



**Development of N-Ce-AC-TiO₂ Composite via Sol-Gel
Assisted Microwave Irradiation for the Adsorption-
Photodegradation of Antibiotics**

by

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TABLE OF CONTENTS

	PAGE
DECLARATION OF THESIS	ii
PERMISSION TO USE	iii
ACKNOWLEDGEMENT	iv
TABLE OF CONTENTS	v
LIST OF TABLES	xi
LIST OF FIGURES	xiii
LIST OF ABBREVIATIONS	xvi
LIST OF SYMBOLS	xix
ABSTRAK	xxii
ABSTRACT	xxiii
CHAPTER 1 : INTRODUCTION	1
1.1 Background	1
1.2 Problem Statement	3
1.3 Research Questions	5
1.4 Research Objectives	6
1.5 Research Scope	7
1.6 Novelty	8
CHAPTER 2 : LITERATURE REVIEW	9
2.1 Antibiotics	9
2.2 Photodegradation	11

2.3	Titanium Dioxide as Photocatalyst	12
2.4	Synthesis of TiO ₂ as Modified Photocatalyst	15
2.4.1	Doping with Non-Metal	15
2.4.2	Doping with Rare Earth Metals	16
2.4.3	Co-doping with Non-Metal and Rare Earth Metal	17
2.5	Mechanism of Photocatalysis	18
2.6	Activated Carbon	19
2.7	Activated Carbon Doped TiO ₂	20
2.8	Sol-Gel Route in Production of AC-TiO ₂ -Based Photocatalyst	21
2.9	Microwave Irradiation Method for Photocatalyst Activation	22
2.10	Factor Effecting Preparation of Photocatalyst	23
2.10.1	Dopant Dosage	23
2.10.2	Microwave Power Radiation	24
2.11	Design of Experiment, DOE	25
2.12	Photocatalytic Activity	27
2.12.1	Operational Factors Influencing the Photocatalytic Activity	27
2.12.2	Effect of Initial Concentration and Contact Time	27
2.12.3	Effect of Temperature	28
2.12.4	Effect of pH	29
2.13	Adsorption Isotherm	33
2.13.1	Langmuir Isotherm	34
2.13.2	Freundlich Isotherm	35
2.13.3	Temkin Isotherm	35
2.13.4	Dubinin-Radushkevich's Model	36
2.14	Degradation Kinetics	37
2.14.1	Pseudo-First Order	37
2.14.2	Pseudo-Second Order	37

2.14.3	Langmuir-Hinshelwood	38
2.15	Adsorption Mechanism in Photocatalyst	39
2.15.1	Intraparticle Diffusion	39
2.15.2	Boyd Model	39
2.16	Thermodynamic Study	40
CHAPTER 3 : METHODOLOGY		42
3.1	Introduction	42
3.2	Materials and Reagents	45
3.3	Synthesis of N-Ce-AC-TiO ₂ as Photocatalyst Composite	46
3.4	Design of Experiment, DOE	47
3.5	Photocatalyst Characterization	50
3.5.1	Crystallographic Structure Analysis	50
3.5.2	Material Identification Analysis	51
3.5.3	Optical Properties Analysis	52
3.5.4	Surface Morphology Analysis	52
3.5.5	Elemental Composition Analysis	53
3.5.6	Surface Area Analysis	53
3.6	Photocatalytic Activity of Antibiotics	54
3.7	Adsorption Experiments	56
3.7.1	Effect of Initial Concentration	56
3.7.2	Effect of Contact Time	57
3.7.3	Effect of Temperature	57
3.7.4	Effect of pH	57
3.8	Adsorption Isotherm	57
3.9	Degradation Kinetics	58
3.10	Adsorption Mechanism by N-Ce-AC-TiO ₂	58
3.11	Scavengers Study	58

