese Green Tea	10	25	1345.41	1620.63	1222.60	1723.11
	10	70	1499.88	1736.31	1514.28	1802.44
	5	80	-	2230	-	1630
	10	80	1577.01	1698.32	1340.77	1968.79
	10	90	1495.47	1765.12	1460.41	1379.82
Green Tea	3	60	697.2		-	
	3	75	938.6		-	
	7.5	80	1557.58		252.41	
	3	90	1066.3		-	
White Tea	3	60	725.3		-	
	3	75	997.3		-	
	3	90	1185.7		-	
Black Tea	7.5	80	1369.70		219.94	

Table 1.5. Catechin concentration ($\pm$ standard error; all reported in mg/g tea)
(Meyer et al., 2023; Zhao et al., 2024)

Brand	Epicatechin	EGC	EGCG	GCG	E-CG
Green tea (365)	6.00 $\pm$ 0.18	13.86 $\pm$ 0.25	23.29 $\pm$ 1.15	2.06 $\pm$ 0.11	9.54 $\pm$ 0.53
Jade Leaf (first harvest)	4.22 $\pm$ 0.33	21.34 $\pm$ 1.30	49.03 $\pm$ 2.95	1.43 $\pm$ 0.15	6.08 $\pm$ 0.65
Jade Leaf (second harvest)	9.36 $\pm$ 0.66	38.04 $\pm$ 1.97	47.95 $\pm$ 3.05	2.52 $\pm$ 0.34	8.80 $\pm$ 1.07
Black tea	0.33 $\pm$ 0.00	-	0.01 $\pm$ 0.01	-	0.35 $\pm$ 0.01

Table 1.6. Contents of selected minerals and trace elements in matcha evaluated by (ICP-MS) (Koláčková et al., 2020)

Analyte	Day spa premium ($\mu\text{g/g}$)	Harmony ($\mu\text{g/g}$)	Don Matcha ($\mu\text{g/g}$)
Na	155 $\pm$ 2	161 $\pm$ 3	131 $\pm$ 2
Mg	2300 $\pm$ 20	2400 $\pm$ 30	2080 $\pm$ 30
Al	11.2 $\pm$ 0.3	113 $\pm$ 1	9.11 $\pm$ 0.20
P	4180 $\pm$ 30	4040 $\pm$ 20	3770 $\pm$ 20
K	4730 $\pm$ 30	2970 $\pm$ 10	2980 $\pm$ 20
Ca	2650 $\pm$ 30	2640 $\pm$ 20	1760 $\pm$ 20
Mn	17.4 $\pm$ 1.0	19.1 $\pm$ 1.2	17.8 $\pm$ 1.2
Fe	111 $\pm$ 3	96.4 $\pm$ 2.5	83.6 $\pm$ 1.5
Cu	7.04 $\pm$ 0.2	22.9 $\pm$ 0.6	25.3 $\pm$ 1.0
Zn	24.7 $\pm$ 0.7	34.7 $\pm$ 1.1	68.5 $\pm$ 1.8
Ba	3.61 $\pm$ 0.1	3.84 $\pm$ 0.10	2.22 $\pm$ 0.1

1.6 Model compound

Methylene blue (MB) is a popular cationic dye commonly used in the extent range of textile industries such as silk, wood and cotton due to its excellent absorption properties and stability. Its chemical formula is $\text{C}_{16}\text{H}_{18}\text{N}_3\text{ClS}$ with a molecular weight of 319.85 g/mol and a maximum wavelength (λ_{max}) of 664 nm (Kerli et al., 2022; Patterson & Patterson, 2011). In 2010, MB was selected by the International Organization for Standardization (ISO Standard 10678: 2010) to be a standard model for evaluating the photocatalytic degradation in aqueous media. It is a well-characterized compound in the literature in terms of degradation pathway

(de Souza Pereira et al., 2023; Mills, 2012). For these reasons, in the current M.Sc. study, MB was selected as a model compound to evaluate the photocatalytic performance of the synthesized TiO₂ photocatalysts.

1.7 Implications of Literature

The existing literature highlights the limitations of chemically synthesized TiO₂ photocatalysts, such as Degussa P-25, in terms of surface morphology and optical properties. These limitations hinder their photocatalytic performance in degrading pollutants in industrial wastewater (H. Dong et al., 2015). To address these challenges, green synthesis methods, which utilize various plant extracts, have emerged as a promising approach to enhance the surface morphology and photocatalytic activity of TiO₂.

The preceding literature review concerning the application of green synthesis of TiO₂ photocatalyst using regular green tea has shown a significant improvement in the surface morphology and optical characteristics for TiO₂ photocatalyst due to the presence of polyphenol compounds. Another type of green tea is matcha Japanese green tea, which has richness in the polyphenol compounds (higher than the regular green tea). A comprehensive literature review revealed a lack of research exploring the application of matcha Japanese green tea extract in the green sol-gel synthesis of TiO₂ photocatalysts. This study aims to bridge this knowledge gap by investigating the potential of using matcha extract for this purpose. By doing so, this research has the potential to be a pioneering contribution in the field of green photocatalysis using TiO₂.

1.8 Aim and objectives

The overall aim of the current M.Sc. study is a major attempt to investigate, for the first time, the application of MJGT extract using the green synthesis to modify the surface morphology of synthesized TiO₂ photocatalyst towards enhancement of its photocatalytic performance. The extracts from the powders of matcha Japanese green tea with first harvest (MJGTF) and second harvest (MJGTS) were separately used for the green synthesis of TiO₂ photocatalyst. To achieve this aim, the work was divided into the following specific objectives:

I. Synthesis

- Chemical synthesis of TiO_2 photocatalyst using the sol-gel method. Titanium (IV) isopropoxide, isopropyl alcohol and deionized water will be used to synthesize the TiO_2 control photocatalyst (CP).
- Green synthesis of TiO_2 photocatalyst using the sol-gel method. Various extracted solutions of MJGTF and MJGTS will be used with titanium (IV) isopropoxide and isopropyl alcohol to synthesize the green TiO_2 photocatalysts.

II. Characterization

A detailed characterization of the structural and surface morphology in terms of crystal structure, functional group, particle size, images of the surface, elemental composition and mapping line, surface topography, surface roughness, surface area, pore properties, thermal stability and optical properties for chemically and greenly synthesized TiO_2 will be carried out using various relevant analytical techniques. Including, X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Field Emission Scanning Electron Microscopy (FE-SEM), Energy-dispersive X-ray (EDX), Atomic force microscopy (AFM), Brunauer-Emmett-Teller (BET) surface area analysis, Transmission electron microscopy (TEM), Thermogravimetric analysis (TGA), and Ultraviolet–visible spectroscopy (UV-vis).

III. Evaluation

The green synthesized TiO_2 photocatalyst's performance will be assessed by measuring its ability to degrade and mineralize methylene blue, a model synthetic industrial wastewater pollutant. This will be done using a batch photocatalysis setup. For comparison, both chemically synthesized TiO_2 and a commercial standard (Degussa P-25) will also be tested. During the photocatalytic process, key parameters such as pH, dissolved oxygen (DO), and color change will be monitored.

2. MATERIALS and METHOD

2.1 Materials

The powders of matcha Japanese green tea (MJGT) with first harvest (denoted as MJGTF) and second harvest (denoted as MJGTS) were used in the green synthesis of TiO_2 photocatalyst, as seen in Table 2.1, which shows the materials used in this study. Titanium (IV) tetra isopropoxide (TTIP) was used as a precursor source of titanium for the chemical and green synthesis of TiO_2 photocatalyst. Isopropyl alcohol was used as a solvent. The commercially available TiO_2 (Degussa, P-25) was used as a benchmark heterogenous photocatalyst (denoted as BM). Methylene blue was used as a synthetic dye model of industrial wastewater (denoted as MB). Deionized (DI) water was used in further experimental processes. All chemical materials were of analytical quality and used directly without additional processing for purification.

Table 2.1. Materials used in the study

No.	Material	Company	Manufacturer	Purity (%)
1	Matcha Japanese green tea	JADE LEAF	USA	NA
2	Titanium (IV) tetra isopropoxide [TTIP, $\text{Ti}(\text{OH}(\text{CH}_3)_2)_4$]	Sigma-Aldrich	Germany	97%
3	Isopropyl alcohol $(\text{CH}_3)_2\text{CHOH}$	THOMAS BAKER	India	99%
4	Degussa P25 powder	Nanografi Nano Technology	Turkey	NA
5	Methylene blue (MB, $\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S} \cdot x\text{H}_2\text{O}$)	Merck	Germany	NA
6	Deionized water micromeg purified system	Elga Labwater, VWR International Ltd	UK	NA

2.2 Instruments and Measurement

A sensitive balance (JOANLAB, FA1004) with a digital indicator was used for measuring purposes, as shown in Figure 2.1 (a). It has AC (100-240 V), with a max capacity of 100 g, a sensitivity of 0.0001 g, and a resolution of 0.1 mg. The magnetic stirrer-heater (SH-2, China), as seen in Figure 2.1 (b), was used for mixing and extracting processes. It has a capacity of 1 L, a maximum temperature range of 49 to 350 °C, and a speed range of 100 to 2000 rpm. The electric centrifuge (80-1,

China) was utilized to separate suspended particles for extracted MJGTF and MJGTS samples, as shown in Figure 2.1 (c). It operated within a speed range of 0 to 4000 rpm. The Heraeus group, Germany, was utilized for the heat treatment of photocatalysts (i.e., drying and calcination), as illustrated in Figure 2.1 (d). The drying specification is 0 to 250 °C, while the annealing temperature for Heraeus ranges from 0 to 1300 °C.

The electrochemical dissolved oxygen (DO, Atlas Scientific, USA) kit measures DO concentrations in the photoreactor, providing interference-free readings, as shown in Figure 2.1 (e). It has a concentration range of 0.00–100 mg/L, an accuracy of ± 0.05 mg/L, a response time of approximately 0.3 mg/L per second, and operates within a temperature range of 1–60 °C. A pH meter (Atlas Scientific, USA) was used to measure pH in the photoreactor, as illustrated in Figure 2.1 (f). It has a range of 0.01 to 14.00, a high resolution of 0.001, an accuracy of ± 0.002 , a response time of 95% within 1 second, and a temperature range of -5 to 99 °C.

These instruments and measurements were used at the Department of Chemical Industries laboratories at the Technical Institute of Anbar, Middle Technical University.





Figure 2.1. The instruments and measurements used in the study: (a) The electrical Balance FA1004, (b) Magnetic stirrer-heater SH-2, (c) The electric Centrifuge 80-1, (d) The annealing furnace Heraeus, (e) Dissolved Oxygen Kit, (f) pH Kit

2.3 Chemical synthesis of TiO_2

This synthesis was performed following the sol-gel method (C. Chang et al., 2023). 10 mL of TTIP precursor was dissolved in 60 mL of alcohol solvent and stirred continuously using a magnetic stirrer at room temperature for 1 h to obtain a homogeneous solution. Then, 30 mL of DI water was added dropwise to the solution and mixed rigorously for 4 h to initiate hydrolysis. The resultant solution (sol) was left for 18 h to obtain a gel. The gel was dried using an oven at 80 °C for 18 h to ensure the evaporation of the used solvent. Afterwards, the dried gel was pulverized to finely powdered TiO_2 by using a mortar. The finely powdered TiO_2 was calcinated at 450 °C for 7 h using an annealing furnace. The schematic representation of the experimental procedure for the chemical synthesis of TiO_2 is shown in Figure 2.2.

This chemically synthesized TiO_2 photocatalyst by the sol-gel method was used as a control photocatalyst for evaluating the greenly synthesized TiO_2 later in terms of characterization and photocatalytic degradation of MB and referred to as CP.

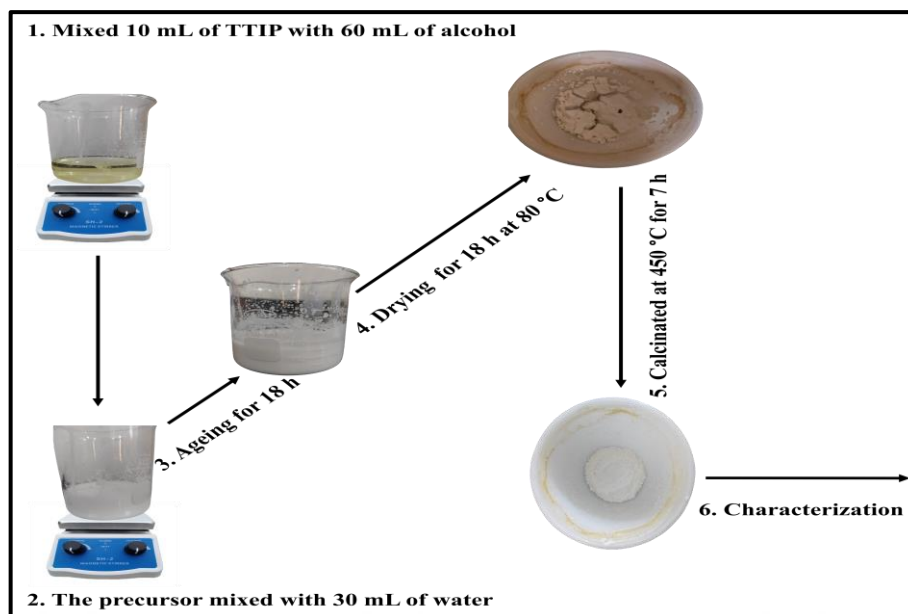


Figure 2.2. Chemical synthesis of TiO_2 via the sol –gel method

2.4 Green synthesis of TiO_2

A conventional solvent extraction method using water as a popular solvent is widely applied for the extraction of bioactive components from plants because it is a simple, effective and economical method (Eddy et al., 2024). In the current study, this method was used to extract the bioactive components from the dry powders of MJGTF and MJGTS.

Three dry powder weights (1, 2, and 3 g) for each MJGTF and MJGTS were separately immersed in 50 mL of DI water and mixed under a constant stirring of 500 rpm and a heating temperature of 80 °C for 5 min using a magnetic stirrer-heater. Then, the six extracted solutions were cooled to room temperature. To remove any impurities found in the extracted solution, a centrifuge was used at 4000 rpm for 15 min. The centrifugation was repeated three times to ensure a complete removal of any impurities. Afterward, the six extracts of MJGTF and MJGTS prepared were used in the green synthesis of TiO_2 photocatalyst.

A mixture of 10 mL of TTIP precursor and 60 mL of alcohol solvent was magnetically stirred at room temperature for 1 h to obtain a homogeneous solution. Then, 30 mL of either MJGTF extract or MJGTS extract was dropwise added to the solution for 4 h for the initiation of hydrolysis. The resultant solution (sol) was left for 18 h to obtain a gel. The gel was dried at 80 °C for 18 h to ensure the evaporation of the used solvent. Afterwards, the dried gel was pulverized to finely powdered

TiO₂ by using a mortar. The finely powdered TiO₂ was calcinated at 450 °C for 7 h using a furnace. The schematic representation of the experimental procedure for the green synthesis of TiO₂ is shown in Figure 2.3.

This greenly synthesized TiO₂ photocatalyst with MJGTF and MJGTS was referred to as GF_x and GS_x, respectively where x=1, 2, and 3 represents the dry powder weight of each MJGTF and MJGTS in gram used in the preparation of their extracts.

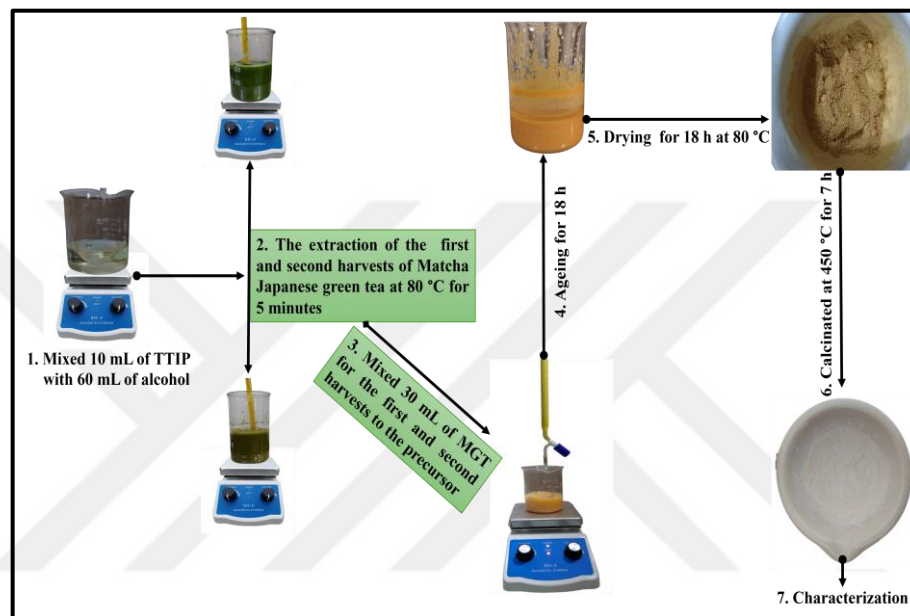


Figure 2.3. Green synthesis of TiO₂ via the sol –gel method

2.5 Experimental setup and procedure

2.5.1 Photoreactor setup

The overall assembly photograph of the batch photoreactor setup is shown in Figure 2.4. This batch photoreactor is a house-custom made from Pyrex-glass cell with a cylindrical shape and total volume of 1 L, an outer radius of 70 mm, an inner radius of 5 mm and a length of 400 mm. A low-pressure mercury UV lamp (model T5-UV, China) with a light intensity of 8 W and a light wavelength of 254 nm was placed in the center of the cylinder. A magnetic stir bar, a pH probe, a dissolved oxygen (DO) probe and a thermocouple were placed inside it. A sampling valve was fitted at the bottom of the photoreactor. This photoreactor was placed above a stirrer-heater and covered with aluminum tin foil to prevent any degradation effects via ambient light in the laboratory. These probes were used to monitor

different investigated reaction conditions and the measuring values were recorded via a data logging program connected to the laptop.

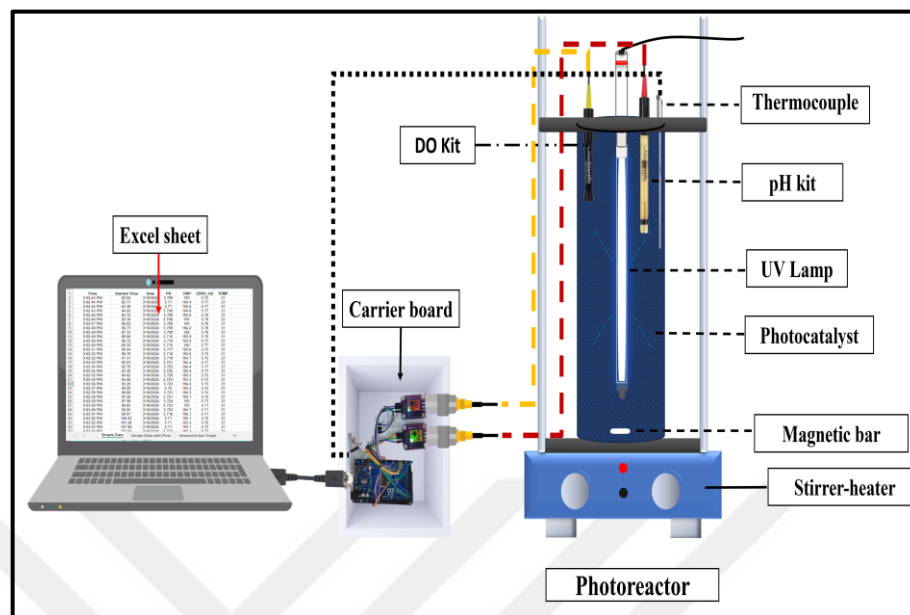


Figure 2.4. A batch photoreactor setup

2.5.2 Calibration curve of MB

The calibration curve for methylene blue (MB) was established using UV-vis spectroscopy (INOVIE LAB, UVVIS-1911DB, UK) to determine the concentrations of standard MB solution prior to and during degradation. The stock solution was prepared at 20 ppm and further diluted to different concentrations (1, 2, 3, 4, 6, 8, 10, and 15 mg/L), as seen in Figure 2.5. The calibration findings showed a good straight line from the calibration curve consisting of 9 points ($R^2 = 0.9994$).

