

# INCORPORATION OF Fe AND $gC_3N_4$ INTO MESOPOROUS TITANIA NANOPARTICLES FOR PHOTODEGRADATION OF DIBENZOTHIOPHENE

NURUL ADILAH BINTI MOHD NOOR

UNIVERSITI PENDIDIKAN SULTAN IDRIS

2024

INCORPORATION OF Fe AND gC<sub>3</sub>N<sub>4</sub> INTO MESOPOROUS TITANIA  
NANOPARTICLES FOR PHOTODEGRADATION OF  
DIBENZOTHIOPHENE

NURUL ADILAH BINTI MOHD NOOR

DISSERTATION PRESENTED TO QUALIFY FOR A  
MASTERS IN SCIENCE  
(RESEARCH MODE)

FACULTY OF SCIENCE AND MATHEMATICS  
UNIVERSITI PENDIDIKAN SULTAN IDRIS

2024



Please tick (✓)

Project Paper

Masters by Research

Master by Mixed Mode

PhD

/

## INSTITUTE OF GRADUATE STUDIES

### DECLARATION OF ORIGINAL WORK

This declaration is made on the .....<sup>1</sup>.....day of.....JULY.....20.....<sup>24</sup>.....

#### i. Student's Declaration:

I, NURUL ADILAH BINTI MOHD NOOR, M20182002270, FACULTY OF SCIENCE AND MATHEMATICS (PLEASE INDICATE STUDENT'S NAME, MATRIC NO. AND FACULTY) hereby declare that the work entitled INCORPORATION OF Fe AND gC3N4 INTO MESOPOROUS TITANIA NANOPARTICLES FOR PHOTODEGRADATION OF DIBENZOTHIOPHENE is my original work. I have not copied from any other students' work or from any other sources except where due reference or acknowledgement is made explicitly in the text, nor has any part been written for me by another person.

Signature of the student

#### ii. Supervisor's Declaration:

I DR. SITI MUNIRAH BINTI SIDIK (SUPERVISOR'S NAME) hereby certifies that the work entitled INCORPORATION OF Fe AND gC3N4 INTO MESOPOROUS TITANIA NANOPARTICLES FOR PHOTODEGRADATION OF DIBENZOTHIOPHENE (TITLE) was prepared by the above named student, and was submitted to the Institute of Graduate Studies as a \* partial/full fulfillment for the conferment of MASTER OF SCIENCE (CHEMISTRY) (PLEASE INDICATE THE DEGREE), and the aforementioned work, to the best of my knowledge, is the said student's work.

1 JULY 2024

Date

DR SITI MUNIRAH SIDIK  
SENIOR LECTURER  
DEPARTMENT OF CHEMISTRY  
FACULTY OF SCIENCE AND MATHEMATICS  
UNIVERSITI PENDIDIKAN SULTAN IDRIS,  
35900 TANJUNG MALIM, PERAK.

Signature of the Supervisor



**INSTITUT PENGAJIAN SISWAZAH /  
INSTITUTE OF GRADUATE STUDIES**

**BORANG PENGESAHAN PENYERAHAN TESIS/DISERTASI/LAPORAN KERTAS PROJEK  
DECLARATION OF THESIS/DISSERTATION/PROJECT PAPER FORM**

Tajuk / Title: INCORPORATION OF Fe AND gC3N4 INTO MESOPOROUS TITANIA NANOPARTICLES  
FOR PHOTODEGRADATION OF DIBENZOTHIOPHENE

No. Matrik /Matric's No.: M20182002270

Saya / I : NURUL ADILAH BINTI MOHD NOOR

(Nama pelajar / Student's Name)

mengaku membenarkan Tesis/Disertasi/Laporan Kertas Projek (Kedoktoran/Sarjana)\* ini disimpan di Universiti Pendidikan Sultan Idris (Perpustakaan Tuanku Bainun) dengan syarat-syarat kegunaan seperti berikut:-

*acknowledged that Universiti Pendidikan Sultan Idris (Tuanku Bainun Library) reserves the right as follows:-*

1. Tesis/Disertasi/Laporan Kertas Projek ini adalah hak milik UPSI.  
*The thesis is the property of Universiti Pendidikan Sultan Idris*
2. Perpustakaan Tuanku Bainun dibenarkan membuat salinan untuk tujuan rujukan dan penyelidikan.  
*Tuanku Bainun Library has the right to make copies for the purpose of reference and research.*
3. Perpustakaan dibenarkan membuat salinan Tesis/Disertasi ini sebagai bahan pertukaran antara Institusi Pengajian Tinggi.  
*The Library has the right to make copies of the thesis for academic exchange.*
4. Sila tandakan ( ☒ ) bagi pilihan kategori di bawah / Please tick ( ☒ ) for category below:-

☐

**SULIT/CONFIDENTIAL**

Mengandungi maklumat yang berdarjah keselamatan atau kepentingan Malaysia seperti yang termaktub dalam Akta Rahsia Rasmi 1972. / Contains confidential information under the Official Secret Act 1972

☐

**TERHAD/RESTRICTED**

Mengandungi maklumat terhad yang telah ditentukan oleh organisasi/badan di mana penyelidikan ini dijalankan. / Contains restricted information as specified by the organization where research was done.