3.12	Thermodynamic Study	59
3.13	Photocatalyst Regeneration	59
CHAPTER 4 : RESULTS & DISCUSSION		61
4.1	Introduction	61
4.2	Experimental Design Approach	61
4.2.1	Impact of Independent Variables on the Response	70
4.2.2	Response Optimization and Model Validation	77
4.3	Characterization of Synthesized Photocatalyst	79
4.3.1	Phase Identification by XRD Analysis	79
4.3.2	Material Identification by FTIR Analysis	81
4.3.3	Optical Properties by Ultraviolet-visible-near-infrared (UV-vis-NIR) Analysis	83
4.3.4	Surface Morphology by Scanning Electron Microscope (SEM) Analysis	87
4.3.5	Elemental Composition by Energy-dispersive X-ray (EDX) Analysis	89
4.3.6	Surface Area Analysis, Brunauer-Emmett-Teller (BET)	90
4.4	Amoxicillin (AMX) and Tetracycline (TC) Removal Efficiency Under Different Experiment Conditions.	94
4.4.1	Effect of Contact Time and Initial Concentration on Adsorption Equilibrium	94
4.4.2	Effect of Temperature on Adsorption Equilibrium	97
4.4.3	Effect of pH on Adsorption Equilibrium	99
4.5	Adsorption Isotherms Study	102
4.6	Degradation Kinetics Study	109
4.7	Investigation on Photocatalytic Mechanism	115
4.7.1	Scavenger Quenching Test	115
4.7.2	Intraparticle Diffusion and Boyd Model	117
4.1	Thermodynamic Study	121

4.2	Adsorption-Photodegradation Mechanism of N-Ce-AC-TiO ₂	123
4.3	Reusability of N-Ce-AC-TiO ₂	126
CHAPTER 5 : CONCLUSION		128
5.1	Conclusion	128
5.2	Recommendations	130
REFERENCES		132
APPENDIX A		162
APPENDIX B		163
APPENDIX C		164
APPENDIX D		165
APPENDIX E		166
APPENDIX F		168
APPENDIX G		170
APPENDIX H		172
APPENDIX I		174
APPENDIX J		176
APPENDIX K		180
APPENDIX L		181
APPENDIX M		185
APPENDIX N		187
APPENDIX O		189
LIST OF PUBLICATIONS		190

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LIST OF TABLES

		PAGE
Table 2.1	Amoxicillin and tetracycline structure and properties.	10
Table 2.2	Photocatalytic activity using TiO ₂ based photocatalyst for antibiotics removal.	13
Table 2.3	Overall mechanism pathway for photocatalysis for TiO ₂ photocatalyst.	17
Table 2.4	Recent study on effect of initial concentration and contact time using various photocatalyst for antibiotics removal.	29
Table 2.5	Recent study on effect of adsorption system temperature range using various photocatalyst for antibiotics removal.	30
Table 2.6	Recent study on effect of pH range using various photocatalyst for antibiotics removal.	31
Table 2.7	Adsorption isotherm and kinetic model for various antibiotic and catalyst.	33
Table 3.1	Chemical properties and description of reagents and antibiotics.	43
Table 3.2	Variable factors and levels.	46
Table 3.3	Factors CCD matrix and experimental data of antibiotics removal.	47
Table 4.1	Factors CCD matrix and experimental data of tetracycline (TC) and amoxicillin (AMX) removal.	62
Table 4.2	Analysis of variance (ANOVA) of quadratic model for removal of TC.	63
Table 4.3	Analysis of variance (ANOVA) of quadratic model for removal of AMX.	64
Table 4.4	Statistical parameters generated from ANOVA for developed model of TC and AMX degradation.	67
Table 4.5	Optimization validation for adsorption and photodegradation of TC and AMX.	78