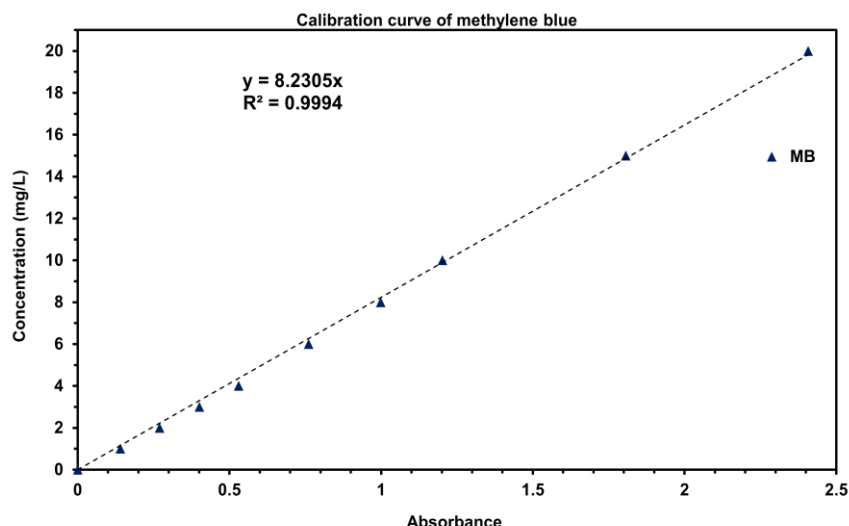


Figure 2.5. The calibration curve of methylene blue

2.5.3 Photolysis experiments

The photolysis process, one of the AOPs, uses UV irradiation to degrade photolytically the refractory pollutants (Khalf et al., 2024). The presence of UV irradiation can act directly as a photolysis process (without using the photocatalyst) and as a photocatalysis process (with using the photocatalyst). To ensure a reliable comparison between chemically and greenly synthesized TiO_2 photocatalysts, it is essential that the contribution of direct photolysis to the overall degradation process be minimized. As suggested by the literature, direct photolysis efficiency decreases with increasing pollutant concentration (Olatunde et al., 2020). To address this, preliminary adsorption-desorption experiments were conducted to determine the optimal dark equilibrium time for MB in the photoreactor. Subsequently, photolysis experiments were performed at various MB concentrations to identify a concentration range where direct photolysis is negligible. By carefully selecting the initial MB concentration, the observed degradation can be confidently attributed to the photocatalytic activity of the TiO_2 photocatalysts.

To determine the optimal initial MB concentration for the photocatalysis experiments, a range of concentrations from 5 to 20 mg/L were prepared. Each concentration was magnetically stirred in the dark for 120 minutes to allow for adsorption-desorption equilibrium. It was determined that 25 minutes was sufficient to reach this equilibrium. Therefore, a 30-minute dark period was selected to ensure complete adsorption-desorption before initiating photolysis. Subsequently, photolysis experiments were conducted at various MB concentrations. Results

indicated that a 20 mg/L initial concentration exhibited negligible degradation via direct photolysis compared to lower concentrations. Consequently, 20 mg/L was chosen as the optimal initial concentration for the subsequent photocatalysis experiments.

2.5.4 Photocatalysis experiments

20 mg of MB was added to 1 L of DI water in the photoreactor to prepare a 20 mg/L MB reactant solution. This reactant solution was magnetically stirred at 300 rpm for 30 min of the adsorption-desorption equilibrium time in the dark. Various doses of photocatalysts (BM, CP, GF2, and GS2) were added to the reactant solution and magnetically stirred at 300 rpm for 30 min to achieve the adsorption-desorption equilibrium between the MB solution and the surface of used photocatalysts. Then, the UV lamp was switched on to start the photocatalytic reactions for 120 min. To baseline a comparison of the photocatalytic performance for these investigated photocatalysts, the photocatalytic experiments were carried out under limited oxygen conditions (i.e., the toughest reaction regime) (Ali et al., 2010). Under these conditions, the oxygen was from the dissolved oxygen (DO) within the MB solution and additional oxygen was provided to the reactant solution through the mass transfer from the ambient air only. During these photocatalytic experiments, the pH of the MB reactant solution changes due to the degradation of MB to form reaction intermediate compounds. As a result, pH gives an indicator to the evaluation of these photocatalytic reactions (Shariffuddin et al., 2013; Zhou et al., 2024). So, the pH and DO were monitored during the course of the reaction. Samples of MB were taken before, after 60 min of adsorption-desorption equilibrium and then every 30 min photocatalytic time to end of photocatalysis experiment. The real photos of these samples were taken to monitor the visual change in color of MB during the reactions.

These samples of treated MB were immediately centrifuged and then quantitatively analyzed for photocatalytic degradation using a UV-vis spectrometer (INOVIE LAB, UVVIS-1911DB, UK) and for photocatalytic mineralization based on the total organic carbon (TOC) using a TOC analyzer (Shimadzu, TOC-LCSN, Jaban). The photocatalytic degradation percentage of MB, D%, (i.e., MB removal percentage) was calculated using equation (2.1). The unknown concentrations of MB in preliminary and these experiments were determined by a linear calibration

curve equation plotted by the known concentrations of standard MB solution versus their absorption values.

$$D (\%) = \frac{C_0 - C_t}{C_0} \times 100 \quad (2.1)$$

Where C_0 is the concentration of MB (mg/L) after the 60 min of adsorption-desorption equilibrium and C_t is the concentration of MB (mg/L) during the photocatalytic reaction time.

The TOC analysis was performed to screen how much MB pollutant was degraded and changed into mineralization. The photocatalytic mineralization percentage was expressed by the TOC removal percentage was calculated using equation (2.2).

$$\text{TOC removal (\%)} = \frac{\text{TOC}_0 - \text{TOC}_t}{\text{TOC}_0} \times 100 \quad (2.2)$$

Where TOC_0 is the concentration of TOC in MB solution (mg/L) after the 60 min of adsorption-desorption equilibrium and TOC_t is the concentration of TOC in MB solution (mg/L) during the photocatalytic reaction time.

Note that the equations (2.1 and 2.2) were used to calculate the photolytic degradation percentage of MB and photolytic mineralization percentage of MB where C_0 is the concentration of MB (mg/L) after the 30 min of adsorption-desorption equilibrium and C_t is the concentration of MB (mg/L) during the photolytic reaction time.

All experiments were performed at room temperature in duplicate, and the figures present the average values of the experimental results, with a standard deviation of ($< 1\%$).

2.6 Characterization Analysis Techniques of TiO_2 Photocatalyst

In the current study, several characterization techniques were used to investigate the structural and morphological properties of the chemically and greenly synthesized TiO_2 photocatalysts. These instruments included XRD, FTIR, FE-SEM, EDX, AFM, BET surface area, TEM, TGA, and UV-Vis. These characteristics were carried out at the University of Tehran, Iran, and Phi Nanoscience Center (PNSC), Baghdad, Iraq.

2.6.1 X-ray Diffraction (XRD)

For analysis of the crystalline structure and crystallite size of synthesized photocatalysts as shown in Figure 2.6, X-ray diffraction (XRD) instrument using a

diffractometer (Panalytical, X' Pert Pr, UK) equipped with a monochromatic CuK α radiation ($\lambda=0.15418$ nm) as X-ray source scanning in 2θ range from 5-80°, acceleration voltage of 30 kV and applied current of 30 mA was conducted. For all synthesized photocatalysts, the XRD data were analyzed for phase analysis by using software (Match!, Version 4, Germany), and indexed by using a standard sample COD Card (Number: 96-900-9087) with the lattice parameters: $a=3.7850$ Å , $c=9.5140$ Å , Cell Volume= 136.300 Å³ and a space group of I41/amd (Al-Taa'y & Hasan, 2021).

The Debye-Scherrer equation (2.3) was used to determine the average crystallite size of synthesized photocatalyst (Muraro et al., 2023) as follows:

$$D_{XRD} = \frac{K \cdot \lambda}{\beta \cdot \cos \theta} \quad (2.3)$$

Where D is average crystallite size, $\lambda = 0.15418$ nm, β is the full width at half maximum (FWHM), K is a shape factor without dimension (0.9) and θ is the Bragg diffraction angle ($^{\circ}$).



Figure 2.6. X-ray diffraction XRD X' Pert Pr

2.6.2 Fourier Transform Infrared (FTIR)

For analysis of identification of functional groups, Fourier Transform Infrared (FTIR) Spectroscopy (Shimadzu, IRAffinity-1, Japan), operating with the infrared radiation range $400-4000$ cm⁻¹ was conducted as illustrated in Figure 2.7.

The software (KnowItAll Informatics System 2024) was used to analyze spectroscopic data in terms of identification, characterization of chemical compounds and access to extensive spectral databases that contain reference spectra of many compounds with annotated functional groups.

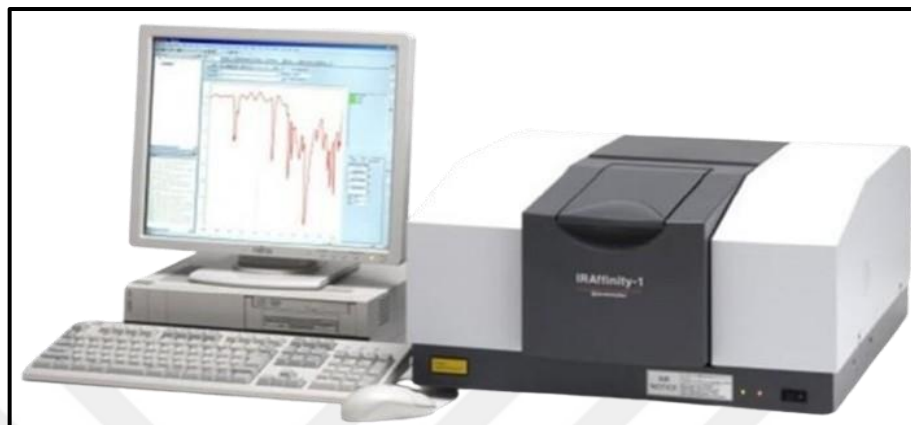


Figure 2.7. Fourier Transform Infrared (FTIR) IRAffinity-1

2.6.3 Field Emission Scanning Electron Microscopy and EDX

Field-emission Scanning Electron Microscopy (FE-SEM) and energy-dispersive X-ray (EDX) (ZEISS SIGMA VP, Germany) were utilized to analyze imaging, energy dispersive spectroscopy (EDS) mapping—line (elemental mapping and composition) of photocatalysts. It has a magnification range of 10.00 to 50.00 KX and an acceleration voltage of 25.00 kV, as illustrated in Figure 2.8. EDX has 10.00 KX magnification at 15 kV and full backscattered electron.

To analyze the mean particle size and size distribution, the ImageJ processing program (version 1.54) and Origin Pro 2024b (student version, Northampton, MA, USA) were used to estimate the mean particle size for each synthesized photocatalyst by fitting the distribution histogram of the particle size to the log-normal distribution function (f) using equation (2.4) (Khelifi et al., 2024).

$$f(D) = \frac{1}{\sqrt{2\pi}\sigma_{sd}} \exp \left[-\frac{(\ln \frac{D}{D_0})^2}{2\sigma^2} \right] \quad (2.4)$$

where D is the mean particle size (nm), D_0 is the median diameter (nm), σ_{sd} is the standard deviation and σ^2 is the median standard deviation.



Figure 2.8. Field Emission Scanning Electron Microscopy ZEISS SIGMA VP

2.6.4 Atomic Force Microscopy (AFM)

Atomic Force Microscopy (AFM, Core AFM, Nanosurf, Switzerland) is a form of scanning probe microscopy that provides three-dimensional images by measuring the forces between a sharp probe and the surface of a sample, allowing the study of surface topography, as shown in Figure 2.9. The images were used to characterize the surface of roughness using MountainsSPIP®Academic 10.0.10510 software.

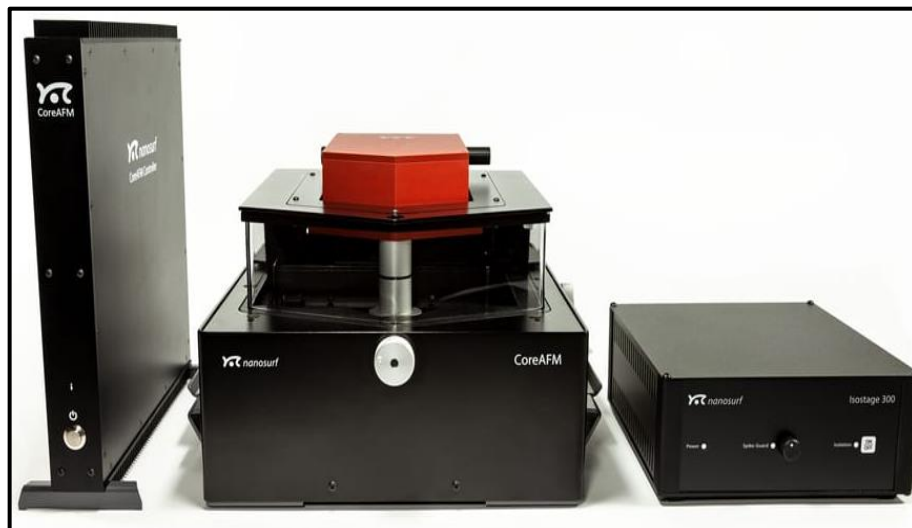


Figure 2.9. Atomic Force Microscopy (AFM)

2.6.5 Brunauer-Emmett-Teller (BET) surface area

For analysis of specific surface area (S_{BET}), BJH pore volume and pore size distribution, N_2 adsorption-desorption isotherm technique using a surface area analyzer as shown in Figure 2.10 (Micromeritics, Gemini VII 2390t, USA) at -196°C micromeritics equipment using the BET/BJH method. Before analysis, the photocatalysts were degassed at 110°C for 2 h to remove weakly adsorbed species (Muraro et al., 2023; Rebollo et al., 2024). The S_{BET} was calculated using the Brunauer-Emmett-Teller (BET) method determined from the relative pressure range between 0.05 and 0.30. The size distribution and volumes were analyzed using the Barrett-Joyner-Halenda (BJH) model.

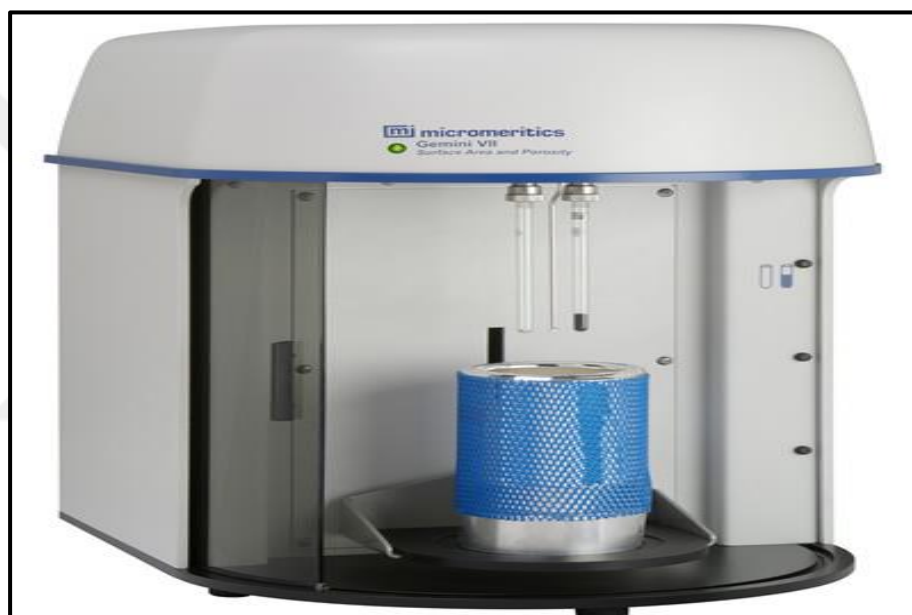


Figure 2.10. The surface area analyzer (Gemini VII 2390t)

2.6.6 Transmission Electron Microscopy (TEM)

An imaging technique was used to further characterize the internal morphological and structural details in terms of the particle size and shape for greenly synthesized photocatalysts (TEM, ZEISS LEO 912 AB, Germany), as seen in Figure 2.11. It has a magnification range of 2.784 to 100.00 KX and an acceleration voltage of 40 to 120 kV with high-resolution point-to-point (0.34 nm) and information limit (< 0.20 nm).



Figure 2.11. Transmission electron microscopy ZEISS LEO 912 AB

2.6.7 Thermogravimetric Analyzer (TGA)

For analysis of thermal stability, thermogravimetric analyzer (TGA) instrument (Mettler—Toledo, USA) with scan temperature of 25 to 609 °C and heating rate of 1 °C/min were used to identify the thermal degradation based on the weight loss vs. temperature, as seen in Figure 2.12.



Figure 2.12. Thermogravimetric Analyzer (TGA) Mettler-Toledo

2.6.8 Ultraviolet–visible spectroscopy (UV-vis)

For analysis of optical properties, the optical properties in terms of wavelength and bandgap energy for investigated photocatalysts were examined. The ultraviolet–visible spectroscopy (UV-vis, Shimadzu 1900i, Japan) was used in the range 200-1000 nm to measure the absorption spectra of the synthesized photocatalysts, as seen in Figure 2.13. The Tauc equation (2.5) was used to identify the bandgap energy of investigated photocatalysts (Sukhadeve & Gedam, 2023; Yahia et al., 2023) by drawing a tangent of the Tauc's plot $((\alpha E)^2$ versus E). The obtained intersection point with the X-axis represented the bandgap energy for each investigated photocatalyst. The software (Origin Pro 2024b) was used to draw the Tauc's plot.

$$(\alpha E)^n = B(E - E_g) \quad (2.5)$$

Where, α is the optical absorption coefficient, E is the photon energy, B is a constant depending on the transition probability, E_g is the optical bandgap energy and n is 2 for direct permitted transitions.



Figure 2.13. Ultraviolet–visible spectroscopy (UV-vis)

2.7 Evaluation Analysis Techniques

2.7.1 UV-vis spectroscopy

For analysis of primary degradation, the primary degradation in terms of the wavelength of MB for evaluating the photocatalysts was examined. The double

beam ultraviolet-visible spectroscopy (INOVIE LAB, UVVIS-1911DB, UK) was used. The absorption spectra were recorded in the range of 200–800 nm to monitor the primary degradation of MB, particularly observing the peak around 644 nm, as seen in Figure 2.14.