☒

**TIDAK TERHAD / OPEN ACCESS**

(Tandatangan Pelajar/ Signature)

DR SITI MUNIRAH SIDIK  
SENIOR LECTURER  
DEPARTMENT OF CHEMISTRY,  
FACULTY OF SCIENCE AND MATHEMATICS,  
UNIVERSITI PENDIDIKAN SULTAN IDRIS,  
35900 TANJUNG MALIM, PERAK.

(Tandatangan Penyelia / Signature of Supervisor)  
& (Nama & Cop Rasmi / Name & Official Stamp)

Tarikh: 1 JULAI 2024

Catatan: Jika Tesis/Disertasi ini **SULIT @ TERHAD**, sila lampirkan surat daripada pihak berkuasa/organisasi berkenaan dengan menyatakan sekali sebab dan tempoh laporan ini perlu dikelaskan sebagai **SULIT** dan **TERHAD**.

*Notes: If the thesis is CONFIDENTIAL or RESTRICTED, please attach with the letter from the organization with period and reasons for confidentiality or restriction.*

## ACKNOWLEDGEMENT

Alhamdulillah, all praise to Allah. Peace and blessing to Prophet Muhammad S.A.W., his families and all muslims. A million thanks dedicated to my beloved family for being the strongest support system and give encouragement during my hard time. Special thanks to my supervisors, Dr. Siti Munirah Binti Sidik for the wiseful advices and help during completing this research project and report. I would also like to thank to my co-supervisors, Dr. Mohamad Saufi Bin Rosmi and Dr. Nur Farhana Binti Jaafar for their support and useful comments during completing the study. Without their guidance, patience, ideas and supports, this research project could not have been accomplished. Special appreciation goes to the staffs of Faculty of Science and Mathematics UPSI for their valuable help and cooperation towards me during completing the research work. My gratitude to the Ministry of Higher Education through financial support from Fundamental Research Grant Scheme for Research Acculturation of Early Career Researchers (FRGS-RACER, no. 2019-0164-103-62). Last but not least, I would like to thank to my labmates and coursemates, Muhammad Shaiful Aidil, Ong Suu Wan, Husna Assaedah, Susana Wong and all my friends that have help me during completing this work either directly or indirectly.



## ABSTRACT

This study aimed to incorporate Fe and  $\text{gC}_3\text{N}_4$  into Mesoporous Titania Nanoparticles (MTN) and investigate photodegradation of Dibenzothiophene (DBT). MTN with various aging time ( $x = 2, 4, 6$  and  $8$  days) were synthesized via sol-gel method before being incorporated with 5wt% Fe (5Fe/MTN- $x$ ) and 5wt%  $\text{gC}_3\text{N}_4$  (5FeMTN- $x/5\text{gC}_3\text{N}_4$ ) using wet-impregnation method. The photocatalysts were characterized using X-ray Diffraction (XRD), Field-Emission Scanning Electron Microscopy (FESEM) with EDX analysis, UV-Visible Diffuse Reflectance Spectroscopy (UV-DRS), Fourier-Transform Infrared Spectroscopy (FTIR), Surface Area Analysis (BET), Photoluminescence Spectroscopy (PL) and Raman Spectroscopy. Photocatalytic performance was evaluated through DBT photodegradation under ultraviolet (UV) light irradiation for 180 min. Parameters such as  $\text{H}_2\text{O}_2$  volume, DBT concentration and photocatalyst dose were manipulated with prolonging the reaction time to 240 min. The results of XRD showed the formation of MTN with the presence of common peaks at  $2\theta$ :  $25.34^\circ - 75.00^\circ$  corresponded to  $\text{TiO}_2$  anatase phase. FTIR and BET analyses also confirmed the formation of MTN and successful incorporation of Fe and  $\text{gC}_3\text{N}_4$  into the hybrid catalysts. UV-DRS and PL results showed the extending of light absorption towards visible light region and lower rate of electron-hole recombination was reached by the addition of Fe and  $\text{gC}_3\text{N}_4$ . The results displayed 5FeMTN-6/5 $\text{gC}_3\text{N}_4$  owned the highest DBT photodegradation with 38.2% compared to the other photocatalysts. At the optimized conditions, 5FeMTN-6/5 $\text{gC}_3\text{N}_4$  reached 57.0% at 40 mg/L DBT concentration with 1 g/L photocatalyst dose and 0.01 mL  $\text{H}_2\text{O}_2$ . The presence of Fe and  $\text{gC}_3\text{N}_4$  enhanced the photocatalytic performance by forming a heterojunction that promoted the generation and inhibit the electron-hole recombination. In conclusion, Fe and  $\text{gC}_3\text{N}_4$  were successfully incorporate into MTN and reached 57.0% DBT photodegradation at optimized conditions. The implication of this study is this photocatalyst has good potential to be further investigated as a low-cost alternative for DBT removal in fuels.