	PAGE
Table 4.6	Optimization validation for adsorption and photodegradation of TC and AMX. 80
Table 4.7	Elemental compositions of synthesized photocatalyst from EDX mapping analysis. 89
Table 4.8	Specific pore parameters and surface area for AC, TiO ₂ , AC-TiO ₂ , N-AC-TiO ₂ , Ce-AC-TiO ₂ , and N-Ce-AC-TiO ₂ . 91
Table 4.9	Comparison of photocatalytic performance influenced by the specific surface area, pore structure, and pore volume for removal of amoxicillin and tetracycline using various photocatalyst in recent study. 93
Table 4.10	Removal efficiency of amoxicillin (AMX) and tetracycline (TC) by AC, AC-TiO ₂ , N-AC-TiO ₂ , Ce-AC-TiO ₂ , and N-Ce-AC-TiO ₂ under system condition: 0.20 g photocatalyst, initial concentration of 10 mg L ⁻¹ , 30 °C of solution temperature, under UV light irradiation. 97
Table 4.11	Isotherms parameters for adsorption of tetracycline (TC) and amoxicillin (AMX) by N-Ce-AC-TiO ₂ photocatalyst with experimental conditions: pH 7 and temperature 30 °C, 45 °C, and 60 °C. 103
Table 4.12	Maximum monolayer adsorptions of AMX and TC onto different AC or TiO ₂ based adsorbents. 106
Table 4.13	Separation factor, R _L on the adsorption of tetracycline (TC) and amoxicillin (AMX) by N-Ce-AC-TiO ₂ composite for three temperature values. 107
Table 4.14	Kinetics model parameters for adsorption of tetracycline (TC) and amoxicillin (AMX) on N-Ce-AC-TiO ₂ photocatalyst at six different initial concentration, pH 7 and 30 °C. 110
Table 4.15	Model parameters for intraparticle diffusion and Boyd model of tetracycline (TC) and amoxicillin (AMX) on N-Ce-AC-TiO ₂ photocatalyst at 6 different initial concentration, pH 7 and temperature of 30 °C. 120
Table 4.16	Thermodynamic parameters for AMX and TC adsorption. 122

LIST OF FIGURES

		PAGE
Figure 2.1	Phase of TiO ₂ (a) rutile; (b) anatase; (c) brookite.	13
Figure 2.2	General electron transfer mechanism in (a) rare earth metal and (b) non-metal.	17
Figure 2.3	Schematic diagram on mechanism of TiO ₂ photocatalyst.	19
Figure 2.4	Difference heating rate between conventional heating and microwave heating.	22
Figure 3.1	Flowchart of methodology in development of N-Ce-AC-TiO ₂ composite for adsorption-photodegradation of antibiotics.	44
Figure 3.2	Schematic diagram of self-assembled photoreactor for photocatalytic study.	55
Figure 4.1	Graphical plot of predicted versus actual values for (a) TC and (b) AMX removal; normal probability of the residuals for (c) TC and (d) AMX removal; studentized residuals versus predicted for (e) TC and, (f) AMX.	68
Figure 4.2	Perturbation plot for (a) TC and (b) AMX removal.	69
Figure 4.3	Surface plots of 3D response and 2D contour of dosage influence of (a) N with Ce (0.02 g – 0.20 g), (b) AC (0.10 g – 0.50 g) with N (0.02 g – 0.20 g), and, (c) AC (0.10 g – 0.50 g) with Ce (0.02 g – 0.20 g) in synthesis of N-Ce-AC-TiO ₂ photocatalyst for TC removal.	71
Figure 4.4	Surface plots of 3D response and 2D contour of dosage influence of (a) N with Ce (0.02 g – 0.20 g), (b) AC (0.10 g – 0.50 g) with N (0.02 g – 0.20 g), and, (c) AC (0.10 g – 0.50 g) with Ce (0.02 g – 0.20 g) in synthesis of N-Ce-AC-TiO ₂ photocatalyst for AMX removal.	72
Figure 4.5	Surface plots of 3D response and 2D contour of microwave power, W influence (600 W – 800 W) with dosage of (a) N (0.02 g – 0.20 g), (b) Ce (0.02 g – 0.20 g), and, (c) AC (0.02 g – 0.20 g), in synthesis of N-Ce-AC-TiO ₂ photocatalyst for TC removal.	75