The UV-vis was calibrated by analyzing five samples of known concentrations for all experiments that used it. This equipment is used at the University of Anbar, College of Science, Department of Chemistry, Consulting Service Laboratory.



Figure 2.14. Ultraviolet–visible spectroscopy UVVIS-1911DB

2.7.2 Total Organic Carbon (TOC)

Total organic carbon (TOC, Shimadzu's TOC-LCSN, Japan) was used as an analytical approach for directly measuring organic carbon content, allowing the evaluation of MB mineralization efficiency into CO_2 and H_2O_2 , as illustrated in Figure 2.15. The TOC uses the 680°C combustion catalytic oxidation method, measuring 4 $\mu\text{g/L}$ to 30,000 mg/L. This equipment is used at the University of Basrah, Maine Science Center, Iraq.



Figure 2.15.TOC-LCSN analyzer

3. RESULTS

3.1 Characterization of synthesized TiO₂ (chemically vs. greenly)

3.1.1 XRD analysis

The XRD analysis for the chemically synthesized TiO₂ (CP) and greenly synthesized TiO₂ (GF1, GF2, GF3, GS1, GS2, and GS3) is shown in Figure 3.1. The XRD spectra in Figure 3.1 for all synthesized TiO₂ photocatalysts show that the position of diffraction peaks located at the orientation of Bragg diffraction angle (2θ value of 25.430) corresponding to the crystalline plane (011) confirms the crystalline anatase phase of TiO₂ according to the anatase TiO₂ standard sample COD Card (Number: 96-900-9087). It is clear to see from this XRD spectra for all synthesized TiO₂ photocatalysts that no diffraction peaks located at the Bragg diffraction angles (2θ values of 27.40 and 30.500) could be identified. Thus, the complete absence of these angles gives further confirmation that the formation of the crystalline phase of TiO₂ is pure anatase. The other Bragg diffraction angles for all synthesized TiO₂ photocatalysts corresponding to their planes are shown in Table 3.1. The crystallite sizes of these synthesized TiO₂ were calculated using the Debye-Scherrer equation (Eq. 2.3) and the obtained crystallite sizes (average values) are presented in Table 3.1.

As shown in Table 3.1, the crystallite sizes of greenly synthesized TiO₂ (GF1, GF2, GF3 and GS1, GS2, GS3) were less than that of the chemically synthesized TiO₂ (i.e., control photocatalyst (CP)). The decreases in the crystallite sizes of greenly synthesized TiO₂ were found to be 40% for GF1, 48% for GF2, 43% for GF3, 47% for GS1, 48% for GS2 and 43% for GS3 when compared with the CP photocatalyst.

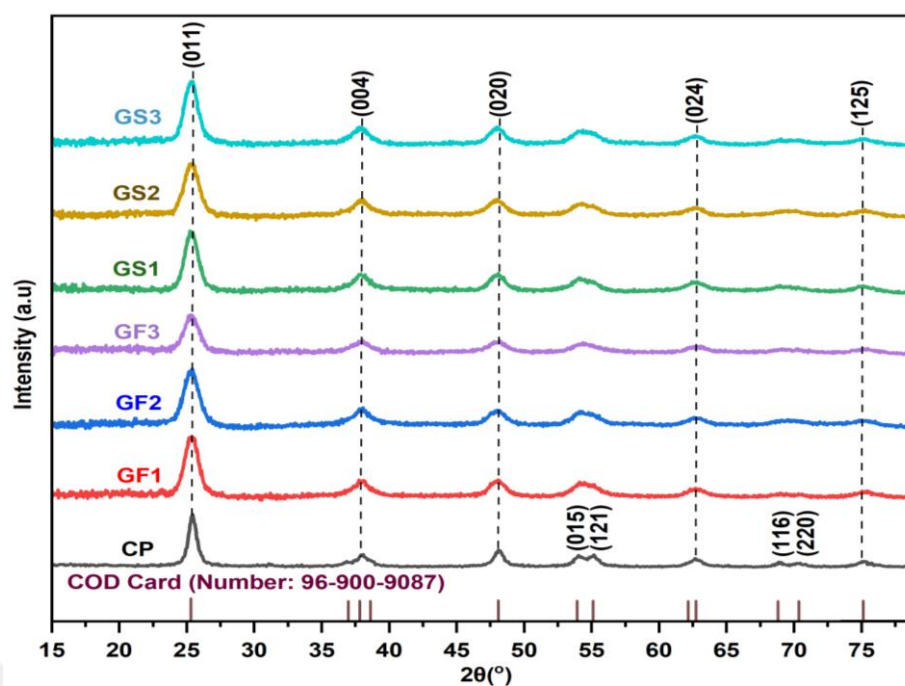


Figure 3.1. XRD spectra of chemically and greenly synthesized TiO₂ photocatalysts

Table 3.1. Average crystallite size of chemically and greenly synthesized TiO₂ (anatase phase)

Photocatalyst	2 ^o (Deg.)	FWHM (Deg.)	hkl	Rwp (%)	FoM	D _{XRD} (nm)
CP	25.43	0.7071	(011)	10.5	0.844373	10
	38.01	1.3494	(004)			
	48.14	0.8357	(020)			
	54.09	0.8812	(015)			
	55.12	0.8739	(121)			
	62.74	1.1132	(024)			
	68.95	0.6325	(116)			
	70.31	1.0914	(220)			
	75.15	1.1803	(125)			
GF1	25.34	1.1605	(011)	9.7	0.776160	6
	37.98	1.3613	(004)			
	47.99	1.2898	(020)			
	54.49	1.9264	(015)			
	62.73	1.4698	(024)			
	68.94	2.7879	(116)			
	70.22	1.1219	(220)			
	75.26	1.8436	(125)			

Table 3.1. (continued). Average crystallite size of chemically and greenly synthesized TiO₂ (anatase phase)

Photocatalyst	2 ^θ (Deg.)	FWHM (Deg.)	hkl	Rwp (%)	FoM	D _{XRD} (nm)
GF2	25.33	1.3346	(011)	6.1	0.760335	5.24
	37.95	1.5004	(004)			
	48	1.3484	(020)			
	54.28	2.0595	(015)			
	62.74	1.5718	(024)			
	69.54	2.8932	(116)			
	75.2	2.014	(125)			
GF3	25.34	1.1719	(011)	9.1	0.804895	5.67
	37.92	1.4796	(004)			
	48.02	1.2921	(020)			
	54.12	2.1081	(015)			
	62.68	1.5679	(024)			
	68.95	2.398	(116)			
	75.07	1.605	(125)			
GS1	25.35	1.3063	(011)	11.5	0.771347	5.32
	37.93	1.8735	(004)			
	48.04	1.4672	(020)			
	54.41	1.9376	(015)			
	62.69	1.543	(024)			
	69.25	1.9877	(116)			
	75.27	1.9556	(125)			
GS2	25.34	1.3187	(011)	3.8	0.763158	5.23
	37.94	1.4603	(004)			
	47.97	1.3936	(020)			
	54.27	1.8176	(015)			
	62.68	1.8670	(024)			
	69.54	2.7382	(116)			
	75.23	1.9752	(220)			
GS3	25.32	1.1298	(011)	4.4	0.788275	5.67
	37.88	1.4594	(004)			
	48.01	1.2024	(020)			
	54.25	1.922	(015)			
	62.7	1.4	(024)			
	68.87	2.9105	(116)			
	75.18	2.0352	(125)			

3.1.2 FTIR analysis

The FTIR analysis for the CP, GF1, GF2, GF3, GS1, GS2, and GS3 photocatalysts is shown in Figure 3.2. The chemical compositions (i.e., chemical bonds) of these photocatalysts were assigned by the peaks that appeared in the FTIR spectra (Figure 3.2) based on the data of transmittance (%) versus wavenumber (cm⁻¹) and then these peaks were identified using the software of KnowltAll Informatics

System 2024. Further detail information about these compounds and their wavenumbers can be found in Appendix 1.

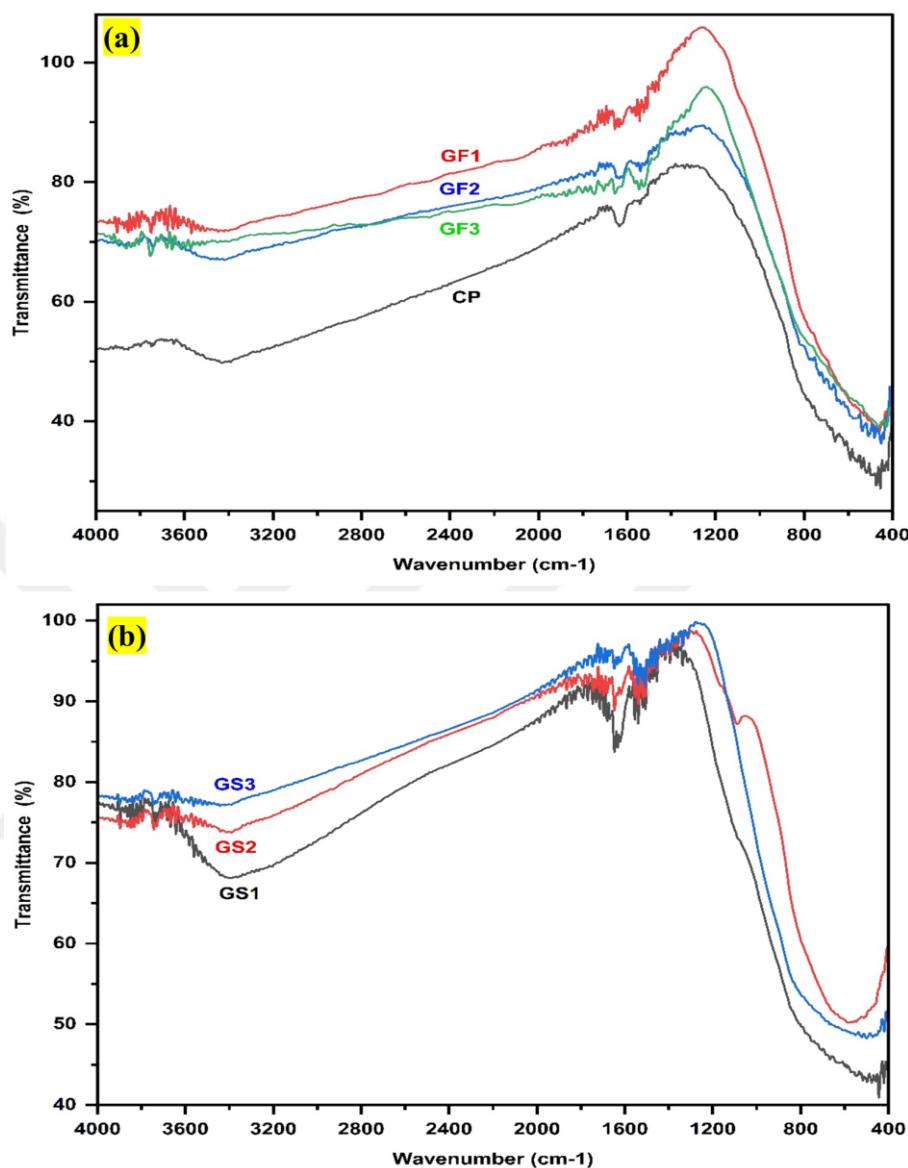


Figure 3.2. FTIR spectra of synthesized TiO₂ photocatalysts: (a) CP, GF1, GF2, GF3 and (b) GS1, GS2, GS3

3.1.3 FE-SEM analysis

The FE-SEM images for the CP, GF1, GF2, GF3, GS1, GS2, and GS3 photocatalyst are shown in Figure 3.3. For the CP photocatalyst, the FE-SEM image shown in Figure 3.3 (a) reveals that the surface morphology of TiO₂ particles was generally spherical in shape with a slight agglomeration to some extent. This slight agglomeration was significantly increased when compared with the GF1, GF2, GF3, GS1, GS2, and GS3 photocatalysts as shown in Figure 3.3 (b-g).

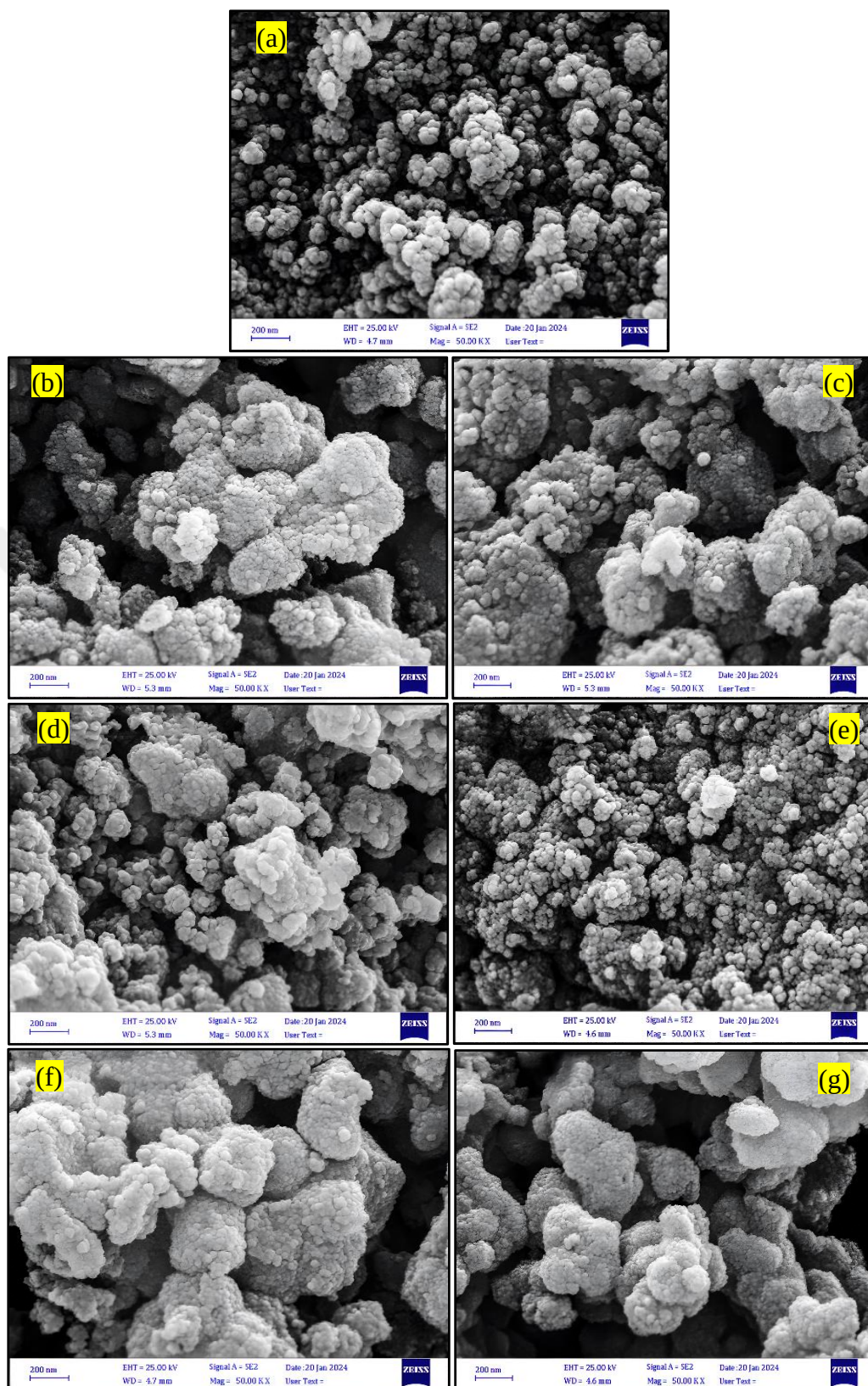
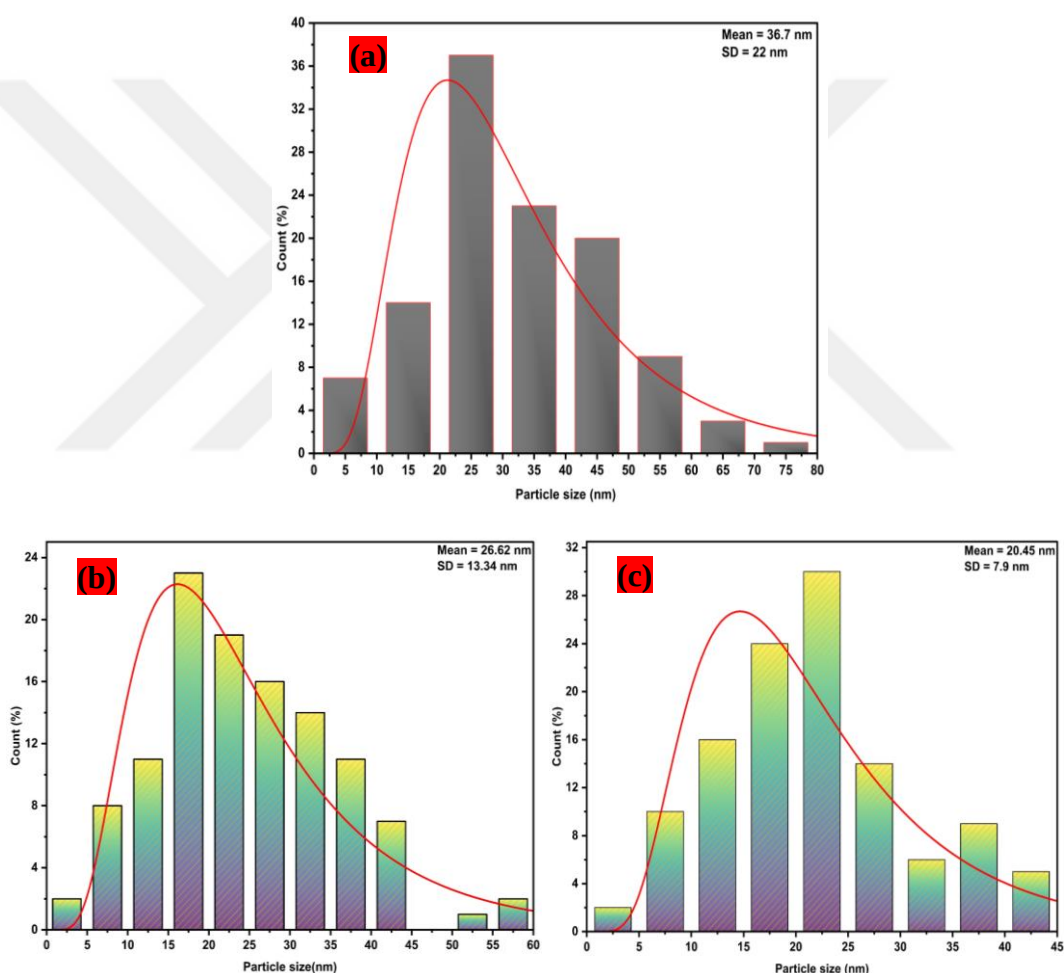


Figure 3.3. FE-SEM spectra of synthesized TiO_2 photocatalysts: (a) CP, (b) GF1, (c) GF2, (d) GF3, (e) GS1, (f) GS2 and (g) GS3

The mean particle size of these synthesized TiO₂ photocatalysts was investigated using equation (2.4) and shown as a distribution histogram in Figure 3.4. This investigation Figure 3.4 showed that the mean particle sizes of synthesized TiO₂ photocatalysts were 36.70 ± 22.00 nm for CP, 26.62 ± 13.34 nm for GF1, 20.45 ± 7.90 nm for GF2, 23.87 ± 11.40 nm for GF3, 18.74 ± 7.00 nm for GS1, 13.20 ± 4.42 nm for GS2, and 25.16 ± 12.33 nm for GS3. An important point to note from these results is that the mean particle sizes for the greenly synthesized TiO₂ photocatalysts were lower than the chemically synthesized TiO₂ photocatalyst (CP).