## PENGGABUNGAN Fe DAN $gC_3N_4$ KE DALAM NANOZARAH TITANIA MESOFORUS UNTUK FOTODEGRADASI DIBENZOTIOFENA

### ABSTRAK

Kajian ini bertujuan untuk menggabungkan Fe dan  $gC_3N_4$  ke dalam Nanozarah Titania Mesoforus (MTN) dan mengkaji fotodegradasi Dibenztiofena (DBT). MTN dengan masa penuaan berbeza ( $x = 2, 4, 6$  dan  $8$  hari) disintesis melalui kaedah sol-gel sebelum digabungkan bersama  $5wt\%$  Fe ( $5Fe/MTN-x$ ) dan  $5wt\%$   $gC_3N_4$  ( $5FeMTN-x/5gC_3N_4$ ) menggunakan kaedah penjejalan basah. Sampel fotopemangkin dicirikan menggunakan analisis Pembelauan Sinar-X (XRD), Mikroskopi Pengimbasan Elektron Pancaran Medan (FESEM) dengan analisis EDX, Spektroskopi Resapan Pantulan Ultralembayung (UV-DRS), Spektroskopi Inframerah Fourier Transformasi (FTIR), Analisis Luas Permukaan (BET), Spektroskopi Fotoluminasi (PL) dan Spektroskopi Raman. Prestasi fotopemangkin dinilai melalui fotodegradasi DBT di bawah sinaran ultralembayung (UV) selama 180 min. Parameter seperti isipadu  $H_2O_2$ , kepekatan DBT dan dos fotopemangkin telah dimanipulasi dengan memanjangkan masa tindak balas kepada 240 min. Dapatan XRD menunjukkan pembentukan MTN dengan kehadiran puncak biasa pada  $2\theta$ :  $25.34^\circ - 75.00^\circ$  sepadan dengan fasa *anatase*  $TiO_2$ . Analisis FTIR dan BET juga mengesahkan pembentukan MTN dan kejayaan penggabungan Fe dan  $gC_3N_4$  ke dalam pemangkin hibrid. Dapatan UV-DRS dan PL menunjukkan lanjutan penyerapan ke arah kawasan cahaya nampak dan kadar penggabungan semula lubang dan elektron yang lebih rendah dicapai dengan penambahan Fe dan  $gC_3N_4$ . Dapatan mempamerkan,  $5FeMTN-6/5gC_3N_4$  memiliki fotodegradasi DBT tertinggi sebanyak  $38.2\%$  berbanding dengan fotopemangkin yang lain. Pada keadaan optimum,  $5FeMTN-6/5gC_3N_4$  mencapai  $57.0\%$  pada  $40\text{ mg/L}$  kepekatan DBT dengan  $1\text{ g/L}$  dos fotopemangkin dan  $0.01\text{ mL}$   $H_2O_2$ . Kehadiran Fe dan  $gC_3N_4$  meningkatkan prestasi fotokatalitik dengan membentuk heterosimpang yang menggalakkan penjanaan dan menghalang penggabungan semula elektron dan lubang. Kesimpulannya, Fe dan  $gC_3N_4$  berjaya digabungkan ke dalam MTN dan mencapai  $57.0\%$  fotodegradasi DBT pada keadaan optimum. Implikasi kajian ini ialah fotopemangkin mempunyai potensi yang baik untuk dikaji dengan lebih lanjut sebagai alternatif kos rendah untuk pembuangan DBT dalam bahan api.



## CONTENTS

	Page
<b>DECLARATION OF ORIGINAL WORK</b>	ii
<b>DECLARATION OF DISSERTATION</b>	iii
<b>ACKNOWLEDGEMENT</b>	iv
<b>ABSTRACT</b>	v
<b>ABSTRAK</b>	vi
<b>CONTENTS</b>	vii
<b>LIST OF TABLES</b>	xi
<b>LIST OF FIGURES</b>	xii
<b>LIST OF ABBREVIATIONS</b>	xv
<b>APPENDIX LIST</b>	xx
<b>CHAPTER 1 INTRODUCTION</b>	1
1.1 Background Research	1
1.2 Problem statement	4
1.3 Research aim	6
1.4 Research objectives	6
1.5 Scope of study	6
<b>CHAPTER 2 LITERATURE REVIEW</b>	8
2.1 Introduction	8
2.2 Sulfur components	13
2.3 Desulfurization methods for the production of clean fuels	15



2.4	Photocatalysis	19
2.5	Photocatalyst	21
2.6	TiO <sub>2</sub> as a photocatalyst	28
2.7	Modification of TiO <sub>2</sub> photocatalyst	29
2.7.1	TiO <sub>2</sub> synthesise method	30
2.7.1.1	Hydrothermal method	30
2.7.1.2	Electrochemical anodization method	31
2.7.1.3	Electrospinning method	32
2.7.1.4	Sol-gel method	34
2.7.2	TiO <sub>2</sub> synthesise materials	35
2.7.3	Mesoporous structure	37
2.7.4	Addition of metal elements into TiO <sub>2</sub>	50
2.7.5	Type of metal elements	51
2.7.5.1	Noble metals	51
2.7.5.2	Transition metals	56
2.7.6	Metal doping method	61
2.7.7	Incorporation of dopant	69
2.8	Addition of Fe and gC <sub>3</sub> N <sub>4</sub> into TiO <sub>2</sub> as composite photocatalyst	70
2.9	Addition of hydrogen peroxide (H <sub>2</sub> O <sub>2</sub> ) as oxidizing agent	72
<b>CHAPTER 3 METHODOLOGY</b>		76
3.1	Introduction	76
3.2	Materials	78
3.2.1	Chemicals	78
3.3	Catalyst preparation	79