	PAGE	
Figure 4.6	Surface plots of 3D response and 2D contour of microwave power, W influence (600 W – 800 W) with dosage of (a) N (0.02 g – 0.20 g), (b) Ce (0.02 g – 0.20 g), and, (c) AC (0.02 g – 0.20 g), in synthesis of N-Ce-AC-TiO ₂ photocatalyst for AMX removal.	76
Figure 4.7	X-ray diffraction patterns of pristine AC, AC-TiO ₂ , N-AC-TiO ₂ , Ce-AC-TiO ₂ , and N-Ce-AC-TiO ₂ photocatalysts.	81
Figure 4.8	FTIR spectra of synthesized photocatalyst, AC, AC-TiO ₂ , N-AC-TiO ₂ , Ce-AC-TiO ₂ , and N-Ce-AC-TiO ₂ .	83
Figure 4.9	The plot of Kubelka-Munk function for determination of band gap energy of (a) TiO ₂ and AC-TiO ₂ , (b) N-Ce-AC-TiO ₂ , N-AC-TiO ₂ and Ce-AC-TiO ₂ .	84
Figure 4.10	The plot of absorption spectra of (a) TiO ₂ , and AC-TiO ₂ , (b) N-AC-TiO ₂ , Ce-AC-TiO ₂ and N-Ce-AC-TiO ₂ .	86
Figure 4.11	SEM images for photocatalyst (a) AC; (b) AC-TiO ₂ ; (c) N-AC-TiO ₂ ; (d) Ce-AC-TiO ₂ ; and (e) N-Ce-AC-TiO ₂ .	88
Figure 4.12	The plots of absorption spectra of N-Ce-AC-TiO ₂ .	90
Figure 4.13	Effect of initial concentration and contact time of (a) TC and (b) AMX on its degradation using N-Ce-AC-TiO ₂ at pH value 7 and 30 °C.	95
Figure 4.14	Effect of temperature on removal efficiency of TC and AMX using N-Ce-AC-TiO ₂ at pH value 7, contact time 190 min, and initial concentration 10 mg L ⁻¹ .	98
Figure 4.15	Point of zero charge (PZC) plot for composite N-Ce-AC-TiO ₂ .	99
Figure 4.16	Effect of pH on degradation of TC and AMX using N-Ce-AC-TiO ₂ composite at temperature 30 °C, contact time 190 min and initial concentration of 10 mg L ⁻¹ .	101
Figure 4.17	Adsorption isotherm model plot for degradation of (a) TC and (b) AMX, using N-Ce-AC-TiO ₂ at temperature 30 °C, contact time 130 min and pH 7.	105
Figure 4.18	Degradation kinetic plot model of pseudo-first order and pseudo-second order for degradation of (a) TC and (b) AMX, using N-Ce-AC-TiO ₂ at temperature 30 °C, contact time 100 min and pH 7 under 7 W UV light irradiation.	111

	PAGE
Figure 4.19 Langmuir-Hinshelwood plot model and kobs versus concentration for degradation of (a) - (b) TC and (c) – (d) AMX, using N-Ce-AC-TiO ₂ at temperature 30 °C, and pH 7 under 7 W UV light irradiation in 100 min.	113
Figure 4.20 Effect of scavenger agent on AMX and TC removal by N-Ce-AC-TiO ₂ at initial concentration 10 mg L ⁻¹ , pH 7 and temperature 30 °C.	116
Figure 4.21 Intraparticle diffusion plot on (a) TC and (b) AMX removal by N-Ce-AC-TiO ₂ at pH 7 and temperature 30 °C.	119
Figure 4.22 Proposed reaction mechanism of N-Ce-AC-TiO ₂ photocatalyst for degradation of TC and AMX under UV light.	125
Figure 4.23 Proposed interaction mechanism of N-Ce-AC-TiO ₂ photocatalyst for degradation of TC and AMX under UV light.	126
Figure 4.24 Regeneration cycle of N-Ce-AC-TiO ₂ in degradation of AMX and TC at initial concentration of 10 mg L ⁻¹ , temperature of 30 °C, and pH 7.	127