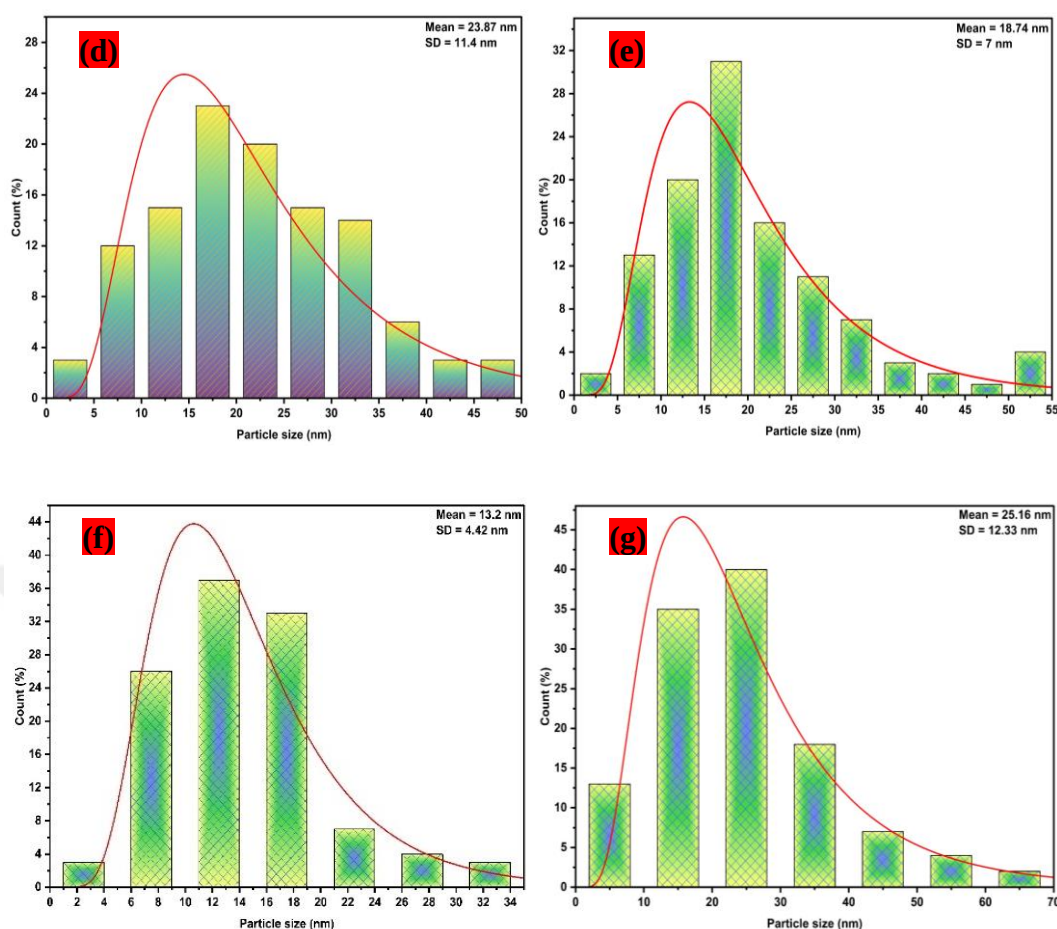


Figure 3.4. FE-SEM distribution histograms of synthesized TiO₂ photocatalysts: (a) CP, (b) GF1, (c) GF2, (d) GF3, (e) GS1, (f) GS2 and (g) GS3

3.1.4 EDX analysis

The EDX analysis was used to investigate the chemical compositions for the CP, GF1, GF2, GF3, GS1, GS2, and GS3 photocatalysts and their results are shown in Figure 3.5. This analysis in Figure 3.5 (a) shows that the titanium (Ti) and oxygen (O) were predominant when compared with other elements (potassium (K) and silicon (Si)) as impurities. The weight percentages of Ti and O were 89.4 and 10.4%, respectively.

The EDX analysis in Table 3.2 presents the chemical compositions of the extracts of MJGTF and MJGTS. These extracts were used to greenly synthesize the TiO₂ photocatalyst. The EDX spectra in Figure 3.5 (b-g) show that the elements of Ti and O were present in the greenly synthesized TiO₂ photocatalysts (GF1, GF2, GF3, GS1, GS2 and GS3). The weight percentages of these elements were less than

that of the chemically synthesized TiO₂ photocatalyst (CP). Appendix 2 show more details about the mapping line of the elements.

Table 3.2. EDX analysis for the chemical compositions of the MJGTF and MJGTS extracts

Element	MJGTF (wt%)	MJGTS (wt%)
C	65.65	64.66
N	0.92	0.00
O	27.99	31.13
Mg	0.25	0.29
Al	0.12	0.34
Si	0.00	0.07
P	0.56	0.33
S	0.47	0.39
K	3.59	1.66
Ca	0.44	1.14
Total	100.00	100.00

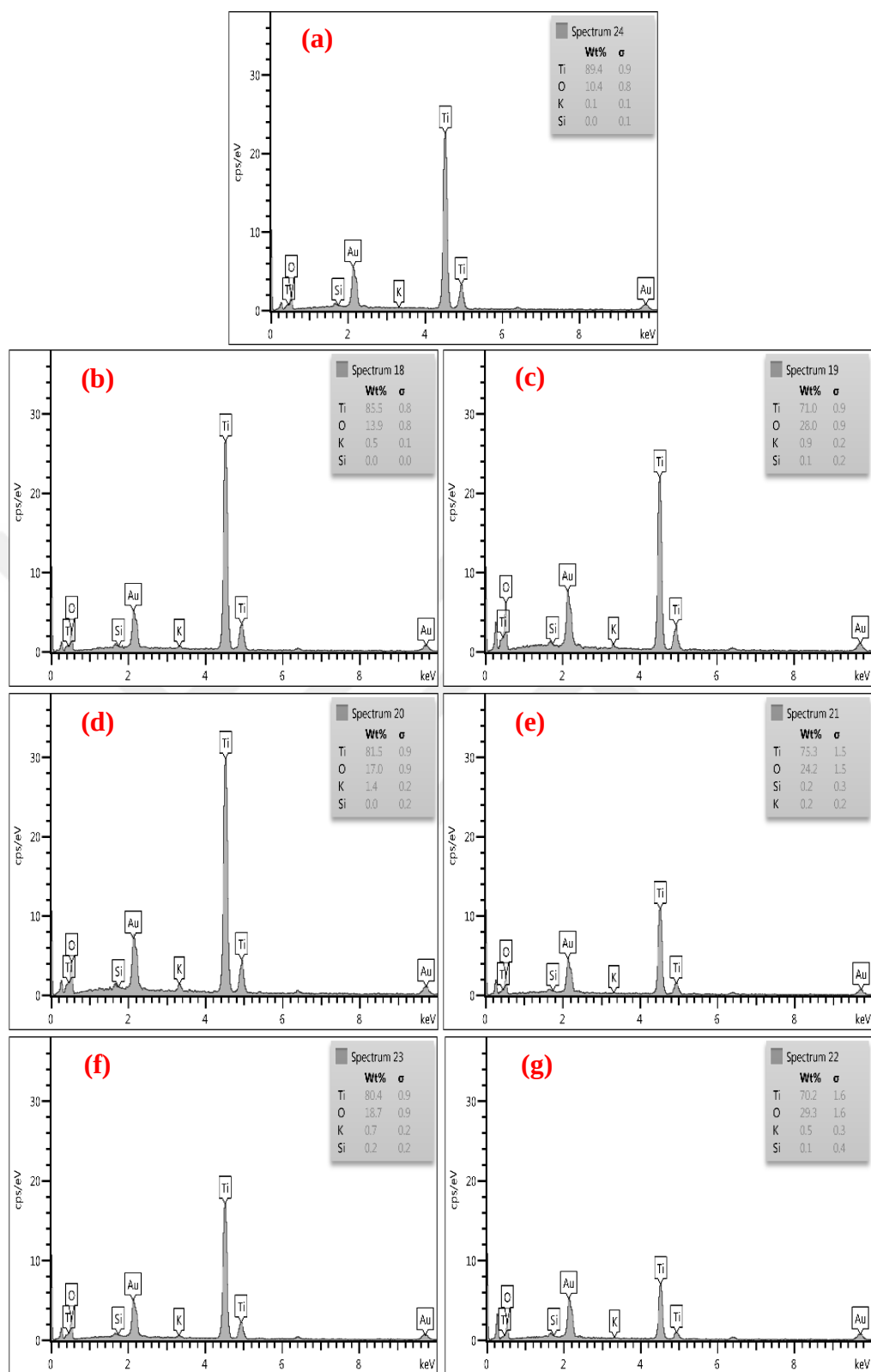


Figure 3.5. EDX spectra of synthesized TiO_2 photocatalysts: (a) CP, (b) GF1, (c) GF2, (d) GF3, (e) GS1, (f) GS2 and (g) GS3

3.1.5 AFM analysis

The AFM analysis was used to characterize the surface topography and roughness for the CP, GF1, GF2, GF3, GS1, GS2, and GS3 photocatalysts. The surface topography of these photocatalysts in terms of the surface skewness (Ssk), coefficient of kurtosis (Sku), arithmetic mean height (Sa) and maximum height (Sz) as well as the surface roughness of these photocatalysts with respect to the root-mean square roughness (Sq) were quantitatively identified by the used software. The three-dimensional (3D) topography micrographs from the AFM analysis are shown in Figure 3.6. These 3D visualizations in Figure 3.6 show the uneven surface morphology between chemically photocatalyst (CP) and greenly photocatalysts (GF1, GF2, GF3, GS1, GS2, and GS3). The presence of topography in terms of hills, valleys and ridges as well as the roughness of the surface is clearly observed in greenly photocatalysts (Figure 3.6 (b-g)) compared with the chemically photocatalyst (Figure 3.6 (a)).

The experimental results of the surface topography and roughness of these 3D visualizations shown in Figure 3.6 are presented in numeric values in Table 3.3. As shown in this Table the surface roughness of synthesized TiO₂ photocatalysts based on the Sq value was 2.3 nm for CP, 9.3 nm for GF1, 3.15 nm for GF2, 3.06 nm for GF3, 5.45 nm for GS1, 36.7 nm for GS2, and 101.2 nm for GS3.

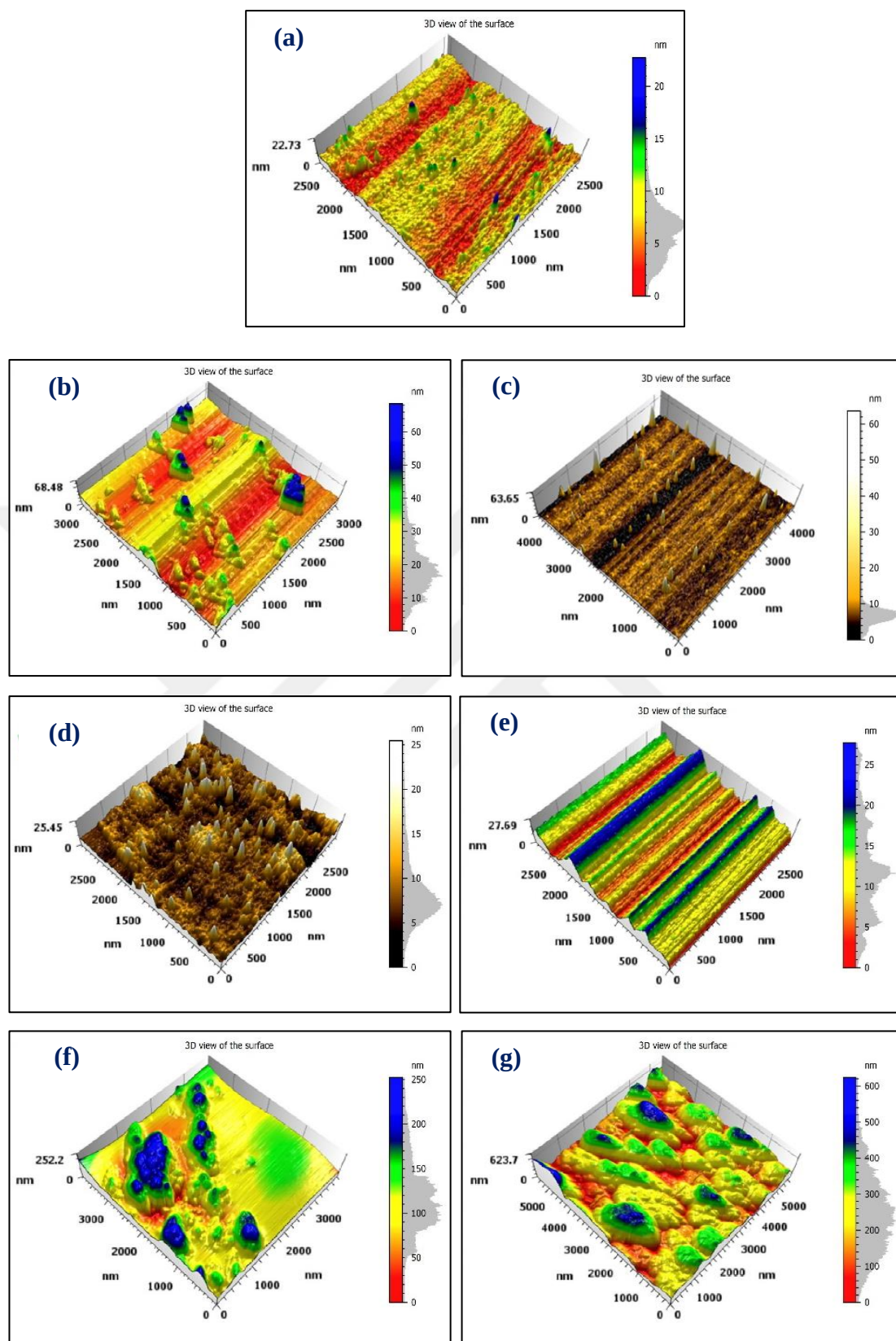


Figure 3.6. AFM spectra of synthesized TiO_2 photocatalysts: (a) CP, (b) GF1, (c) GF2, (d) GF3, (e) GS1, (f) GS2 and (g) GS3

Table 3.3. The AFM analysis of surface topography and roughness

Parameters	CP	GF1	GF2	GF3	GS1	GS2	GS3
Sq (nm)	2.31	9.33	3.15	3.06	5.45	36.74	101.2
Sz (nm)	22.73	68.48	63.65	25.45	27.69	252.2	623.7
Sa (nm)	1.81	6.87	1.88	2.23	4.28	28.36	81.88
Ssk	0.52	1.32	5.67	1.30	0.47	0.62	0.30
Sku	4.79	5.73	61.22	5.77	2.91	3.58	2.77

3.1.6 BET analysis

The BET analysis was used to characterize the textural characteristics in terms of specific surface area, average pore size and pore volume for the CP, GF1, GF2, GF3, GS1, GS2, and GS3 photocatalysts. The characteristic plot of the N₂ adsorption-desorption isotherm and pore distribution curves of these synthesized photocatalysts are shown in Figure 3.7. These photocatalysts exhibited the isotherm of a type III with a hysteresis loop of H3 in shape according to the IUPAC classification (Sing et al., 1985; Thommes et al., 2015).

The results of BET specific surface area (S_{BET}), BJH average pore size (dp) and pore volume (V_p) calculated from BET analysis (Figure 3.7) are summarized in Table 3.4 . For the CP photocatalyst, Table 3.4 , the S_{BET} was found to be 13.78 m²/g. It is obvious to see from Table 3.4 that this S_{BET} was greatly increased in comparison with the GF1, GF2, GF3, GS1, GS2 and GS3 photocatalysts. The percentage increases in the S_{BET} were found to be 125% for GF1, 151% for GF2, 129% for GF3, 156% for GS1, 204% for GS2 and 127% for GS3 when compared with the CP photocatalyst. As shown in Table 3.4, the BJH average pore sizes for the these greenly photocatalysts recorded in the range (1.66-2.14 nm) were lower than the CP photocatalyst. The pore volumes of for these greenly photocatalysts recorded in the range (2.75-3.64 cm³/g) were higher than the CP photocatalyst.