3.3.1	Synthesize of Mesoporous Titania Nanoparticles (MTN)	79
3.3.2	Synthesize of graphitic carbon nitride ( $\text{gC}_3\text{N}_4$ )	79
3.3.3	Synthesize of MTN-x with addition of 5wt% Fe (5Fe/MTN-x)	80
3.3.4	Synthesize of 5Fe/MTN-x with addition of 5wt% $\text{gC}_3\text{N}_4$ (5FeMTN-x/5 $\text{gC}_3\text{N}_4$ )	80
3.4	Catalyst characterization	81
3.4.1	X-ray diffraction (XRD)	81
3.4.2	Surface area analysis (BET)	82
3.4.3	UV-Visible diffuse reflectance spectroscopy (UV-DRS)	83
3.4.4	Field-Emission scanning electron microscopy (FESEM) with EDX analysis	84
3.4.5	Fourier-transform infrared spectroscopy (FTIR)	85
3.4.6	Photoluminescence (PL)	86
3.4.7	Raman spectroscopy	87
3.5	Photodegradation of DBT	87

## CHAPTER 4 RESULTS AND DISCUSSION 91

4.1	Effect of Mesoporous Titania Nanoparticles (MTN) aging time	91
4.1.1	Crystallinity	92
4.1.2	Surface morphology with Elemental Analysis	94
4.1.3	Functional group	96
4.1.4	Surface area/pore structure	98
4.1.5	Structural phases	100
4.1.6	DBT degradation	102
4.2	Effect of Fe addition into various MTN	104

4.2.1	Crystallinity	105
4.2.2	Surface morphology with Elemental Analysis	107
4.2.3	Measured band gap	109
4.2.4	Functional group	112
4.2.5	Surface area/pore structure	114
4.2.6	Structural phases	116
4.2.7	DBT degradation	118
4.3	Effect of dopant addition	120
4.3.1	Crystallinity	121
4.3.2	Surface morphology with Elemental Analysis	123
4.3.3	Measured band gap	126
4.3.4	Functional group	129
4.3.5	Surface area/pore structure	131
4.3.6	Photochemical properties	133
4.3.7	Structural phases	135
4.3.8	DBT degradation	136
4.4	Optimization parameters	140
4.4.1	Effect of addition of Hydrogen peroxide (H <sub>2</sub> O <sub>2</sub> )	141
4.4.2	Effect of catalyst dosage	145
4.4.3	Effect of DBT initial concentration	147
<b>CHAPTER 5 CONCLUSION AND RECOMMENDATIONS</b>		151
<b>REFERENCES</b>		154
<b>APPENDIX</b>		177



## LIST OF TABLES

Table No.		Page
2.1	List of catalysts that have been used for PODS of DBT	25
2.2	Summary of modification of bare TiO <sub>2</sub> photocatalyst	44
2.3	Summary of addition of metal elements into TiO <sub>2</sub> photocatalyst	65
3.1	List of Chemicals	78
4.1	Pore structural informations of MTN-2, MTN-4, MTN-6 and MTN-8 photocatalysts	99
4.2	Photodegradation of DBT using MTN-2, MTN-4, MTN-6 and MTN-8 photocatalysts	103
4.3	Pore structural informations of 5Fe/MTN-2, 5Fe/MTN-4, 5Fe/MTN-6 and 5Fe/MTN-8 photocatalysts	115
4.4	Photodegradation of DBT using 5Fe/MTN-2, 5Fe/MTN-4, 5Fe/MTN-6 and 5Fe/MTN-8 photocatalysts	119
4.5	Pore structural informations of MTN-6, 5Fe/MTN-6 and 5FeMTN-6/5gC <sub>3</sub> N <sub>4</sub> photocatalysts	132
4.6	Photodegradation of DBT using MTN-6, 5Fe/MTN-6, gC <sub>3</sub> N <sub>4</sub> and 5FeMTN-6/5gC <sub>3</sub> N <sub>4</sub> photocatalysts	138
4.7	Effect of addition of H <sub>2</sub> O <sub>2</sub> for photodegradation of DBT	144
4.8	Effect of catalyst dosage for photodegradation of DBT	146
4.9	Effect of DBT initial concentration for photodegradation of DBT	148
4.10	Optimum conditions for photodegradation of DBT using 5FeMTN-6/5gC <sub>3</sub> N <sub>4</sub> under UV light	150