LIST OF ABBREVIATIONS

AC	Activated carbon
AC-TiO ₂	Activated carbon doped titanium dioxide
Alg	Alginate
AMX	Amoxicillin
ANOVA	Analysis of variance
AP	Adeq precision
Av	Aloe vera
BEN	Bentonite
BET	Brunauer-Emmett-Teller
Bi	Bismuth
C	Carbon
C-LDH	Concrete-based hydrotalcites
C-N=O	Nitroso
C ₃ N ₄	Carbon nitride
CB	Conduction band
CCD	Central composite design
Ce	Cerium
Ce-AC-TiO ₂	Cerium doped AC-TiO ₂
Ce ₂ O ₃	Cerium (III) oxide
Ce ³⁺	Cerium ion
Ce ⁴⁺	Cerium ion
CeO ₂	Ceric oxide
Cl	Chlorine
CO ₂	Carbon dioxide
Cu	Copper
DOE	Design of Experiment
EDTA	Ethylenediaminetetraacetic acid
EDX	Energy dispersive X-ray
EPs	Emerging pollutants
et al.,	And others
eV	Electron volt
F	Fluorine

Fe	Iron
FTIR	Fourier transform infrared
FWHM	Full width at half maximum
H	Hydrogen
H ₂ O	Water
H ₂ O ₂	Hydrogen peroxide
H ₃ PO ₄	Phosphorus acid
HCl	Hydrochloric acid
HDTMA	Hexadecyltrimethylammonium
HO-C=O	Carboxyl
<i>hν</i>	Having energy
I	Iodine
IPA	Isopropyl alcohol
JCPDS	Joint Committee on Powder Diffraction Standards
K	Potassium
KBr	Potassium bromide
KOH	Potassium hydroxide
MBC	Biochar
min	Minute
Mo	Molybdenum
MWNTs	Multi-Walled Carbon Nanotubes
N	Nitrogen
N-AC-TiO ₂	Nitrogen doped AC-TiO ₂
N-Ce-AC-TiO ₂	Nitrogen-Cerium co-doped AC-TiO ₂
NaOH	Sodium hydroxide
Ni	Nickle
No.	Number
O	Oxygen
P	Phosphorus
pBQ	p-Benzoquinone
Pc	Phthalocyanine
Pd	Palladium
PFO	Pseudo-first order
PPCPs	Pharmaceutical and personal care products

PSO	Pseudo-second order
PVFD	Polyvinylidene fluoride
RE	Rare earth
RSM	Response surface methodology
S	Sulfur
SEM	Scanning electron microscope
TC	Tetracycline
TD	Triazine dendrimer
Ti	Titanium
TiO ₂	Titanium dioxide
TTIP	Titanium (IV) isopropoxide
UV	Ultraviolet
UV-vis-NIR	Ultraviolet vis near infrared region
V	Vanadium
V	Visible li
VB	Valence band
VL	Visible light
Vo	Oxygen vacancies
Xe	Xenon lamp
XRD	X-ray diffraction
Zn	Zinc
ZnCl ₂	Zinc chloride
ZnO	Zinc oxide

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LIST OF SYMBOLS

b_i	Linear coefficient
b_{ii}	Quadratic coefficient
b_{ij}	Interaction coefficient
b_o	Constant coefficient
B_t	Boyd's equation
C_{BL}	Boundary layer thickness
C_e	Final antibiotic concentration
C_t	Antibiotic concentration at time t
C_0	Initial antibiotic concentration
D_i	Diffusion coefficient
e^-	Electrons
e_{CB}^-	Electron on conduction band
E_g	Energy band gap
h^+	Holes
h_{VB}^+	Holes on valence band
HO_2^-	Hydroperoxide ion
k_2	Equilibrium rate constant
k_{eq}	Equilibrium constant
N_A	Avogadro Number
n_m	Monolayer activity
$\frac{P}{P_o}$	Relative pressure
P_o	Pressure at equilibrium phase
q_e	Amount of antibiotic adsorbed on photocatalyst surface
q_t	Amount of antibiotic adsorbed on photocatalyst surface at time t
S_{BET}	Specific surface area
x_1	Urea dose
x_2	Cerium (III) nitrate hexahydrate dose
x_3	Activated carbon dose
x_4	Microwave power
X_i	Factor variable and response
X_j	Independent factor
α'	Initial adsorption rate