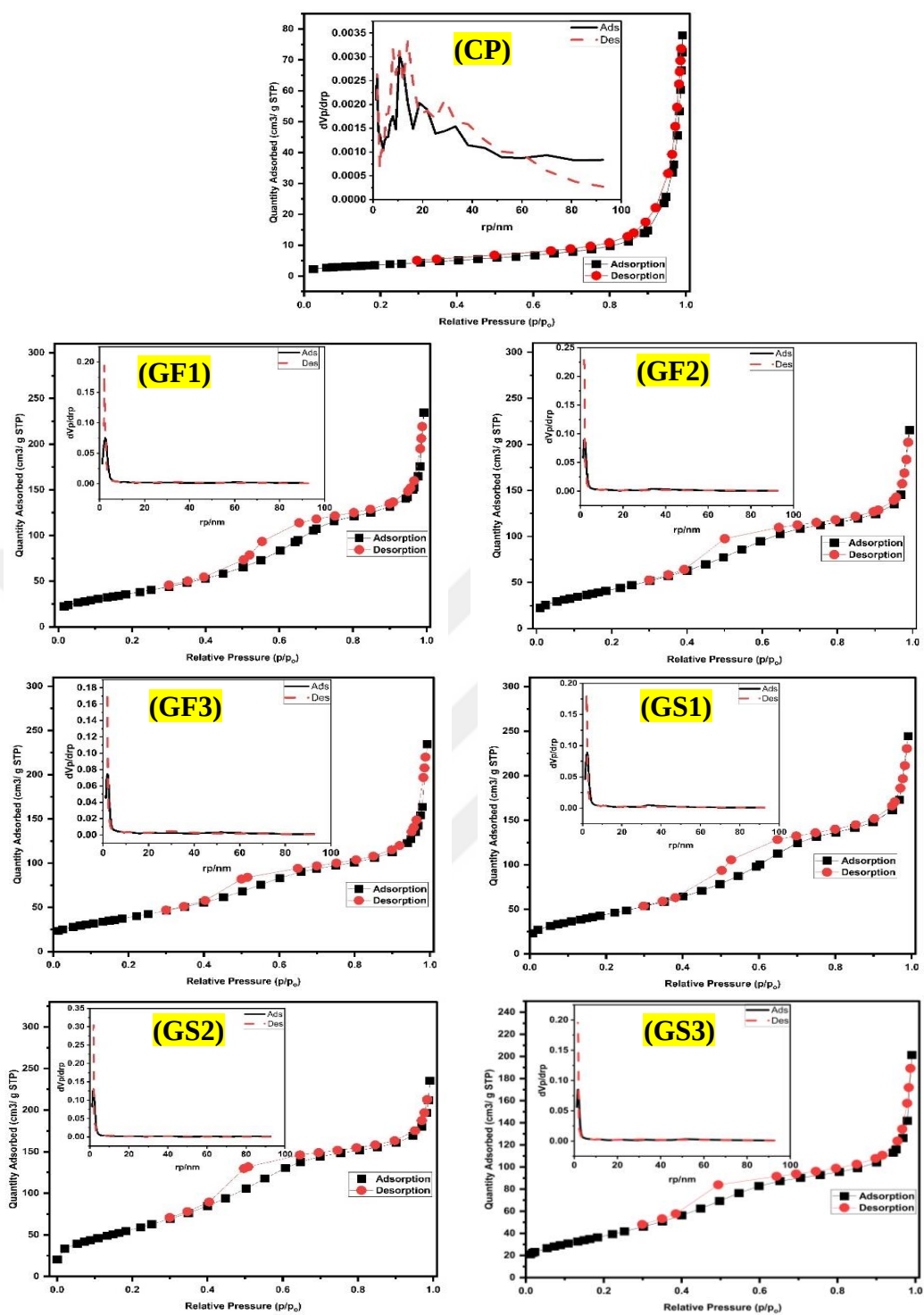


Figure 3.7. BET analysis of synthesized TiO_2 photocatalysts

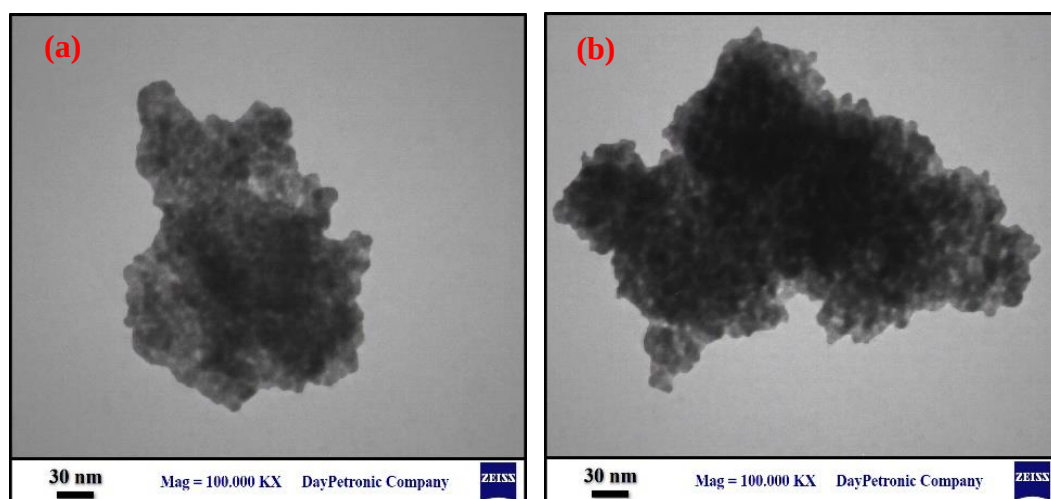
Table 3.4. The BET analysis of chemically and greenly synthesized TiO₂ photocatalysts

Photocatalyst	S _{BET} (m ² /g)	d _p (nm)	V _p (cm ³ /g)
CP	13.78	14.03	0.1179
GF1	139.00	2.14	0.347
GF2	164.44	1.66	0.301
GF3	142.53	1.88	0.327
GS1	169.92	1.66	0.364
GS2	217.66	1.88	0.320
GS3	140.78	1.66	0.275

3.2 Further characterization of greenly synthesized TiO₂ (GF2 vs. GS2)

3.2.1 TEM analysis

The TEM analysis was carried out to further characterize the internal morphological and structural details in terms of the particle size and shape for the GF2 and GS2 photocatalysts. The TEM analysis for these photocatalysts is shown in Figure 3.8 (a, b). The distribution histograms of the average particle sizes of the GF2 and GS2 photocatalysts are shown in Figure 3.8 (c, d). The average particle sizes of these photocatalysts calculated from the TEM analysis were found to be 7.33 ± 3.26 nm for GF2 and 5.38 ± 1.83 nm for GS2.



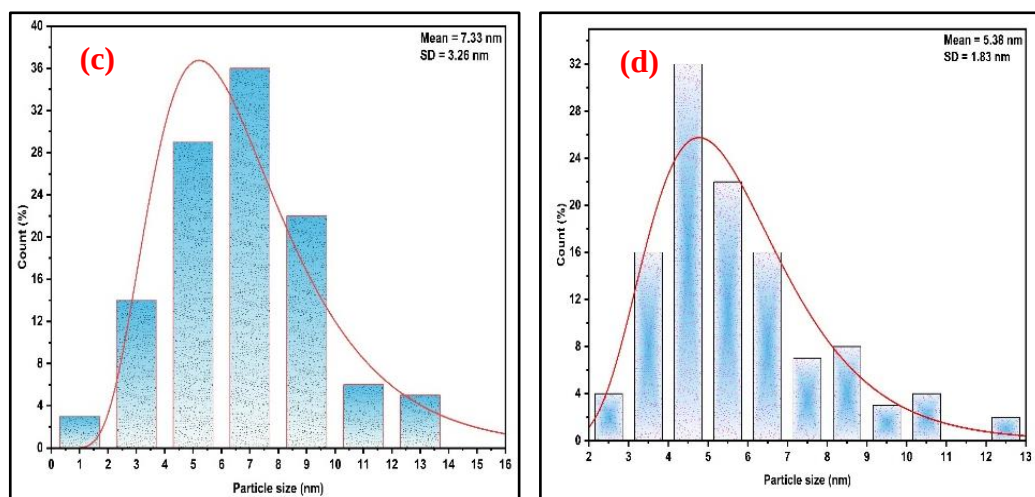


Figure 3.8. TEM images of greenly synthesized TiO₂ photocatalysts: (a) GF2, (b) GS2 and TEM distribution histograms of the average particle sizes: (c) GF2, (d) GS2

3.2.2 TGA analysis

The TGA analysis was performed to investigate the thermal stability of the GF2 and GS2 photocatalysts based on the weight loss as a function of the temperature, as shown in Figure 3.9. The TGA thermograms in Figure 3.9 reveal that three stages of thermal degradation were identified.

For the GF2 photocatalyst, Figure 3.9 (a), the percentages of weight loss were found to be 3.45% for the first stage (temperature range 25-119 °C), 2.37% for the second stage (temperature range 119-366 °C), 1.00% for the third stage (temperature range 366-605 °C).

For the GS2 photocatalyst, Figure 3.9 (b), the percentages of weight loss were found to be 4.01% for the first stage (temperature range 25-96 °C), 1.78% for the second stage (temperature range 96-370 °C), 0.83% for the third stage (temperature range 370-605 °C). Generally, a similar trend of thermal degradation for both photocatalysts was observed in Figure 3.9.

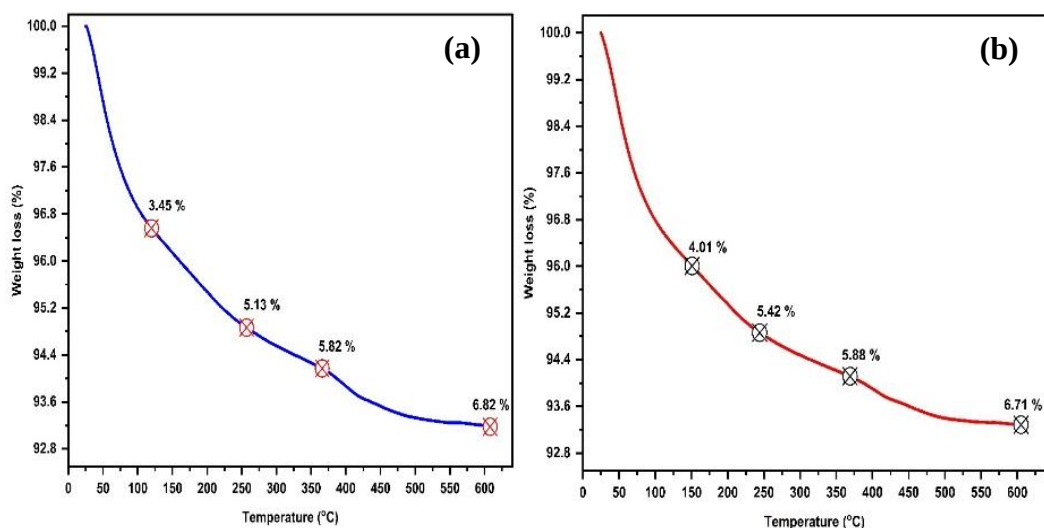


Figure 3.9. TGA analysis of greenly synthesized TiO₂ photocatalysts: (a) GF2 and (b) GS2

3.2.3 Optical analysis

The optical analysis was used for identifying the optical properties in terms of the wavelength and optical bandgap energy (E_g) for the GF2 and GS2 photocatalysts. This analysis for these photocatalysts is shown in Figure 3.10. The wavelengths of the GF2 and GS2 photocatalysts in Figure 3.10 (a, c) were found to be 443 and 494 nm, respectively. The E_g value for GF2 and GS2 identified from the Tauc's plots in Figure 3.10 (b, d) was found to be 1.55 eV. The results of wavelength for GF2 and GS2 shown in Figure 3.10 (a, c) state that the wavelength of these photocatalysts shifted from the UV light-blue region (< 400 nm) to the visible light-red region (> 400 nm). These are valuable results for the modification of the optical properties of greenly synthesized TiO₂ photocatalysts.

It is interesting to compare these results by green synthesis of TiO₂ with that of chemical synthesis of TiO₂. Therefore, further optical analysis was performed on the chemically synthesized TiO₂ as a control photocatalyst (CP) and shown in Appendix 3. It was found that the wavelength and E_g for CP were 333 nm and 2.66 eV, respectively.

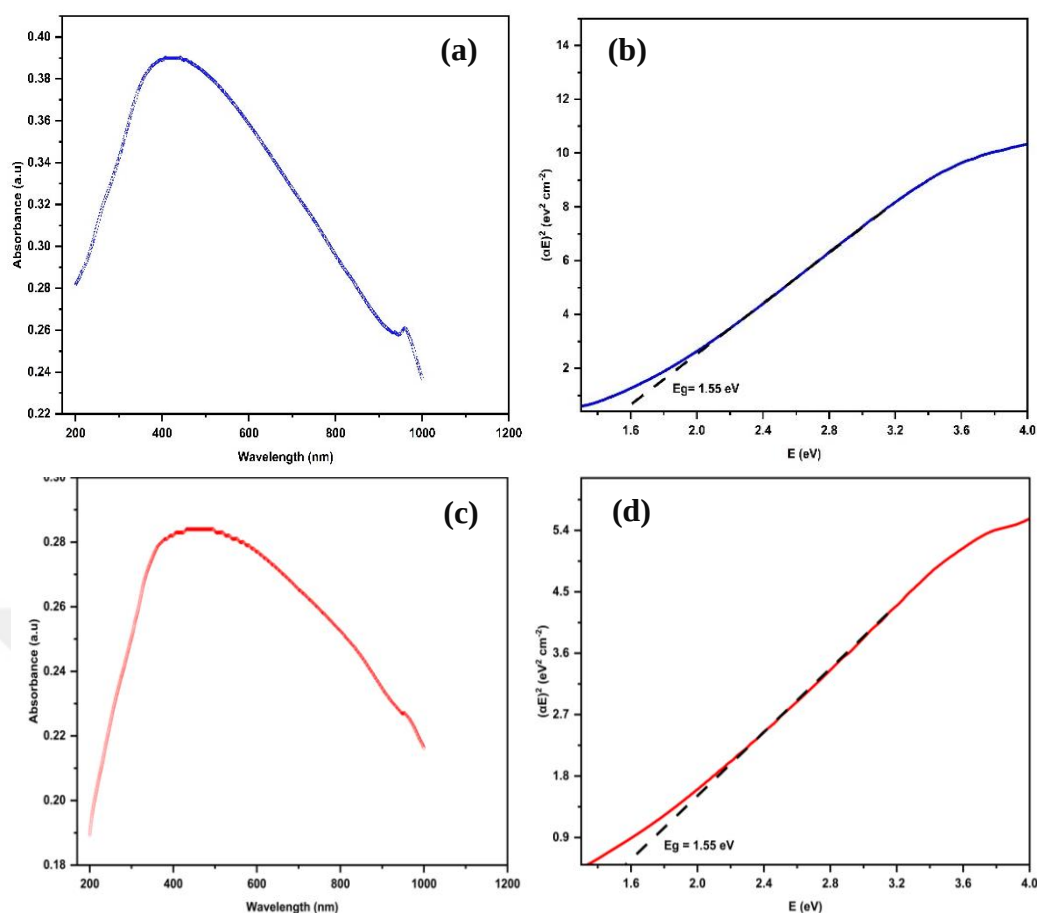


Figure 3.10. Optical analysis of greenly synthesized TiO₂ photocatalysts: (a) GF2 and (b) GS2

3.3 Degradation of MB

3.3.1 Photolysis

To ensure a fair comparison between the photocatalytic performances of the chemical and greenly synthesized TiO₂ photocatalysts, it was crucial to minimize the contribution of direct photolysis to the overall degradation process. To achieve this, a series of photolysis experiments were conducted after a 30-minute adsorption-desorption equilibrium period. Various initial MB concentrations (5, 10, 15, and 20 mg/L) were tested under 120 minutes of UV irradiation. The results indicated that the extent of photolytic degradation decreased with increasing initial MB concentration. Specifically, 40%, 19%, 9%, and 2% degradation was observed for the 5, 10, 15, and 20 mg/L concentrations, respectively, after 120 minutes of photolysis.

3.3.2 Photocatalysis

3.3.2.1 Photocatalytic degradation of MB by synthesized TiO_2 (chemical vs. green)

Various doses of applied photocatalysts from 200 to 450 mg/L were investigated as a function of the D% of MB versus the photocatalytic time of 120 min to find the optimum dose of each applied photocatalyst.

For the chemically synthesized TiO_2 photocatalyst (CP), Figure 3.11 shows that the D% of MB increased from 9 to 22% with increasing the doses of CP from 200 to 350 mg/L. Higher doses of 400 and 450 mg/L showed a decrease in the D% of MB to be 14 and 11%, respectively. Therefore, the dose of 350 mg/L is the optimum dose for the CP photocatalyst.

For the greenly synthesized TiO_2 photocatalysts (GF2 and GS2), Figure 3.12 and Figure 3.13 demonstrate that increasing the photocatalyst dose from 50 to 125 mg/L resulted in a corresponding increase in MB degradation efficiency. However, further increasing the dose to 150 mg/L led to a decrease in degradation efficiency. The optimal photocatalytic degradation was observed at a photocatalyst dose of 125 mg/L for both GF2 and GS2, achieving 90% and 98% MB degradation, respectively.

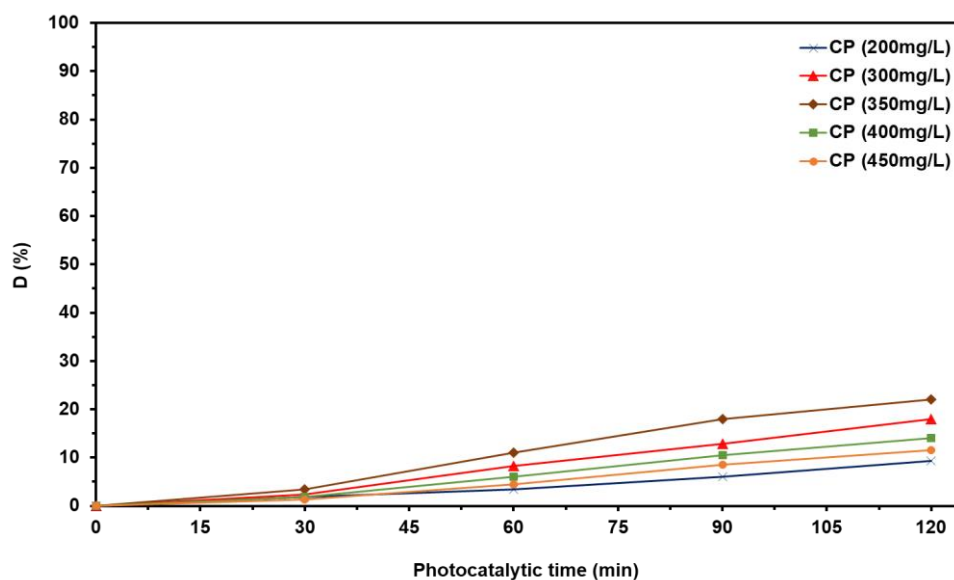


Figure 3.11. Effect of various doses of the synthesized CP photocatalyst on the D (%) of MB

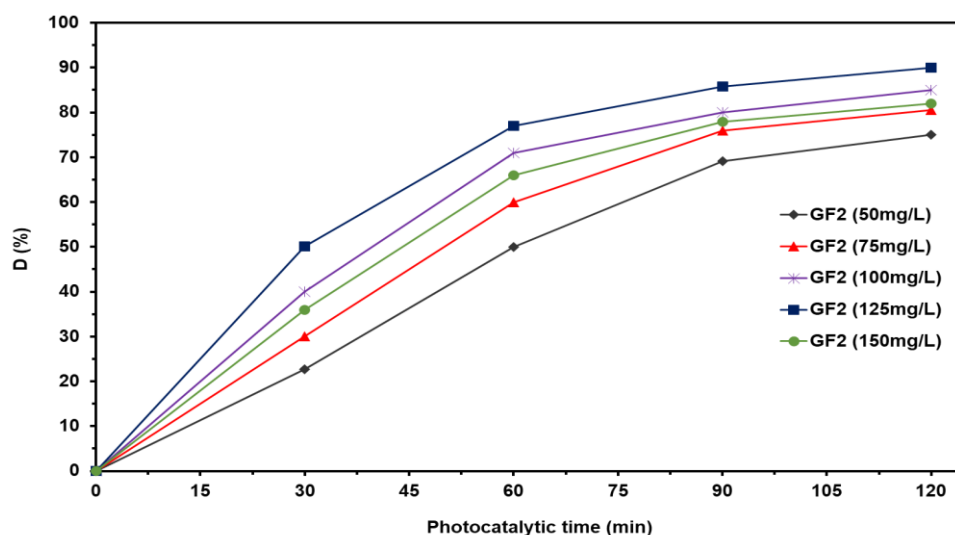


Figure 3.12. Effect of various doses of the synthesized GF2 photocatalyst on the D (%) of MB

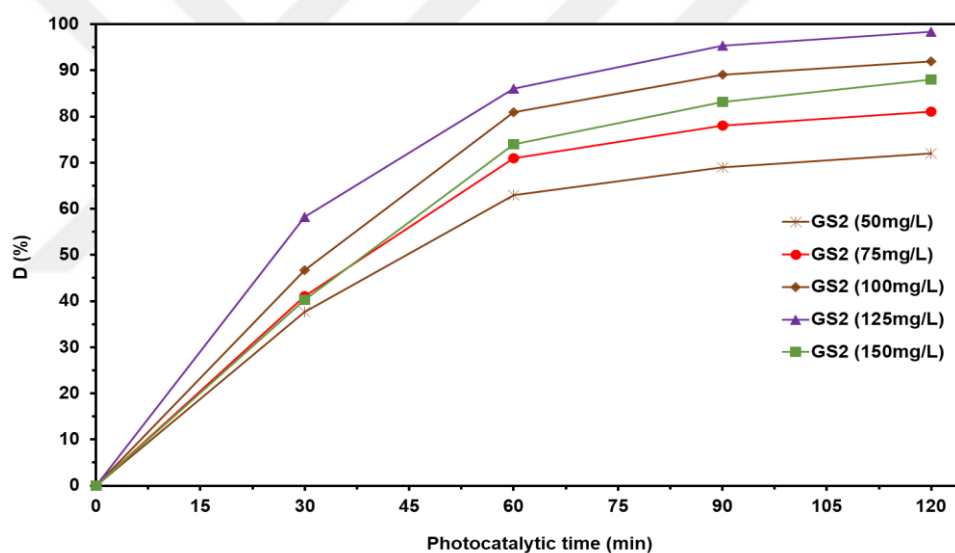


Figure 3.13. Effect of various doses of the synthesized GS2 photocatalyst on the D (%) of MB

3.3.2.2 Photocatalytic mineralization of MB by synthesized TiO₂ (chemical vs. green)

The degree of photocatalytic mineralization expressed by the TOC removal using CP, GF2 and GS2 photocatalysts at their optimum photocatalytic doses over the photocatalytic time of 120 min was investigated with respect to the pH and DO monitoring parameters.