## LIST OF FIGURES

No. Figures		Page
2.1	Chemical Structure of DBT	14
2.2	General photocatalytic process of semiconductor Based on Adaptation From Saravanan et al. (2017)	20
2.3	Schematic illustration of synthesizing process of $\text{TiO}_2$ via hydrothermal method	30
2.4	Schematic illustration of electrochemical anodization process with three-electrode measurement system	31
2.5	Schematic illustration of the setup of electrospinning process	33
2.6	Schematic illustration of sol-gel process	34
2.7	Schematic illustration of synthesizing MTN via microwave- assisted method	40
2.8	Schematic illustration of photocatalytic mechanism of MTN via microwave-assisted method Based on Adaptation From Jaafar et al. (2015)	41
2.9	Schematic illustration of synthesizing mesoporous $\text{TiO}_2$ via solvothermal method	42
2.10	Schematic illustration of photodegradation mechanism of doped $\text{TiO}_2$	51
2.11	Plasmon nanoparticles enhanced the photocatalytic activity of semiconductor photocatalyst	52
2.12	Schematic illustration of synthesizing catalyst via wet- impregnation method	63
3.1	Detailed methodology flowchart	77
4.1	XRD patterns of MTN-2, MTN-4, MTN-6 and MTN-8	93
4.2	FESEM images of (a) MTN-2, (b) MTN-4, (c) MTN-6 and (d) MTN-8	94





4.3	EDX dot-mapping images of MTN-4 consist of (a) O, (b) Ti	95
4.4	FTIR spectra of MTN-2, MTN-4, MTN-6 and MTN-8	96
4.5	(a) N <sub>2</sub> adsorption-desorption linear isotherms and (b) pore size distribution of MTN-2, MTN-4, MTN-6 and MTN-8	98
4.6	Raman spectra of MTN-2, MTN-4, MTN-6 and MTN-8	101
4.7	% degradation of DBT for MTN-2, MTN-4, MTN-6 and MTN-8	102
4.8	XRD patterns of 5Fe/MTN-2, 5Fe/MTN-4, 5Fe/MTN-6, 5Fe/MTN-8 and Fe	105
4.9	FESEM images of the samples (a) 5Fe/MTN-2, (b) 5Fe/MTN-4, (c) 5Fe/MTN-6 and (d) 5Fe/MTN-8	107
4.10	EDX dot-mapping images of 5Fe/MTN-6 consist of (a) Ti, (b) O and (c) Fe	108
4.11	UV-DRS spectra of (a) 5Fe/MTN-2, (b) 5Fe/MTN-4, (c) 5Fe/MTN-6 and (d) 5Fe/MTN-8	109
4.12	The band gap of prepared (a) 5Fe/MTN-2, (b) 5Fe/MTN-4, (c) 5Fe/MTN-6 and (d) 5Fe/MTN-8 photocatalysts	111
4.13	FTIR spectra of 5Fe/MTN-2, 5Fe/MTN-4, 5Fe/MTN-6, 5Fe/MTN-8 and Fe	112
4.14	(a) N <sub>2</sub> adsorption-desorption linear isotherms and (b) pore size distribution of 5Fe/MTN-2, 5Fe/MTN-4, 5Fe/MTN-6 and 5Fe/MTN-8	114
4.15	Raman spectra of (a) 5Fe/MTN-2, 5Fe/MTN-4, 5Fe/MTN-6 and 5Fe/MTN-8 (b) Fe	117
4.16	% degradation of DBT for 5Fe/MTN-2, 5Fe/MTN-4, 5Fe/MTN-6 and 5Fe/MTN-8	118
4.17	XRD patterns of Fe, MTN-6, 5Fe/MTN-6, 5FeMTN-6/5gC <sub>3</sub> N <sub>4</sub> and gC <sub>3</sub> N <sub>4</sub>	121
4.18	FESEM images of the samples (a) Fe, (b) gC <sub>3</sub> N <sub>4</sub> , (c) MTN-6, (d) 5Fe/MTN-6 and (e) 5FeMTN-6/5gC <sub>3</sub> N <sub>4</sub>	123
4.19	EDX dot-mapping images of 5FeMTN-6/5gC <sub>3</sub> N <sub>4</sub> consist of (a) Ti, (b) O, (c) Fe, (d) C and (e) N	125





4.20	UV-DRS spectra of (a) MTN-6, (b) 5Fe/MTN-6 and (c) 5FeMTN-6/5gC <sub>3</sub> N <sub>4</sub>	126
4.21	The band gap of prepared (a) MTN-6, (b) 5Fe/MTN-6 and (c) 5FeMTN-6/5gC <sub>3</sub> N <sub>4</sub> photocatalysts	128
4.22	FTIR spectra of Fe, MTN-6, 5Fe/MTN-6, 5FeMTN-6/5gC <sub>3</sub> N <sub>4</sub> and gC <sub>3</sub> N <sub>4</sub>	129
4.23	(a) N <sub>2</sub> adsorption-desorption linear isotherms and (b) pore size distribution of MTN-6, 5Fe/MTN-6 and 5FeMTN-6/5gC <sub>3</sub> N <sub>4</sub>	131
4.24	PL spectra of gC <sub>3</sub> N <sub>4</sub> , MTN-6, 5FeMTN-6/5gC <sub>3</sub> N <sub>4</sub> and 5Fe/MTN-6	134
4.25	Raman spectra of (a) MTN-6, 5Fe/MTN-6 and 5FeMTN-6/5gC <sub>3</sub> N <sub>4</sub> (b) Fe	135
4.26	(a) UV-Vis absorption spectra of photodegradation of DBT solution (40 mg/L) in the presence of 5FeMTN-6/5gC <sub>3</sub> N <sub>4</sub> photocatalyst (b) % degradation of DBT for MTN-6, 5Fe/MTN-6, gC <sub>3</sub> N <sub>4</sub> and 5FeMTN-6/5gC <sub>3</sub> N <sub>4</sub>	137
4.27	Proposed mechanism of heterojunction-type photocatalytic system of TiO <sub>2</sub> incorporated with Fe and gC <sub>3</sub> N <sub>4</sub> for photodegradation of DBT Based on Adaptation From Zhu et al. (2018)	139
4.28	% degradation of DBT using 5FeMTN-6/5gC <sub>3</sub> N <sub>4</sub> with addition of 0.00, 0.01, 0.03, 0.06 and 0.09 mL of H <sub>2</sub> O <sub>2</sub>	141
4.29	% degradation of DBT using 5FeMTN-6/5gC <sub>3</sub> N <sub>4</sub> with addition of 1, 3, 5, 7 and 9 g/L of catalyst dosage	145
4.30	% degradation of DBT using 5FeMTN-6/5gC <sub>3</sub> N <sub>4</sub> with 20, 30, 40, 50 and 60 mg/L concentration of DBT solution	147
4.31	The MS product of DBTO <sub>2</sub>	149