β'	Elovich desorption constant
β	Beta
ε	Error
$^{\circ}$	Degree
λ	X-ray wavelength
β	Full width at half maximum
θ	Bragg angle
&	And
%	Percentage
$^{\circ}\text{C}$	Celcius
ΔG	Gibbs free energy
ΔH	Enthalphy
ΔS	Entropy
$\cdot\text{HO}_2$	Hydroperoxyl radicals
$\cdot\text{O}_2^-$	Superoxide radicals or radical species
$\cdot\text{OH}$	Hydroxyl radicals
2θ	2 theta
2D	Two-dimensional object
3D	Three-dimensional object
a	Section area of molecule adsorbed by adsorbent
A	Initial adsorption rate or desorption constant
A_T	Temkin constant for heat adsorption
B	Elovich constant
B_{DR}	Dubinin-Radushkevich constant
B_T	Temkin constant for adsorption potential
C	BET constant
cm	Centimeter
Cu $K\alpha$	Copper K-alpha
D	Crystalline sizes
df	Degree of freedom
E	Adsorption energy
$F(R)$	Kubelka-Munk function
g	Gram
GHz	Gigahertz
h	Hour
h	Initial adsorption rate

h^+	Holes
k	Constant
K	Absorption coefficient
K	Kelvin
K_F	Freundlich constant
kJ	Kilojoule
K_L	Langmuir constant
kV	Kilovolt
L	Liter
m^2	Square meter
mA	Miliampere
mg	Miligram
mL	Mililiter
mm	Milimeter
mol	Mole
n	Nucleophile donates lone-pair
n_f	Heterogeneity factor
nm	Nanometer
P	Pressure in gas phase
pH_{pzc}	Isoelectric point
Q_{DR}	Amount of antibiotic adsorbed by photocatalyst
Q_m	Saturation capacity
R	Reflectance
R	Universal gas constant
R_L	Separation factor
rpm	Rotation per minute
S	Scattering coefficient
s	Second
t	Time
T	Temperature
W	Watt
W	Volume of gas adsorbed at relative pressure
wt	Weight
Y	Quadratic regression response
π	Pi

Pembangunan Komposit N-Ce-AC-TiO₂ Melalui Pendekatan Sol-Gel Dengan Bantuan Radiasi Gelombang Mikro Dalam Penjerapan-Fotodegradasi Antibiotik

ABSTRAK

Pencemaran antibiotik yang merebak secara meluas di dalam persekitaran telah menyebabkan munculnya cabaran global disebabkan oleh kesan negatifnya kepada ekologi, kesihatan dan kesejahteraan manusia. Oleh itu, fotodegradasi menjadi kaedah yang baik bagi menyingkirkan bahan cemar ini dalam merawat pencemaran air. Dengan itu, kajian ini bertujuan untuk mensistesis N-Ce-AC-TiO₂ fotomangkin melalui pendekatan sol-gel dengan bantuan radiasi gelombang mikro dalam penjerapan-fotodegradasi *amoxicillin* (AMX) dan *tetracycline* (TC). Kaedah Rangsangan Permukaan (RSM) digunakan bagi menentukan kondisi optimum dalam proses penyediaan fotomangkin. N-Ce-AC-TiO₂ menunjukkan fasa anatase yang stabil dengan size kristal 5.48 nm, kawasan permukaan Brunauer-Emmett-Teller (BET) yang bagus iaitu 278.87 m² g⁻¹ dan jurang tenaga yang rendah yang mana signifikasinya dikurangkan daripada TiO₂ asli 3.20 eV kepada 2.16 eV. Daripada kajian pengoptimuman, N-Ce-AC-TiO₂ yang disintesis dengan 0.02 g nitrogen, 0.20 g cerium, 0.50 g karbon teraktif dan diaktifkan dengan 600 W sinaran kuasa gelombang mikro dalam masa 15 minit dapat mencapai tahap degradasi maksimum bagi TC dan AMX pada nilai 93% ± 0.23 dan 96% ± 0.16 dalam masa 100 minit dibawah sinaran UV, bagi tahap kepekatan pemula 10 mg L⁻¹, pada suhu 30 °C, dengan larutan pH 7 bagi TC, dan pH 6 bagi AMX. Spesis aktif yang paling menyumbang kepada proses fotodegradasi adalah lohong (h⁺) dan radikal superoksida (·O₂⁻). Degradasi TC mematuhi isoterma Langmuir, model kinetik pseudo-tertib pertama (PFO) (R²: 0.999), dan Langmuir-Hinshelwood (R²: 0.988). Manakala AMX mematuhi isoterma Langmuir, model kinetik pseudo-tertib pertama (PFO) (R²: 0.999), dan Langmuir-Hinshelwood (R²: 0.976). Perubahan pada entalpi (ΔH) (TC: 27.65 kJ mol⁻¹, AMX: 15.50 kJ mol⁻¹), entropi (ΔS) (TC: 0.09 kJ mol⁻¹, AMX: 0.05 kJ mol⁻¹), dan tenaga pengaktifan bebas Gibbs (ΔG) (TC: -1.05 kepada -3.88 kJ mol⁻¹, AMX: -1.16 kepada -2.80 kJ mol⁻¹) mencadangkan proses penjerapan adalah endoterma, bersesuaian dan spontan bagi kedua-dua antibiotik. Antara interaksi yang berkemungkinan terlibat diantara TC dan AMX dengan N-Ce-AC-TiO₂ termasuk *kation* – *π*, interaksi elektrostatik, ikatan hidrogen, *n* – *π*, dan *π* – *π*. Selain itu, kestabilan N-Ce-AC-TiO₂ disahkan melalui 80% kecekapan penyingkiran selepas kitaran yang ke-empat (AMX) dan ke-lima (TC). Secara asasnya, hasil kerja ini menawarkan perspektif baru dalam mencipta fotomangkin yang efektif, boleh diulang pakai, dan ditambah baik, menggunakan pendekatan sintesis dengan bantuan gelombang mikro untuk penyahlumusan antibiotik.