For the chemically synthesized TiO₂ photocatalyst (CP), Figure 3.14 shows that the TOC removal was found to be 21% at 120 min.

For the greenly synthesized TiO_2 photocatalysts (GF2 and GS2), Figure 3.15 and Figure 3.16 shows that the TOC removal at the end of photocatalytic time was found to be 88% for GF2 and 97% for GS2. Figure 3.17 shwos the color change of the CP, GF2, and GS2 was monitored at their optimum photocatalytic doses of photocatalytic degradation.

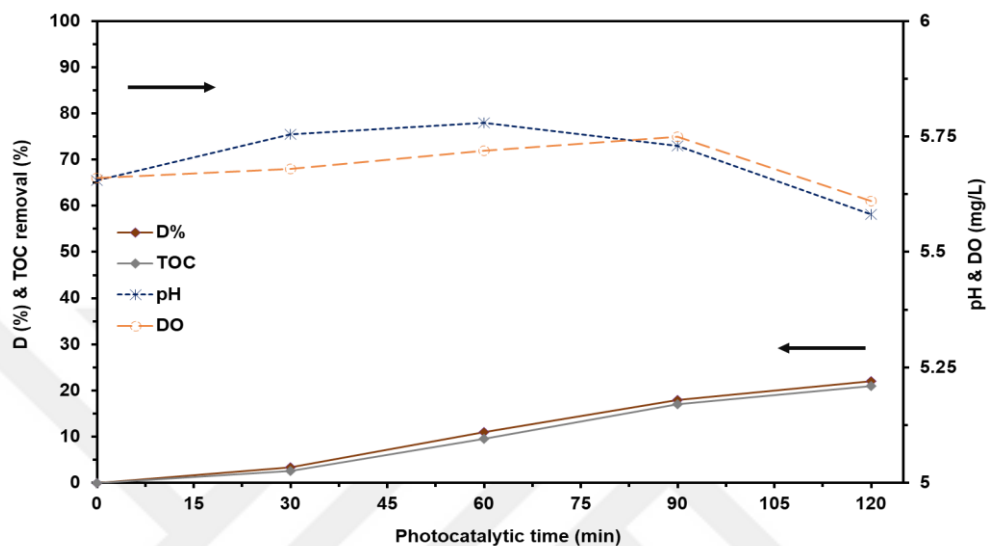


Figure 3.14. Effect of synthesized TiO_2 photocatalysts at their optimum photocatalytic doses on the D% of MB and TOC removal (%) with respect to photocatalytic time, and pH and DO monitoring parameters of CP

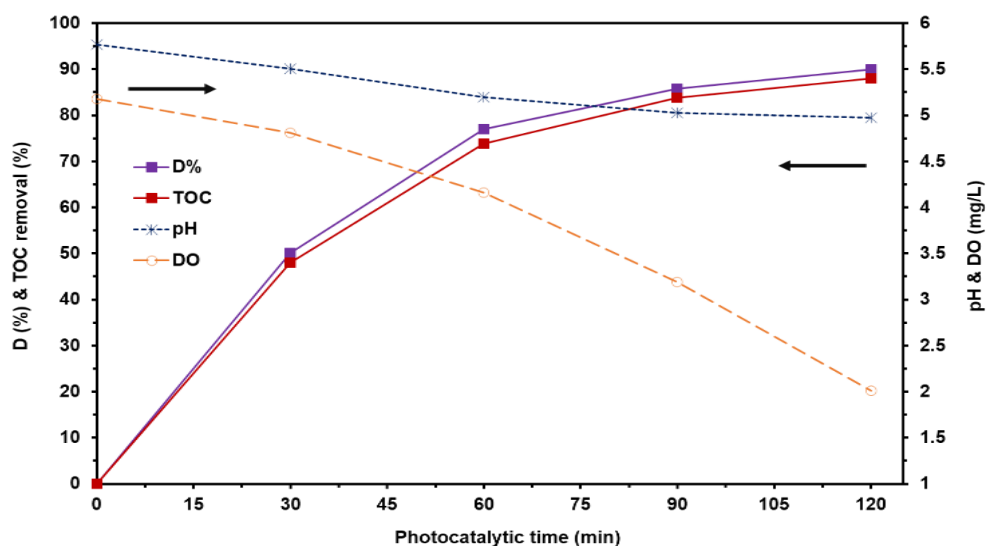


Figure 3.15. Effect of synthesized TiO_2 photocatalysts at their optimum photocatalytic doses on the D% of MB and TOC removal (%) with respect to photocatalytic time, and pH and DO monitoring parameters of GF2

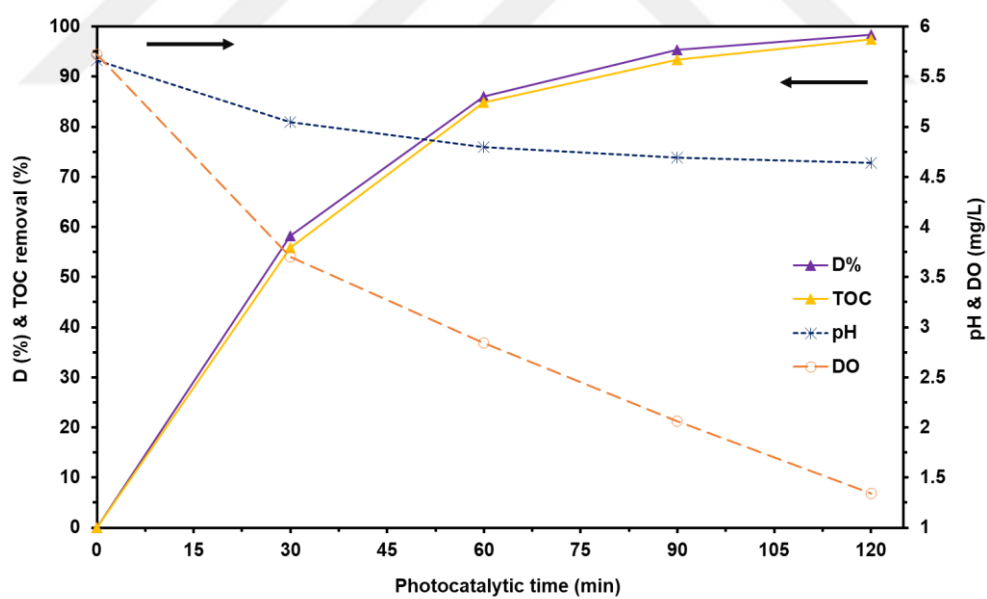


Figure 3.16. Effect of synthesized TiO_2 photocatalysts at their optimum photocatalytic doses on the D% of MB and TOC removal (%) with respect to photocatalytic time, and pH and DO monitoring parameters of GS2

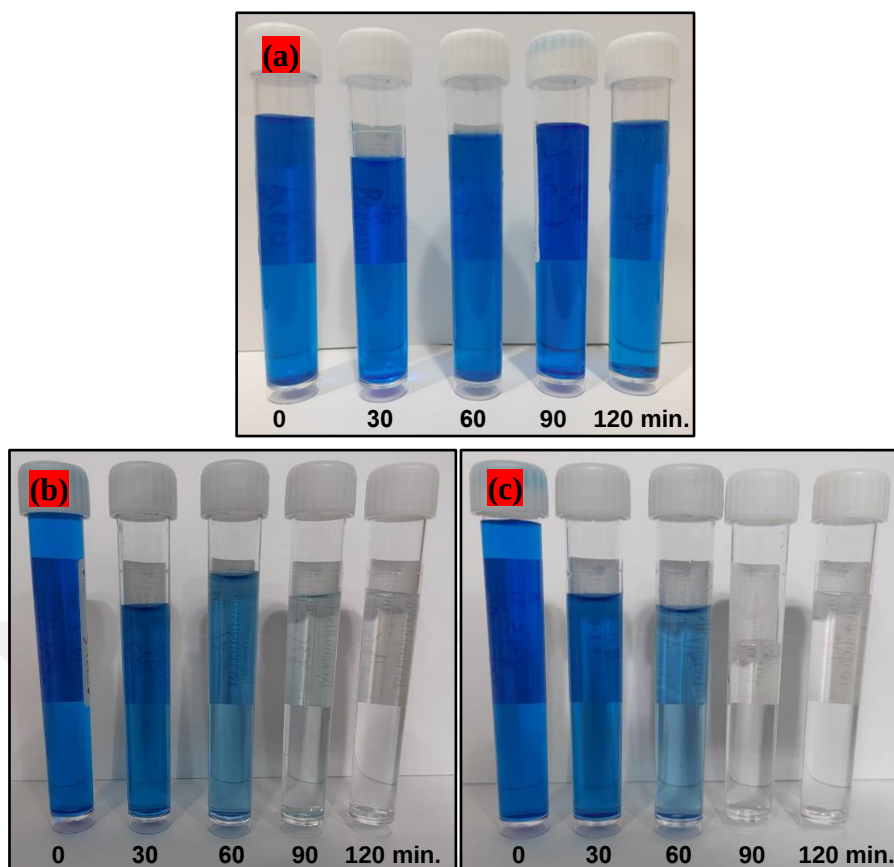


Figure 3.17. Change in color of MB aqueous solution using synthesized TiO_2 photocatalysts at their optimum photocatalytic doses: (a) CP, (b) GF2 and (c) GS2

3.3.2.3 Further evaluation of synthesized TiO_2 photocatalyst (benchmark vs. green)

To establish a benchmark for comparison, the performance of the greenly synthesized TiO_2 photocatalysts (GF2 and GS2) was compared to a commercially available TiO_2 photocatalyst (Degussa P-25, or BM). A range of BM photocatalyst doses (150-450 mg/L) were investigated in Figure 3.18 to determine the optimal dose for maximizing MB degradation. It was found that a dose of 300 mg/L yielded the highest degradation efficiency (30% D%) after 120 minutes of photocatalytic reaction. At this optimal dose, Figure 3.19, the BM photocatalyst achieved 29% mineralization of MB, accompanied by a 3% decrease in pH and a 6% reduction in dissolved oxygen (DO). Figure 3.20 also shows the monitored color change of BM.

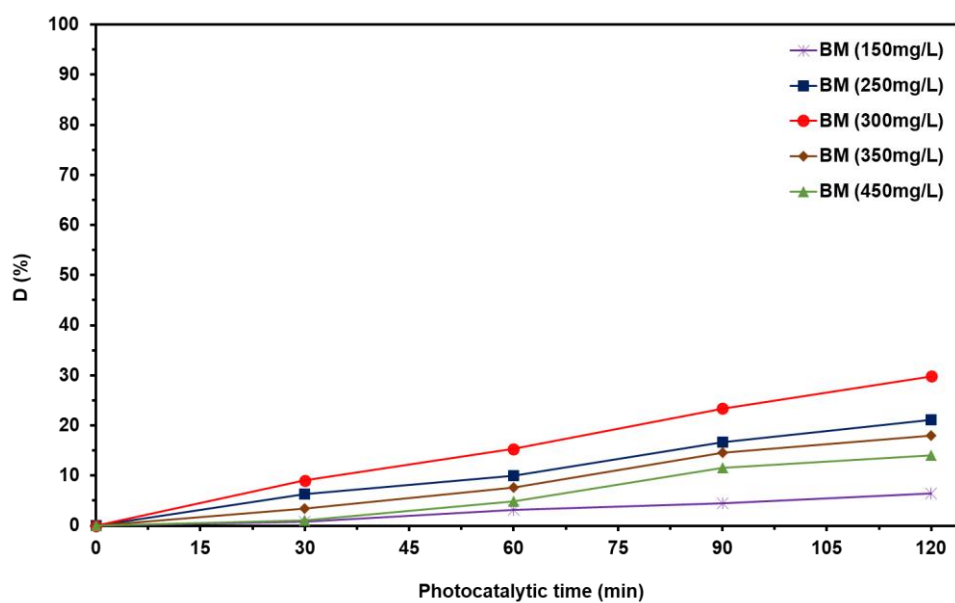


Figure 3.18. A commercial photocatalyst TiO_2 (BM): investigation of the optimum dose

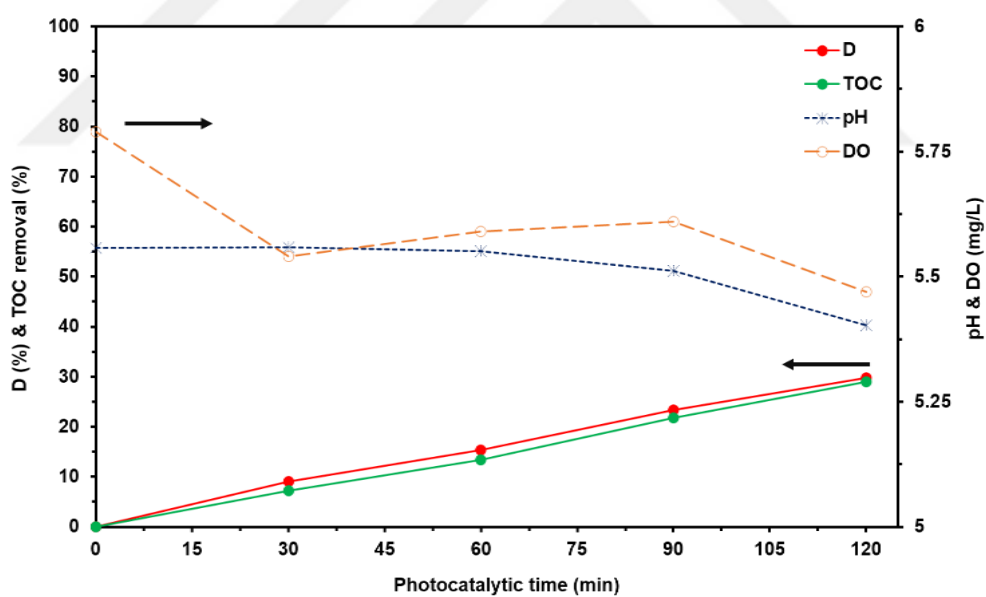


Figure 3.19. Commercial photocatalyst TiO_2 (BM): TOC removal (%) of MB, pH and DO monitoring

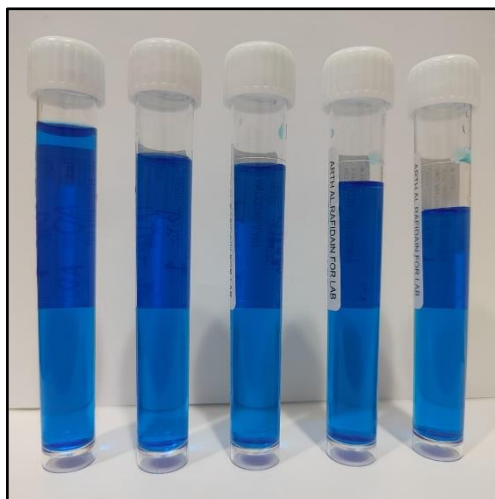


Figure 3.20. Commercial photocatalyst TiO_2 (BM) color change monitoring

4. DISCUSSION

4.1 Characterization of synthesized TiO₂ (chemically vs. greenly)

4.1.1 XRD analysis

The XRD analysis showed the anatase phase of chemically and greenly synthesized TiO₂ and a reduced crystallite size of GF1, GF2, GF3, GS1, GS2, and GS3 compared with CP photocatalyst. This is the same result of studies as found by (Helmy et al., 2021) on *Malva parviflora* plant extract and (Eddy et al., 2024) on various extract plants. The possible mechanism was explained by Saikumarai et al., (Saikumari et al., 2019) who showed that the reduction of crystallite sizes of greenly synthesized TiO₂ with green tea extract by 16.4% when compared with that of chemically synthesized TiO₂ is related to the presence of polyphenols as active components in green tea extract that played a significant role in chelating, stabilizing, capping and reducing agents of titanium ions, and thus controlling the crystallite size of green synthesis of TiO₂.

The effect of added weights from 1 to 3 g for each MJGTF and MJGTS as extracts on the crystallite sizes of the greenly synthesized TiO₂ photocatalysts (GF1, GF2, GF3 and GS1, GS2, GS3) is shown in Table 3.1. As observed in Table 3.1, the added weight of MJGTF increased from 1 to 2 g, the crystallite sizes of GF1 (6 nm) and GS1 (5.32 nm) photocatalysts decreased to 5.24 nm at GF2 and 5.23 nm at GS2. Further increase in the added weight to 3 g led to increase the crystallite sizes of GF3 and GS3 photocatalysts to be 5.67 nm, respectively. Thus, at 2 g of MJGTF and MJGTS extracts, the crystallite sizes of GF2 and GS2 photocatalysts were found to be minimum. This general trend of data is similar to that observed by Nguyen et al., (C. H. Nguyen et al., 2018) who studied the effect of various contents of Pd in the range from 0.25 to 1 wt% on the crystal size of chemically synthesized Pd-TiO₂ photocatalyst. The experimental results indicated that the crystal size decreased with increasing the Pd content to become minimum at a critical Pd content. After this Pd critical, the crystal size increased due to the reduction of either particle nucleation during hydrolysis and condensation steps in the sol-gel synthesis of Pd-TiO₂ or grain boundaries during the sintering process.

4.1.2 FTIR analysis

The identified peaks as chemical bonds by The FTIR analysis were compared with the KnowltAll Informatics System 2024 and published literature (Agus et al., 2017; Albaidani et al., 2023; Chougala et al., 2017; Hui & Chao, 2006; Magdalane et al., 2019).

For the CP photocatalyst, the FTIR spectrum in Figure 3.2 (a) shows that the peak identified at the wavenumbers of 455.20 cm^{-1} is attributed to the Ti-O bond. The peaks identified at the wavenumbers of 540.07 and 659.66 cm^{-1} are related to the Ti-O-Ti bond. Generally, these identified peaks are usually found by the FTIR spectra in the range $400\text{--}800\text{ cm}^{-1}$ for the chemical synthesis of TiO_2 photocatalyst as reported in the literature (Kumaravel et al., 2023; Verma et al., 2016). The other peaks identified at the wavenumbers of 3406.29 , 1543.05 and 1635.64 cm^{-1} can be allocated to the characteristic bonds of hydroxyl groups (O-H), which are originated from isopropyl alcohol and water used in the chemical synthesis of TiO_2 . These identified peaks are in agreement with the literature (Agus et al., 2017; Albaidani et al., 2023; Chougala et al., 2017; Hui & Chao, 2006; Magdalane et al., 2019).