## LIST OF ABBREVIATIONS

ADS	Adsorptive desulfurization
AFM	Atomic Force Microscope
AO	Auto-oxidation
AOPs	Advanced Oxidation Processes
AO7	Acid Orange 7
AO10	Acid Orange 10
BaSO <sub>4</sub>	Barium sulfate
BDS	Biodesulfurization
BET	Brunnauer-Emmett-Teller
BJH	Barrett-Joyner-Halenda
BPA	Bisphenol A
BT	Benzothiophene
CAL	Calibration volume
CB	Conduction band
CCDs	Charge-coupled devices
CIDs	Charge-injection devices
CM	Conventional sol-gel
2-CP	2-chlorophenol
4-CP	4-chlorophenol
CR	Congo red
Cr(VI)	Hexavalent chromium





CSTiO <sub>2</sub>	Core-shell TiO <sub>2</sub> nanomaterials
CTAB	Hexadecyltrimethyl-ammonium bromide
CTDs	Charge transfer devices
Cu <sub>2</sub> (OH) <sub>2</sub> CO <sub>3</sub>	Copper hydroxycarbonate
	Initial concentration
C <sub>t</sub>	Concentration at a specific time
2D	Two-dimensional
3D	Three-dimensional
DBT	Dibenzothiophene
DBTO <sub>2</sub>	DBT sulfone
2,4-D	2,4-dichlorophenoxyacetic acid
2,4 DNP	2,4 dinitrophenol
2,4-DP	2,4-dichlorophenoxypropionic acid
E	Band gap energy
e <sup>-</sup>	Electrons
EDS	Extractive desulfurization
EDX	Energy-Dispersive X-ray
FCC	Fluidized catalytic cracking
FEG	Field emission gun
FESEM	Field-Emission Scanning Electron Microscopy
FTIR	Fourier-Transform Infrared
Fe <sub>2</sub> O <sub>3</sub>	Iron (III) oxide
GC	Gas Chromatography
GC-MS	Gas Chromatography-Mass Spectrometer
gC <sub>3</sub> N <sub>4</sub>	Graphitic carbon nitride



$h^+$	Holes
$h$	photon energy
HCl	Hydrochloric acid
HDS	Hydrodesulfurization
He-Ne	Helium-Neon
$HNO_3$	Nitric acid solution
$HO\bullet_2$	Hydroperoxyl radicals
$H_2O_2$	Hydrogen peroxide
$H_2S$	Hydrogen sulphide
IR	Infrared
IWI	Incipient wet impregnation
KBr	Potassium bromide
MB	Methylene Blue
MG	Malachite Green
MO	Methyl Orange
MS	Mass spectrometry
MTN	Mesoporous $TiO_2$ Nanoparticles
MW	Microwave assisted sol-gel
NaOH	Sodium hydroxide
Nd:YAG	Neodymium-Yttrium Aluminium Garnet
Nd: $YVO_4$	Neodymium-Yttrium Ortho-Vanadate
$NH_4F$	Ammonium fluoride
$NH_4OH$	Ammonium hydroxide
4-NP	para-nitrophenol
$O_2\bullet^-$	Superoxide radicals





•OH	Hydroxyl radicals
ODS	Oxidative desulfurization
OV	Oxygen vacancies
Pc	Phthalocyanine
PL	Photoluminescence
PMT	Photomultiplier Tube
PODS	Photocatalytic Oxidative Desulfurization
PTFE	Polytetrafluoroethylene
PVP	Polyvinylpyrrolidone
RhB	Rhodamine B
RR	Remazol Red
RR198	Reactive Red 198



SEM	Scanning Electron Microscopy
SO <sub>x</sub>	Sulfur oxides
SPR	Surface Plasmon Resonance
STM	Scanning Tunneling Microscope
TBOT	Titanium (IV) butoxide
TEM	Transmission Electron Microscopy
TiO <sub>2</sub>	Titanium oxide
TIOS	Titanium (IV) oxysulfate
TNF	TiO <sub>2</sub> nanofiber
TNR	TiO <sub>2</sub> nanorod
TNT	TiO <sub>2</sub> nanotube
TS	Thiophene