Development of N-Ce-AC-TiO₂ Composite via Sol-Gel Assisted Microwave Irradiation for the Adsorption-Photodegradation of Antibiotics

ABSTRACT

The widespread antibiotic pollution in the environment has emerged as a global challenge due to its adverse impacts on ecology, human health, and well-being. Hence, photodegradation is the promising method to remove this pollutant in polluted water treatment. Therefore, this study aims to synthesize N-Ce-AC-TiO₂ photocatalyst via the sol-gel approach with microwave irradiation assistance in the adsorption-photodegradation of amoxicillin (AMX) and tetracycline (TC). Response surface methodology (RSM) was used to determine the optimum conditions in preparing the photocatalyst. N-Ce-AC-TiO₂ showed a stable anatase phase with a crystallite size of 5.48 nm, a good Brunauer-Emmett-Teller (BET) surface area of 278.87 m² g⁻¹ and a low band gap energy, which was reduced significantly from 3.20 eV of pristine TiO₂ to 2.16 eV. From the optimization studies, N-Ce-AC-TiO₂ synthesized with 0.02 g nitrogen, 0.20 g cerium, 0.50 g activated carbon, and activated with irradiation power of 600 W in 15 mins achieved maximum degradation for TC and AMX at 93% ± 0.23 and 96% ± 0.16 within 100 min under UV light irradiation for an initial concentration of 10 mg L⁻¹, at 30 °C, with solution pH 7 for TC and pH 6 for AMX. Active species that contribute to the photodegradation process the most are holes (h⁺) and superoxide radicals (·O₂⁻). The TC degradation was appropriately obeyed by Langmuir isotherms, pseudo-first order (R²: 0.999), and Langmuir-Hinshelwood (R²: 0.988) kinetic models. The AMX degradation obeyed Langmuir isotherms, pseudo-first order (R²: 0.999), and Langmuir-Hinshelwood (R²: 0.976) kinetic models. The change in enthalpy (ΔH) (TC: 27.65 kJ mol⁻¹, AMX: 15.50 kJ mol⁻¹), entropy (ΔS) (TC: 0.09 kJ mol⁻¹, AMX: 0.05 kJ mol⁻¹), and Gibbs free energy (ΔG) (TC: -1.05 to -3.88 kJ mol⁻¹, AMX: -1.16 to -2.80 kJ mol⁻¹) suggested that the adsorption process was endothermic, favourable, and spontaneous for both antibiotics. Possible interactions involved between TC and AMX with N-Ce-AC-TiO₂ include *cationic* – π, electrostatic interaction, hydrogen bonding, *n* – π, and π – π interactions. Additionally, N-Ce-AC-TiO₂ stability was confirmed through 80% removal efficiency after the fourth (AMX) and fifth (TC) cycles. In essence, this work offers new perspectives on creating effective, reusable, and improved photocatalysts using a convenient microwave-assisted synthesis approach for antibiotic decontamination.