In the FTIR spectra (Figure 3.2 (a, b)), the Ti-O bonds were identified by the peaks at the wavenumbers of 424.34 cm^{-1} for GF1, 451.34 and 632.65 cm^{-1} for GF2, 424.34 and 459.06 cm^{-1} for GF3, 443.63 and 640.37 cm^{-1} for GS1, 422.41 and 619.15 cm^{-1} for GS2, and 418.55 cm^{-1} for GS3. The Ti-O-Ti bonds were identified by the peaks at the wavenumbers of 474.49 cm^{-1} for GF1, 536.21 cm^{-1} for GF2 and 580.57 cm^{-1} for GS3. The bonds of Ti-O and Ti-O-Ti obtained by the FTIR analysis are responsible for confirming the successful synthesis of TiO_2 (H. Kaur et al., 2021).

Some important compounds for the GF1, GF2, GF3, GS1, GS2 and GS3 photocatalysts such as amines, aldehydes, amides, alkenes and aromatics were identified by their bonds NH, C=O, NH, C=C and CH, respectively that correspond to their assigned wavenumber in the FTIR spectra Figure 3.2 (a, b).

4.1.3 FE-SEM analysis

The FE-SEM showed a spherical morphology with a tendency to build large agglomerates on the TiO_2 particles by using the MJGT exact was observed in Figure 3.3. These agglomerates were not evenly distributed (i.e., non-uniformity) over the

surface particles of TiO_2 due to the attractive forces between these particles and the use of different concentrations and types of MJGT extracts in the green synthesis of TiO_2 . This is the same finding as observed by Kaur et al., (H. Kaur et al., 2021) who used an aqueous leaf extract of *L. siceraria* for the green synthesis of TiO_2 photocatalyst.

The particle size results indicate that the green synthesis of TiO_2 photocatalysts played a significant role in improving (i.e., decreasing) the mean particle size. This finding is similar to that reported in the literature concerning the reduction of mean particle size by using the green synthesis of TiO_2 photocatalyst due to the interaction effect between the extract and precursor (Eddy et al., 2024). Interestingly, at 2 g of MGTF and MJGTS extracts, the mean particle sizes of the GF2 and GS2 photocatalysts were minimum. This is because the interaction effect between MJGT extract and the precursor was maximum. Further increase in the weight of their extracts at 3 g increased the mean particle sizes of the GF3 and GS3 photocatalysts. At this weight, the interaction effect between their extract and the precursor became less effective, thus increasing the mean particle sizes (Wellia et al., 2024). This result is consistent with the results obtained from the XRD analysis shown earlier at this weight of MJGTF and MJGTS extracts. As known in the literature, controlling the mean particle size of synthesized photocatalysts is vitally important for obtaining higher photocatalytic performance (Rincón Joya et al., 2019).

4.1.4 EDX analysis

The EDX finding confirms that the TiO_2 photocatalyst was successfully synthesized using chemical and green sol-gel method. It is interesting to note from these spectra in Figure 3.5 (b-g) that the K element was found in all greenly synthesized TiO_2 photocatalysts. The existence of K element in the green synthesis of TiO_2 using the leaf extract of *L. siceraria* played a significant role in capping and reducing agents as reported by Kaur et al., (H. Kaur et al., 2021) who showed that the K element is one of the minerals that represents the phytochemical compounds. While, the Si element was found in GF2, GS1, GS2 and GS3 photocatalysts where this result is in agreement with the results obtained from the FTIR analysis shown earlier. The maximum weight percentage of Si was recorded at GS2 (0.7%). In the current analysis, it is expected that the presence of K and Si together plays a

significant role in improving the specific surface area for the GF2 and GS2 photocatalysts. Therefore, further investigation is required to confirm this improvement.

4.1.5 AFM analysis

The AFM experimental results show that the S_q values of the surface topography and roughness of greenly synthesized TiO_2 photocatalysts are higher than the chemically synthesized TiO_2 photocatalyst (CP). Generally similar trends of results in terms of S_{sk} , S_{ku} , S_a and S_z were recorded for the greenly synthesized TiO_2 photocatalysts when compared with the chemically synthesized TiO_2 photocatalyst. These results confirm that the surface topography and roughness were significantly increased by the green synthesis of TiO_2 photocatalyst. It has been reported in literature that the increased surface roughness based on the values of S_q plays a significant role in increasing the adsorption of pollutants and then the overall surface area of the photocatalyst increases accordingly (A. Kumar et al., 2024). To confirm these interesting findings, the analysis of BET surface area is required to support these findings.

4.1.6 BET analysis

The BET surface area showed a large S_{BET} of greenly synthesized TiO_2 compared with chemically (CP). The findings with respect to the BJH average pore sizes and pore volumes give strong evidence that the green synthesis of TiO_2 photocatalyst at the extracts of MJGTF with GF1, GF2, GF3 and MJGTS with GS1, GS2 and GS3 using the sol-gel method was successfully effective in enhancing significantly the S_{BET} of the chemically synthesized TiO_2 as a control photocatalyst (CP). A similar observation was recorded by Nateq et al., (Nateq & Ceccato, 2019) who showed that the porosity features in terms of the pore volume with respect to the pore diameter via the BJH method participated in increasing the BET surface area of the synthesized TiO_2 photocatalyst using the reverse micelle solution. The general trend of the S_{BET} data for the green synthesis of TiO_2 photocatalyst was similar to that found in the FE-SEM analysis based on the investigation of mean particle sizes of synthesized TiO_2 photocatalysts due to the same reason explained earlier pertaining to the interaction effect between the extract and precursor (Wellia et al., 2024). The maximum S_{BET} of greenly synthesized TiO_2 photocatalysts

recoded in Table 3.4 was found at 2 g of MJGTF and MJGTS extracts for the GF2 and GS2 photocatalysts, corresponding to the highest percentage of increases in the S_{BET} for them. These interesting results are expected and agree with the results obtained from the analysis of FE-SEM and XRD shown earlier. As reported in literature, the larger surface area can provide more active sites on the surface of synthesized photocatalyst, thus increasing the adsorption process of the molecules of pollutant onto these sites. As a result, enhancing the photocatalytic degradation efficiency (Athar & Muneer, 2023; Helmy et al., 2021; H. Kaur et al., 2021; Liu et al., 2023).

At the current stage, the experimental results based on the previous analyses confirmed the maximum S_{BET} was recorded at the GF2 and GS2 photocatalysts. To examine their characteristics deeply, further characterization was proposed in the coming section.

4.2 Further characterization of greenly synthesized TiO₂ (GF2 vs. GS2)

4.2.1 TEM analysis

The TEM analysis can be observed from the magnified images in Figure 3.8 that the crystal structure of the GF2 and GS2 photocatalysts has a spherical shape with crystalline phase. These findings agree with the results obtained from the XRD analysis. Both confirmed a crystalline phase of synthesized TiO₂ photocatalysts. The average particle sizes of these photocatalysts obtained from the TEM analysis in the range 5.38-7.33 nm are consistent with the results obtained by the XRD analysis.

4.2.2 TGA analysis

The TGA analysis showed that the weight loss by the thermal degradation that occurred at previously mentioned stages can be attributed to the moisture loss with respect to evaporating the adsorbed water molecules on the surface of these photocatalysts (Kumaravel et al., 2023; Wellia et al., 2024) for the first stage and the dehydroxylation of Ti-OH groups (i.e., removal of hydroxyl groups from the surface of the photocatalyst) (Kumaravel et al., 2023) for the second stage. It is clear to see from TGA thermograms in Figure 3.9 that no significant weight loss was found at stage three for both photocatalysts, indicating the formation of anatase-phase TiO₂ photocatalyst (Wellia et al., 2024). The results obtained from

the FTIR analysis shown earlier confirmed the presence of these compounds that were exposed to thermal degradation at these stages of TGA analysis.

It is important to note that the photocatalysts were calcined at a temperature of 450 °C. Thermogravimetric analysis (TGA) confirmed the thermal stability of the greenly synthesized GF2 and GS2 photocatalysts up to 600 °C.

4.2.3 Optical analysis

The optical analysis confirm the enhancement in the electrical and optical properties for GF2 and GS2 in terms of narrowing their bandgap energy by the green sol-gel synthesis. This finding gives evident that the wavelength of CP was significantly increased in comparison with GF2 and GS2. The percentage increase in the wavelength was 33% for GF2 and 48% for GS2. A similar trend of results based on the E_g was found where the percentage decrease in the E_g was 42% for GF2 and GS2 compared with CP.

One possible explanation for this enhancement may be attributed to the decrease in crystallite sizes by green sol-gel synthesis of TiO_2 as reported by Saikumari et al., (Saikumari et al., 2019) and Mohamad M Ahmed (Ahmad et al., 2021). In the current study, a significant decrease in crystallite sizes of greenly synthesized TiO_2 (48% for GF2 and GS2) was found when compared with the CP photocatalyst as reported earlier by the XRD analysis. Another possible explanation for this enhancement may be attributed to the presence of K and Si elements as reported earlier by the EDX analysis and confirmed by the FTIR analysis. It is more likely that the presence of K and Si elements replaced Ti atoms and occupied them effectively, changing the conduction band (CB) of the TiO_2 photocatalyst due to the change of Ti (d) orbital of the photocatalyst by the replaced element (d) atoms, thus modifying its electrical and optical properties in terms of narrowing its bandgap energy as well as structural properties (M. M. Khan, 2023; C. H. Nguyen et al., 2018; Zaleska, 2008).

The green synthesis of TiO_2 played a significant role in enhancing the electrical and optical properties for the GF2 and GS2 photocatalysts. This valuable finding can have the potential for applying these photocatalysts in the visible light region and then will be beneficial for the economic considerations.

4.3 Degradation of MB

4.3.1 Photolysis

The photolysis showed that the 20 mg/L MB concentration exhibited minimal degradation via direct photolysis compared to lower concentrations. These findings align with previous studies that have reported a decrease in photolytic efficiency with increasing pollutant concentration (Olatunde et al., 2020).

Therefore, the 20 mg/L MB concentration was selected as the optimal initial concentration for subsequent photocatalysis experiments.

4.3.2 Photocatalysis

4.3.2.1 Photocatalytic degradation of MB by synthesized TiO₂ (chemical vs. green)

The increase in applied dose led to an increase in the number of active sites on the photocatalyst surface, thus the adsorption of MB molecules on these sites and the photon absorption increased accordingly. As a result, the photocatalytic degradation of MB increased (Chaudhary et al., 2023; Helmy et al., 2021; Yahia et al., 2023).

However, further increasing the dose led to a decrease in degradation efficiency due to a well-known phenomenon in the field of photocatalysis (effects of light scattering and screening via the increase in the aggregation of the photocatalyst's particles, which acts as barriers for the light irradiation) (Moeini et al., 2024; Vasiljevic et al., 2020).

Figure 4.1 compares the photocatalytic degradation efficiency (% degradation, D%) of MB achieved by the chemically and greenly synthesized TiO₂ photocatalysts at their optimal doses. Notably, both GF2 (90% D%) and GS2 (98% D%) significantly outperform the commercially available CP photocatalyst (22% D%). This superior performance of the green photocatalysts can be attributed to the increased surface area (S_{BET}) observed in Figure 4.1. GF2 and GS2 exhibit significantly higher S_{BET} values (164.44 m²/g and 217.66 m²/g, respectively) compared to CP (13.78 m²/g). This improvement, achieved through the green sol-gel synthesis method, translates to enhanced MB degradation. Compared to CP, the S_{BET} increases by 151% for GF2 and a remarkable 204% for GS2. These substantial increases in surface area are the primary factor behind the observed 309% and 346%

enhancements in MB degradation for GF2 and GS2, respectively. Interestingly, despite using the same optimal dose (125 mg/L), GS2 demonstrates a higher photocatalytic performance than GF2. This can be directly attributed to its higher S_{BET} , achieved through the green synthesis process.

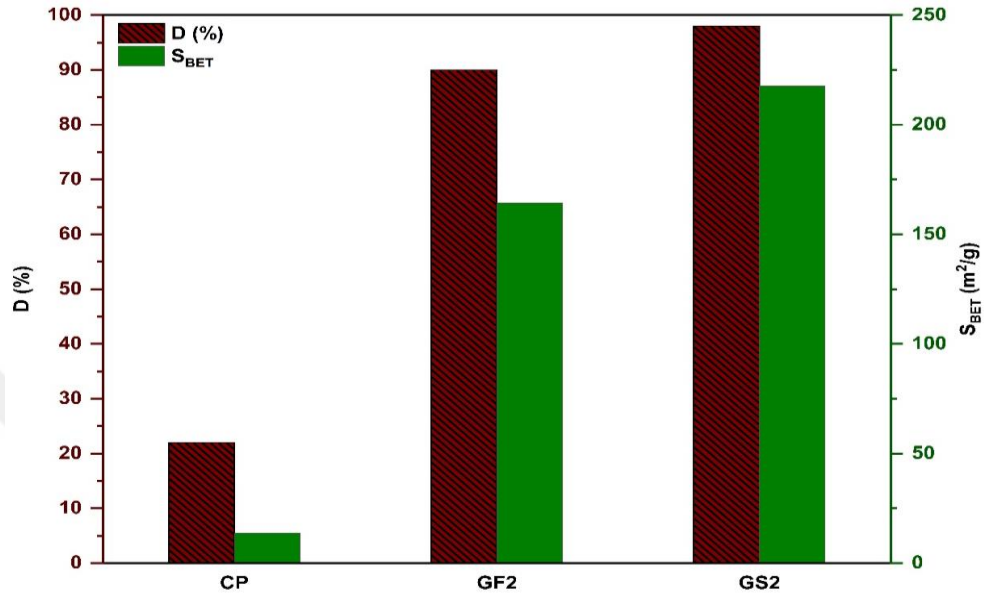


Figure 4.1. The D% of MB and the S_{BET} for the synthesized TiO_2 photocatalysts (CP, GF2 and GS2)

4.3.2.2 Photocatalytic mineralization of MB by synthesized TiO_2 (chemical vs. green)

The degree of photocatalytic mineralization expressed by the TOC removal using CP, GF2 and GS2 photocatalysts at their optimum photocatalytic doses over the photocatalytic time of 120 min was investigated with respect to the pH and DO monitoring parameters.

For the chemically synthesized TiO_2 photocatalyst (CP), Figure 3.14 shows that the TOC removal was found to be 21% at 120 min. This lower mineralization is expected and can be attributable to lower photocatalytic performance obtained by the CP photocatalyst (D% of MB was 22% only). This finding can be supported by the results obtained by monitoring the pH and DO parameters. In terms of monitoring the pH, a slight reduction in pH values was recorded by 1%. This implies that MB is resistant to further degrade photocatalytically under the examined conditions by CP (Yahia et al., 2023). In terms of monitoring the DO, there was an insignificant reduction in the DO as conventional oxidant

concentration (< 1%). This gives strong evidence that the consumption of oxidant concentration in terms of DO during the photocatalytic reactions was so limited, indicating that the overall photocatalytic degradation of MB was weak. The obtained results from the pH and DO monitoring are in agreement with the photocatalytic performance of degradation and mineralization of MB by CP.

For the greenly synthesized TiO₂ photocatalysts (GF2 and GS2), Figure 3.15 and Figure 3.16 shows that the TOC removal at the end of photocatalytic time was found to be 88% for GF2 and 97% for GS2. Higher photocatalytic mineralization by these photocatalysts can be related to their higher photocatalytic degradations (90% for GF2 and 98% for GS2). This photocatalytic mineralization was positively associated with monitoring the pH and DO parameters. A drop of pH was found to be 14 and 18% for GF2 and GS2, respectively. This finding is interesting from the heterogenous photocatalysis point of view where the photocatalytic reactions are significantly affected by pH. The drop in pH refers to the generation of free hydroxyl radicals (HO•) during these reactions, which plays a significant role in degrading the MB into reaction intermediate compounds and then mineralizing them (Shariffuddin et al., 2013; Zhou et al., 2024). In parallel, a significant reduction in the DO as conventional oxidant concentration for GF2 and GS2 was found to be 61 and 77%, respectively. This is an interesting result from the mechanism of heterogenous photocatalysis point of view where the presence of the adsorbed DO molecules on the outer surface of the synthesized TiO₂ plays a significant role as an electron acceptor to generate the superoxide radical ions (O₂⁻) as shown in equation (4.1) (Zhou et al., 2024). These radical ions can significantly degrade the MB molecules in conjunction with the free hydroxyl radicals (HO•) as strongly oxidizing agents. Hence, improving the overall photocatalytic degradation of MB (García-Prieto et al., 2022).



The general trend of photocatalytic degradation of MB by GF2 and GS2 is similar to the photocatalytic mineralization by these photocatalysts based on their equal optimum doses of 125 mg/L. The GF2 photocatalyst showed lower photocatalytic mineralization than that of the GS2 photocatalyst. One probable reason for this is the generation of reaction intermediate compounds such as Azure A, Azure B, Azure C and Thionin during the photocatalytic degradation of MB

(Garg et al., 2023). As reported in the literature, the intermediate compounds generated during the photocatalytic degradation process are often resistant to further degradation (Ali et al., 2010).

In the current study, it is anticipated that these recalcitrant intermediates may form and hinder complete mineralization when using the GF2 photocatalyst under the specified conditions. This hypothesis is supported by the observed pH changes in the MB solution, which suggests the formation of acidic or basic intermediates. A 14% change in pH was recorded during the reaction. The visual changes observed in the MB solution during the photocatalytic process further support the quantitative degradation and mineralization data.

As shown in Figure 3.17, the color of the MB solution remained largely unchanged when using the CP photocatalyst, indicating minimal degradation. In contrast, the blue color of the MB solution gradually faded over time when treated with GF2 and GS2, ultimately becoming transparent after 120 minutes. These visual observations corroborate the high D% values obtained for GF2 and GS2, demonstrating the effectiveness of these green synthesized photocatalysts in degrading MB. Thus, color monitoring can be employed as a simple, qualitative indicator of photocatalytic degradation.

4.3.2.3 Further evaluation of synthesized TiO₂ photocatalyst (benchmark vs. green)

Overall, the BM photocatalyst exhibited significantly lower photocatalytic performance compared to the green synthesized GF2 and GS2 photocatalysts. Additionally, the blue color of the MB solution remained largely unchanged, further confirming the limited photocatalytic activity of the BM photocatalyst as shown in Figure 3.20, highlighting the potential of green synthesis methods for developing efficient and sustainable photocatalysts.