TSD	Ti <sup>3+</sup> site defects
TTIP	Titanium Tetraisopropoxide
T20	Tween 20
TX100	Triton X100
US	Ultrasound-assisted impregnation
UV	Ultraviolet
UV-DRS	UV-Visible Diffuse Reflectance Spectroscopy
XRD	X-Ray Diffraction
VB	Valence band
WO <sub>3</sub>	Tungsten oxide
ZnO	Zinc oxide



## APPENDIX LIST

- A UV-Vis Absorption Spectra of DBT Solution at Initial Time
- B Calibration Curve of the Standard DBT in Acetonitrile Solution
- C List of Publications
- D List of Conferences



## CHAPTER 1

### INTRODUCTION

#### 1.1 Background Research

Desulfurization of fuel oils such as diesel, fluidized catalytic cracking (FCC) gasoline, kerosene, jet fuel and heating oil has become an important topic in oil refining industry. Sulfur compounds in fuel oils were encouraged to be removed as they create problems during refining as well as during their commercial use. During refining, these sulfur compounds can cause corrosion problems in pumping, pipeline and refining equipment and also poisoning some of catalysts used in oil processing (Bhutto et al., 2016). During the commercial use of fuel oils, sulfur compounds has released the sulfur oxides ( $\text{SO}_x$ ) through combustion process which lead to

environmental problems such as acid rain, global warming and atmospheric pollution. Besides, the human health was also exposed to negative impact such as respiratory illness, heart disease and asthma (Hitam, Jalil, & Triwahyono, 2018). With the heightened interest for cleaner air and increased stringent environmental regulations for sulfur concentration in fuel worldwide, the plan to achieve little-to-no sulfur fuels (S-content<10 ppm) has been implementing by many developed and developing countries in order to reduce the negative effects on environment and health (Mandizadeh, Salavati-Niasari, & Sadri, 2017; Bhutto et al., 2016). Therefore, the removal of sulfur in fuel has become the hot topic for many researchers nowadays, as intensive studies were needed to find more economical and viable deep desulfurization technologies.

for sulfur removal in fuel oils (Bhutto et al., 2016). HDS process was indeed an efficient method in eliminating acyclic and aliphatic sulfur compounds such as thiols, sulfides and disulfides but it was difficult to reduce heterocyclic sulfur compounds such as thiophene (TS), dibenzothiophene (DBT) and its alkylated derivatives due to their steric hindrance (Hitam, Jalil, & Abdurashed, 2019). Besides, HDS method employs the use of hydrogen at an elevated pressure (20-100 atm of H<sub>2</sub>) and high operating temperature (300-400 °C) which were very costly option for deep desulfurization (Zeelani, Ashrafi, Dhakad, Gupta, & Pal, 2016; Zaid, Kait, & Mutalib, 2016). Therefore, alternative ultra-deep desulfurization processes such as extractive desulfurization (EDS), adsorptive desulfurization (ADS), biodesulfurization (BDS) and oxidative desulfurization (ODS) were necessary to be developed (Mandizadeh et al., 2017).



Among those various desulfurization techniques, ODS was considered as one of the most encouraging techniques for deep desulfurization due to its mild operating conditions which can be operated under low temperature and ambient pressure, as well as its high ability to oxidize and convert refractory sulfur compound such as DBT without the hydrogen utilization (Ding et al., 2015). In fact, photocatalytic oxidative desulfurization (PODS) has gained attention as the promising technique to improve the performance of ODS, since photocatalysis was one of the advanced oxidation processes (AOPs) that can promote outstanding performance in degrading a wide range of toxic compounds under light irradiation. Besides, photocatalysis also provides other advantages such as easy operation, low-cost, sustainable technology, ability to perform at room temperature, environmental friendliness and capability to transform toxic contaminants into harmless products with high selectivity (Hitam et al., 2019). PODS was assumed to be a potential method to solve this problem since it promotes high catalytic activity, safety, low energy consumption and recycling ability (Zhu et al., 2014). This finding was supported by Miao et al. (2016) which stated that, PODS has been known to be a promising method as it provides a green path to photooxidize sulfur species to highly polar sulfoxides or sulfone product with the presence of ultraviolet (UV) or visible light as the energy source.

In order to improve the PODS activity, some modifications of the existing catalysts have been done by researchers. Generally, the photocatalytic efficiency can be improved by several techniques such as synthesise of high surface area materials, the use of support material, coupling with other semiconductors, formation of a defect structure to improve charge-carrier separation and coupling with organic or inorganic materials (Hitam et al., 2019).