CHAPTER 1 : INTRODUCTION

1.1 Background

Antibiotics are a type of medicine that is used to fight or treat bacterial infection. It is widely used in human medicine, agriculture, and livestock. However, due to uncontrolled usage of antibiotics worldwide, it led to pollution that contributed to the potential harm in the ecological environment and raised concern when discussing on maintaining environmental sustainability (Coronado-Apodaca et al., 2023; Noorani et al., 2024; Suhan et al., 2023). Antibiotic pollution usually originates from the pharmaceutical industry (Ranjan et al., 2022), excretion of incomplete metabolism of antibiotics in humans or animals from bodies after consumption (Haffiez et al., 2022), hospital waste (Barathe et al., 2024), and pharmaceutical and personal care products (PPCPs) from daily use (Gautam et al., 2024). Antibiotic traces can be found in sediment, wastewater, and water surfaces (Aguilar-Aguilar et al., 2023; Ahmad et al., 2022; Lu et al., 2023).

Antibiotics like amoxicillin (AMX) (Al-Musawi et al., 2023; Palacio et al., 2021), ciprofloxacin (Rodríguez-González et al., 2022; Thuan et al., 2022), erythromycin (Low et al., 2021), and tetracycline (TC) (Leichtweis et al., 2022; Zhang et al., 2024) are the most common antibiotics associated with the pollutants found in the environment. It was reported that 80-90% of consumed antibiotics were discharged into the environment in their original form (Obayomi et al., 2023). Improper management can lead to resistance development, which can affect our ecology (Domingo-Torner et al., 2023), wildlife and aquatic systems, and bring negative impacts on human health and well-being (Zhao et al., 2024). The increase in detection of antibiotics is challenging due to the lack specific established regulations to monitor their removal and treatment process. Therefore, the

development of plausible methods for managing antibiotic traces in polluted water is a crucial matter for environmental sustainability.

There are several established methods used to remove excess antibiotics in water, such as membrane treatment (Hassan et al., 2021), advanced oxidation process (Akbari et al., 2021), reverse osmosis (Zare et al., 2021), membrane separation (Wang et al., 2023), biological treatment (Pu et al., 2022), adsorption (Stylianou et al., 2021), constructed wetlands (Zhao et al., 2023), and photocatalytic (Marinho et al., 2022). However, these methods have shortcomings such as high cost, long treatment duration, fouling, low removal rates, and incomplete degradation of antibiotics (Wu et al., 2023; Chin et al., 2023). Currently, a combination of adsorption and photodegradation techniques is the best alternative method due to its simple operation, low energy consumption, and high efficiency in antibiotic removal (Ammar et al., 2024; Lan et al., 2024). Degradation of antibiotics using adsorption and photodegradation was observed in the removal of AMX (Wahyuni et al., 2024), ciprofloxacin (Ammar et al., 2024), norfloxacin (Lan et al., 2024), TC (Khanmohammadi et al., 2024), and quinolone antibiotics (Almasi Jaf et al., 2024).

Titanium dioxide (TiO_2) is widely used as a photocatalyst for its non-toxicity, stability, low cost, and high photocatalytic activity (Abdullah et al., 2023; Gloria et al., 2023; Negoescu et al., 2023). However, since TiO_2 is a non-porous material, it often has limitations in adsorption capacity and is prone to agglomeration during catalytic process, hence reducing the photocatalyst degradation efficiency (Suhan et al., 2023). In order to overcome these drawbacks, carbon-based materials such as activated carbon (AC), biochar, carbon nanotubes, and graphene are among the materials used as TiO_2