5. CONCLUSION

The current M.Sc. study aimed, for the first time, to investigate the possibility of applying the matcha Japanese green tea extracts from the first harvest and the second harvest for the green synthesis of TiO₂ photocatalyst. This aim was achieved in three separate stages, including synthesis, characterization, and evaluation. The overall findings of this investigation to draw the following main conclusions are summarized into the following sections:

1. Synthesis and characterization of chemically and greenly TiO₂ photocatalysts

- The FTIR analysis confirmed that the CP, GF1, GF2, GF3, GS1, GS2, and GS3 photocatalysts were successfully synthesized by identifying the peaks of FTIR spectrum at the wavenumbers corresponding to the bonds of Ti-O and Ti-O-Ti, which are responsible for synthesizing the TiO₂ photocatalyst.
- The XRD analysis showed that the formation of the crystalline phase of chemically and greenly synthesized TiO₂ photocatalysts is pure anatase. Also, this analysis showed that the effect of added weights from 1 to 3 g for each MJGTF and MJGTS as extracts on the crystallite sizes of the GF1, GF2, GF3, GS1, GS2, and GS3 photocatalysts played a significant role in decreasing their crystallite sizes when compared with the CP photocatalyst. This decrease is attributed to the presence of polyphenols as active compounds in these extracts, which in turn control the crystallite size via acting as stabilizing, capping, and reducing agents of Ti ions. At 2 g of these extracts, the crystallite sizes of GF2 and GS2 photocatalysts were found to be minimum due to the reduction of either particle nucleation during hydrolysis and condensation steps in the green sol-gel synthesis of TiO₂ or grain boundaries during the sintering process.
- The FE-SEM analysis revealed that the surface morphology of the chemically and greenly synthesized photocatalysts was spherical in shape. The FE-SEM images showed that the agglomeration in terms of non-uniformity in distribution over the surface particles of the GF1, GF2, GF3, GS1, GS2, and GS3 photocatalysts was higher than that of the CP photocatalyst due to the attractive forces between these particles and the use of different concentrations and types of MJGT extracts in the green synthesis of TiO₂. The mean particle size of these

synthesized TiO₂ photocatalysts obtained by this analysis was similar in general trend as found by the XRD analysis.

- The EDX analysis gave further confirmation that the chemical and green TiO₂ photocatalysts were successfully synthesized using the sol-gel method because the presence of the Ti element and O element were predominant in comparison with other elements (K and Si) as impurities.
- The AFM analysis revealed that the presence of topography in terms of hills, valleys and ridges as well as the roughness of the surface was clearly visualized in the 3D topography micrographs and numerically obtained with respect to the Sq values. The surface topography and roughness for the greenly photocatalysts were higher than that of the chemically photocatalyst. The increased surface roughness based on the values of Sq played a significant role in increasing the adsorption of pollutants and then the overall surface area of the photocatalyst increased accordingly (this can be explained below).
- The BET analysis showed that the percentage increase in the S_{BET} was found to be 125% for GF1, 151% for GF2, 129% for GF3, 156% for GS1, 204% for GS2, and 127% for GS3 when compared with the CP photocatalyst. The maximum S_{BET} of greenly synthesized TiO₂ photocatalysts was found at 2 g of MJGT1 and MJGT2 extracts for the GF2 and GS2 photocatalysts. One possible explanation for this is the existence of K and Si together as identified by the EDX analysis, which played a significant role in improving their S_{BET} . The BET results are generally consistent with the results obtained from the analyses of FE-SEM and XRD.
- The TEM analysis based on their results obtained for the GF2 and GS2 photocatalysts was supportive of the results from the XRD analysis with respect to the spherical shape of the crystal structure and within the range of average particle sizes.
- The TGA analysis showed the thermal stability of the GF2 and GS2 photocatalysts over a wide range of investigated temperatures (up to 600 °C). The TGA results gave further confirmation to the results obtained by the XRD analysis where the phase of formation of these green photocatalysts was anatase.
- The optical analysis showed that the wavelengths of the GF2 and GS2 photocatalysts were found to be 443 and 494 nm, respectively, with the identified

Eg value of 1.55 eV for both photocatalysts. These results confirmed that the wavelength for these photocatalysts shifted from the UV light-blue region (< 400 nm) to the visible light-red region (> 400 nm). This means that the optical properties for the GF2 and GS2 photocatalysts were significantly enhanced by the green synthesis of TiO_2 photocatalyst. This enhancement in their optical properties could be related to two possible reasons. First reason, the decrease in crystallite sizes by green sol-gel synthesis of TiO_2 as reported in the literature where a significant decrease in crystallite sizes of greenly synthesized TiO_2 (48% for GF2 and 47% for GS2) was found. Second reason, the presence of K and Si elements as found by the EDX analysis and confirmed by the FTIR analysis. They replaced Ti atoms and occupied them effectively, changing the conduction band (CB) of the TiO_2 photocatalyst due to the change of Ti (d) orbital of the photocatalyst by the replaced element (d) atoms, thus modifying its electrical and optical properties in terms of narrowing its bandgap energy as well as structural properties.

2. Evaluation of photolysis and photocatalysis of MB

- ❖ The direct photolysis process had a limited effect on the selected concentration of MB (20 mg/L) when compared with other investigated concentrations (i.e., 2% photolytic degradation at 120 min photolytic time). Thus, this effect was excluded as a photolytic degradation mechanism under the photocatalysis process.
- ❖ For the chemically synthesized photocatalyst (CP), the optimum photocatalytic dose was found at 350 mg/L. At this dose, the D% of MB was 22%. While, for the greenly synthesized photocatalysts (GF2 and GS2), the optimum photocatalytic dose was found at 125 mg/L. At this dose, the D% of MB was 90% for GF2 and 98% for GS2. This could be related to a significant improvement in the S_{BET} for GF2 ($164.44 \text{ m}^2\text{g}^{-1}$) and GS2 ($217.66 \text{ m}^2\text{g}^{-1}$), when compared with that of CP ($13.78 \text{ m}^2\text{g}^{-1}$). As reported in the literature, the larger surface area can provide more active sites on the surface of synthesized photocatalyst, thus increasing the adsorption process of the molecules of pollutants onto these sites. As a result, the photocatalytic degradation efficiency is significantly increased. This was supported by the AFM analysis concerning the increased surface roughness. Based on this, the GS2 showed higher

photocatalytic performance than that of GF2 due to its higher S_{BET} obtained by the green synthesis.

- ❖ The degree of photocatalytic mineralization expressed by the TOC removal using the CP, GF2 and GS2 photocatalysts at their optimum photocatalytic doses was found to be 21, 88 and 97%, respectively. The performance of photocatalytic mineralization by these photocatalysts could be related to their photocatalytic performance. This performance was supported by the results obtained from monitoring the pH and DO parameters. The drop in pH referred to the generation of free hydroxyl radicals ($\text{HO}^\bullet$) during photocatalytic reactions, which plays a significant role in degrading the MB into reaction intermediate compounds and then mineralizing them. In parallel, a significant reduction in the DO as conventional oxidant concentration played a significant role as an electron acceptor to generate the superoxide radical ions. These radical ions could significantly degrade the MB molecules in conjunction with the free hydroxyl radicals as strongly oxidizing agents. Hence, improving the overall photocatalytic degradation of MB.
- ❖ Monitoring the visual change in color of MB solution samples as real photos during the photocatalysis process using CP, GF2 and GS2 could be used as an indicator of the photocatalytic degradation of MB.
- ❖ The performance of the greenly synthesized TiO_2 photocatalysts (GF2 and GS2) was better than that of the typical and standard commercial photocatalyst TiO_2 (Degussa, P-25) as a benchmark photocatalyst (BM) in all investigated cases.
- ❖ Finally, the greenly synthesized TiO_2 photocatalysts with respect to GF2 and GS2 by the sol-gel method were superior in terms of characterization and photocatalytic degradation of MB under all examined conditions when compared with the chemically synthesized TiO_2 as a control photocatalyst and commercial TiO_2 (Degussa, P-25) as a benchmark photocatalyst. This value performance of the GF2 and GS2 photocatalysts can be considered novel green photocatalysts in the field of green photocatalysis.

5.1 Recommendations

There are still general limitations arising from the wide range of investigations into the green sol-gel synthesis of TiO₂ photocatalyst using matcha Japanese green tea conducted in the current M.Sc. study. A number of suggestions for future work can be recommended below:

- Investigating the ingredients of matcha Japanese green tea with first and second harvests using the relevant analytical techniques to identify the active components such as polyphenol and flavonoid that are expected to enhance the surface morphology of green TiO₂ photocatalysts. This will give insight into deeply understanding the role of these components in this enhancement.
- Applying the design of experiments (DOE) to optimize the operating parameters used in the green sol-gel method such as mixing speed, mixing time, reaction temperature, extraction time, ingredient ratio and others. This will help to find the best conditions for synthesis.
- Investigating the reusability of greenly synthesized photocatalysts in terms of separation and recycling by using a photocatalytic membrane reactor under continuous operation. This will make the greenly synthesized photocatalysts feasible in real applications.
- Utilizing the solar light as a source of UV irradiation to verify the ability of the greenly synthesized photocatalysts to be effectively activated in degradation of target pollutant under these conditions. This will make these photocatalysts to satisfy the economic considerations.
- Studying the photocatalytic degradation kinetic modeling for the greenly synthesized photocatalysts to establish an insight into better understanding the photocatalytic reaction conditions.
- Examining the complete mineralization of MB by controlling the pH or/and adding conventional oxidants such as H₂O₂ or dissolved oxygen (DO). This will significantly increase the generation of free hydroxyl radicals (HO[•]) as a strong and powerful oxidizing agent to further degrade the target pollutant.

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APPENDICES

APPENDIX 1 Explanation: FTIR Results Using The KnowItAll Informatics System 2024 Program For Photocatalysts

Type	Wavenumber (cm ⁻¹)	Classification	Group	Bond	Intensity	Mode	Notes
CP	3406.29	Alcohols	hydroxyl	OH	Strong	Stretching	Asymmetrical and symmetrical vibrations of hydroxyl group
	1635.64	Water moisture	hydroxyl	O-H	Weak	Deformation	
	1543.05	Water molecules	OH	O-H	Medium	Deformation	The bending vibrations of surface-adsorbed water molecules on TiO ₂ .
	659.66	Titanium	O-Ti-O	O-Ti-O	Strong	Stretching	Anatase phase
	540.07	Titanium	O-Ti-O	O-Ti-O	Strong	Stretching	Anatase phase
	455.20	Titanium	Ti-O	Ti-O	Strong	Stretching	
GF1	3402.43	Amines	CH ₂ -NH-CH ₂	NH	Weak	Stretching	Secondary amine
	1654.92	Aldehydes	HO-C=C-CH	C=O	Strong	Stretching	Alpha beta, beta hydroxy aldehyde
	1543.05	Amides	R-CO-NH-C	NH	Strong	Combination	Amide II, combination of C-N stretching and N-H bond

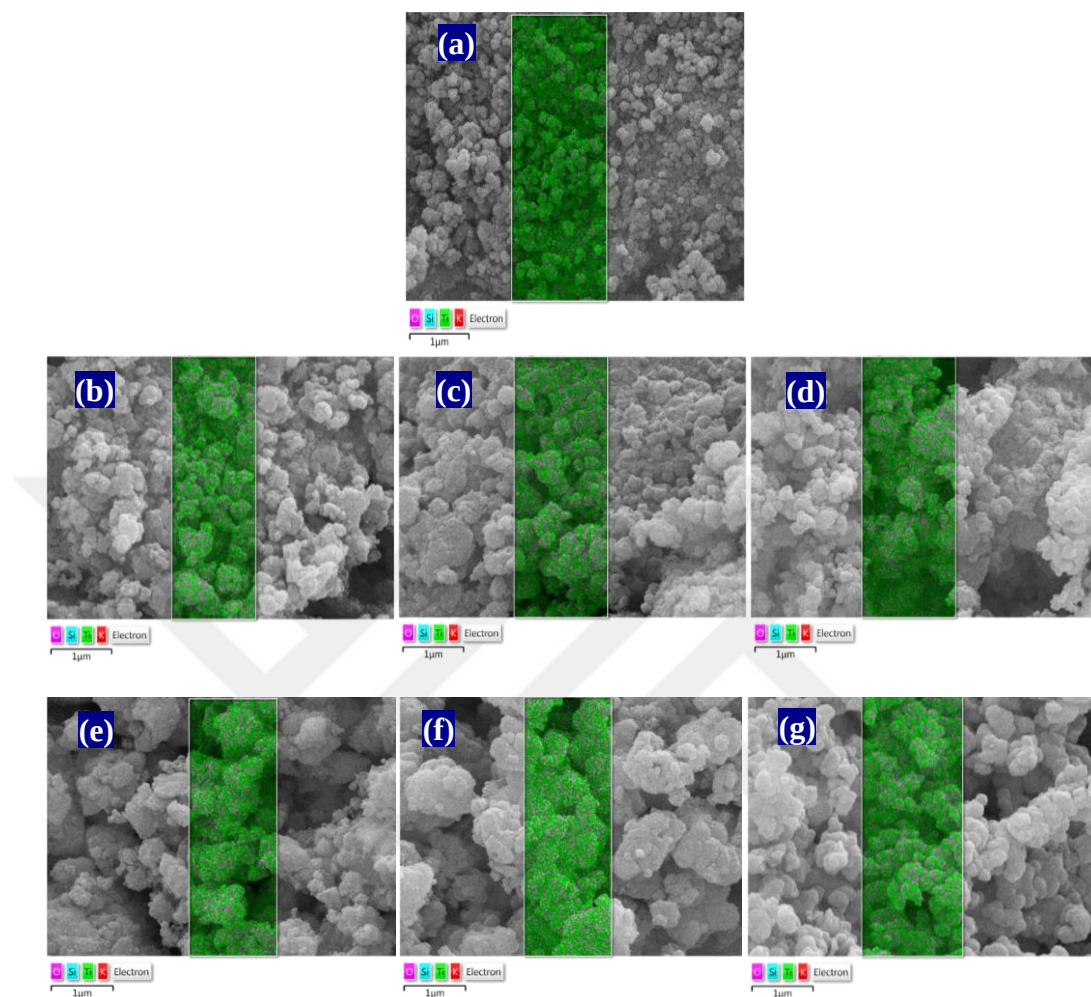
	1419.61	Alkenes	RCH=C H ₂	CH	medium	Deformation	CH ₂ in-plane deformation
	1319.31	Amides	R-CO- NH-C	C-N	medium	Stretching	
	763.81	Aromatics	1,2,4- trisubstituted	CH	Strong	Deformation	2 adjacent H out-of-plane deformation
	474.49	Titanium	O-Ti-O	O-Ti-O	Strong	Stretching	
	424.34	Titanium	Ti-O	Ti-O	Strong	Stretching	
GF2	3444.87	Amines	CH ₂ - NH-CH ₂	NH	Weak	Stretching	Secondary amine
	1635.64	Alkenes	CCCH=C HCC	C=C	Variable	Stretching	Non-conjugated C=C
	1539.20	Amides	R-CO- NH-C	NH	Strong	Combination	amide II, combination of C-N stretching and N-H bond
	1458.18	Alkanes	C-(CH ₃) ₃	CH	Medium	Antisymmetric deformation	
	810.10	Silicon Compounds	(R) ₃ SiH	Si-H	Strong	Wagging	
	709.80	Aromatics	1,2,3- trisubstituted	Ring	Strong	Bending	Out-of-plane ring bending
	632.65	Titanium	Ti-O	Ti-O	Strong	Stretching	Anatase phase
	536.21	Titanium	O-Ti-O	O-Ti-O	Strong	Stretching	
	451.34	Titanium	Ti-O	Ti-O	Strong	Stretching	
GF3	3124.68	Amides	R-CO- NH-CO- N	NH	Medium	Stretching	

	1701.22	Aldehydes	CH=CH-CHO	C=O	Strong	Stretching	Alpha beta unsaturated aldehyde
	1651.07	Aldehydes	HO-C=C-CHO	C=O	Strong	Stretching	alpha beta, beta hydroxy aldehyde
	1543.05	Amides	R-CO-NH-C	NH	Strong	Combination	Amide II, combination of C-N stretching and N-H
	1458.18	Alkanes	C-(CH ₃) ₃	CH	Medium	Antisymmetric deformation	
	1369.46	Alkanes	C-(CH ₃) ₃	CH	Medium	Deformation	
	459.06	Titanium	Ti-O	Ti-O	Strong	Stretching	
	424.34	Titanium	Ti-O	Ti-O	Strong	Stretching	
GS1	3313.71	Silicon Compounds	(R) ₃ Si-OH	O-H	Medium	Stretching	Broad peak
	1712.79	Aldehydes	Ph-CHO	C=O	Strong	Stretching	Aryl aldehyde
	1647.21	Alkenes	CCCH=CH	C=C	Variable	Stretching	Non-conjugated C=C
	1622.13	Alkenes	CCCH=CH	C=C	Variable	Stretching	Non-conjugated C=C
	1539.20	Amides	R-CO-NH-C	NH	Strong	Combination	Amide II, combination of C-N stretching and N-H
	1454.33	Alkanes	C-(CH ₃) ₃	CH	Medium	Antisymmetric deformation	
	1394.53	Alkanes	C-(CH ₃) ₃	CH	Medium	Deformation	

	1336.67	Alkanes	(R)3CH	CH	Weak	Deformation	
	806.25	Silicon Compounds	(R)3SiH	Si-H	Strong	Wagging	
	640.37	Titanium	Ti-O	Ti-O	Strong	Stretching	
	443.63	Titanium	Ti-O	Ti-O	Strong	Stretching	
GS2	3392.79	Silicon Compounds	(R)3Si-OH	O-H	Medium	Stretching	Broad peak
	2933.73	Alkanes	Cyclohexyl	CH	Medium	Symmetric stretching	
	1714.72	Aldehydes	Ph-CHO	C=O	Strong	Stretching	Aryl aldehyde
	1649.14	Aldehydes	HO-C=C-CHO	C=O	Strong	Stretching	Alpha beta, beta hydroxy aldehyde
	1539.20	Amides	R-CO-NH-C	NH	Strong	Combination	Amide II, combination of C-N stretching and N-H
	1490.97	Aromatics	1,2,3,4,5,6 trisubstituted	Ring	Medium	Stretching	
	1417.68	Alkenes	RCH=CH ₂	CH	Medium	Deformation	CH ₂ in-plane deformation
	1338.60	Alkanes	(R)3CH	CH	Weak	Deformation	
	1089.78	Silicon Compounds	Si-O-Si	Si-O-Si	Variable-strong	Stretching	Open chain
	619.15	Titanium	Ti-O	Ti-O	Strong	Stretching	Anatase phase
GS3	422.41	Titanium	Ti-O	Ti-O	Strong	Stretching	
	3196.05	Amides	R-CO-NH ₂	NH	Medium	antisymmetric	Primary amide
	1697.36	Aldehydes	CH=CH-CHO	C=O	Strong	Stretching	Alpha beta unsaturated aldehyde

	1647.21	Aldehydes	HO-C=C-CH	C=O	Strong	Stretching	Alpha beta, beta hydroxy aldehyde
	1539.20	Amides	R-CO-NH-C	NH	Strong	Combination	Amide II, combination of C-N stretching and N-H
	1506.41	Aromatics	1,2,3,4,5, 6-trisubstituted	Ring	Variable	Stretching	
	1456.26	Alkanes	C-(CH ₃) ₃	CH	Medium	Antisymmetric deformation	
	1394.53	Alkanes	C-(CH ₃) ₃	CH	Medium	Deformation	
	1338.60	Alkanes	(R) ₃ CH	CH	Weak	Deformation	
	758.02	Silicon Compounds	R-Si(CH ₃) ₃	Si-C	Variable	Stretching	
	580.57	Titanium	O-Ti-O	Ti-O	Strong	Stretching	
	418.55	Titanium	Ti-O	Ti-O	Strong	Stretching	

**APPENDIX 2 Explanation: The Mapping Line Of Synthesized TiO₂
Photocatalysts: (a) CP, (b) GF1, (c) GF2, (d) GF3, (e) GS1, (f) GS2 And (g)GS3**



APPENDIX 3 Explanation: The Optical Properties Of Chemically Synthesized