Over the last few decades, various photocatalysts have been developed for PODS and semiconductor-based catalysts such as zinc oxide (ZnO), titanium oxide (TiO<sub>2</sub>), tungsten oxide (WO<sub>3</sub>), etc were known to exhibit excellent photocatalytic performance (Kang et al., 2019). The presence of photocatalyst in PODS was crucial as it promotes the oxidation of sulfur-containing compounds by enhancing the rate of active species formation and improving the charge transfer. From previous studies, the instantaneous increased of sulfur removal depends on the increasing amount of photocatalyst (Aazam, 2014; Abdelaal & Mohamed, 2014). However, the decreasing in sulfur removal was occurred as the further addition of photocatalyst was beyond the optimum value. It was due to the excess amount of catalyst tends to inhibit the light source and decrease photoelectron productivity which results in reducing the photocatalytic oxidation efficiency (Li et al., 2016). In this perspective, TiO<sub>2</sub> as semiconductor photocatalyst has received considerable attention due to its commercial availability, high chemical stability and excellent catalytic properties (Petronella et al., 2017). This finding was supported by Hosseini and Faghihian (2019) which stated that, TiO<sub>2</sub> was one of various semiconductors that has been widely utilized in photodegradation experiments due to its elevated photocatalytic activity, photochemical stability, affordability and safe to use.

## 1.2 Problem Statement

TiO<sub>2</sub> has been widely used in the PODS of DBT in fuel due to its promising photoactivity, non-toxicity, chemical stability and low cost (Hitam et al., 2019). However, TiO<sub>2</sub> has several drawbacks that limit its practical application such as has





narrow spectrum utilization due to its wide band gap (3.2 eV) and rapid recombination of electron-hole pairs (Jaafar, Jalil, & Triwahyono, 2017). Modification of  $\text{TiO}_2$  into a mesoporous structure was reported successfully increased the stability and photoactivity of the photocatalyst (Zhang et al., 2020). Besides that, the modification of  $\text{TiO}_2$  with transition metal and polymeric carbon material can also enhance the photoactivity of the photocatalyst (Sadanandam, Zhang, & Scurrrell, 2018; Zaid et al., 2016). Among those various metallic dopants, Fe was considered to be the promising candidate for this research due to the ionic radius of  $\text{Fe}^{3+}$  (0.69 Å) was nearly similar to  $\text{Ti}^{4+}$  (0.745 Å), which in turn can help the  $\text{Fe}^{3+}$  ions to be easily incorporated into  $\text{TiO}_2$  crystal lattice. As a result,  $\text{Fe}^{3+}$  will restrict the recombination of electron-hole pairs by performing as a charge carrier trap, which can significantly enhance the photoactivity (Marami, Farahmandjou, & Khoshnevisan, 2018). In recent years,  $\text{gC}_3\text{N}_4$  as a well-known polymer has got much attention from researchers due to its advantages such as low cost, electronic characteristics, high chemical and thermal stability, and also an efficient non-metallic photocatalyst (Gahlot, Dappozze, Mishra, & Guillard, 2021; Abedini, Allahyari, & Rahemi, 2021). The incorporation of both Fe and  $\text{gC}_3\text{N}_4$  can improve the separation of photogenerated electron-hole pairs as it can form heterojunction known as Z-scheme mechanism that allow the reduction and oxidation reactions occurred from different sites of photocatalyst (Zhu, Murugananthan, Gu, & Zhang, 2018). Nevertheless, there was no study has been done to investigate the potential of mesoporous  $\text{TiO}_2$  with incorporation of Fe and  $\text{gC}_3\text{N}_4$  in the degradation of DBT under UV light yet.





### 1.3 Research aim

The aim of this research was to investigate the photocatalytic efficiency of mesoporous  $\text{TiO}_2$  nanoparticles (MTN) with addition of Fe and  $\text{gC}_3\text{N}_4$  for the photodegradation of DBT in model fuel under UV light irradiation.

### 1.4 Research Objectives

The objectives of this research are:

- 1) To synthesize MTN via sol-gel method and modification with Fe and  $\text{gC}_3\text{N}_4$  via wet-impregnation method.
- 2) To study the physicochemical properties of prepared photocatalysts.
- 3) To elucidate the photocatalytic activities of prepared photocatalysts in photodegradation of DBT under UV light.

### 1.5 Scope of study

In this research, MTN was synthesized via sol-gel method and modified with Fe and  $\text{gC}_3\text{N}_4$  as a photocatalyst for the photodegradation of DBT in model oil under UV light irradiation. Different aging time ( $x = 2, 4, 6$  and  $8$  days) were used to prepare the bare MTN- $x$ . Then, 5wt% of Fe was added into MTN- $x$  to form 5Fe/MTN- $x$  before being modified with 5wt% of  $\text{gC}_3\text{N}_4$  dopant by wet-impregnation method and denoted





as 5FeMTN-x/5gC<sub>3</sub>N<sub>4</sub>. Then, the physicochemical properties of prepared photocatalysts were characterized using X-ray diffraction (XRD), Surface area analysis (BET), UV-Visible diffuse reflectance spectroscopy (UV-DRS), Field-Emission scanning electron microscopy (FESEM), Fourier-transform infrared spectroscopy (FTIR), Photoluminescence (PL) and Raman spectroscopy. The photocatalytic activity of 5FeMTN-x/5gC<sub>3</sub>N<sub>4</sub> was compared with undoped MTN-x and also 5Fe/MTN-x in order to determine the effectiveness of the combination of Fe and gC<sub>3</sub>N<sub>4</sub> into MTN for photodegradation of DBT in model oil under UV light. After photocatalytic reaction, the degraded DBT solution was characterized by GC-MS to determine the degradation product.

