

**SYNTHESIS OF SILVER NANOPARTICLES
USING *KYLLINGA BREVIFOLIA* EXTRACT AND
IMMOBILISATION ON TiO₂ NANOTUBES FOR
METHYL BLUE DYE REMOVAL**

NORAIN ISA

UNIVERSITI SAINS MALAYSIA

2020

**SYNTHESIS OF SILVER NANOPARTICLES
USING *KYLLINGA BREVIFOLIA* EXTRACT AND
IMMOBILISATION ON TiO₂ NANOTUBES FOR
METHYL BLUE DYE REMOVAL**

by

NORAIN ISA

**Thesis submitted in fulfilment of the
requirements for the degree of
Doctor of Philosophy**

April 2020

DECLARATION

I hereby declare that i have conducted, completed the research work and written the thesis entitle “Synthesis of Silver Nanoparticles using *Kyllinga Brevifolia* Extract and Immobilisation on TiO₂ Nanotubes for Methyl Blue Dye Removal”. I also declare that it has not been previously submitted for the award of any degree or diploma or other similar title of this for any other examining body or university.

Candidate : Norain Bt Isa

Signature:

Date : 28 March 2020



Witnessed by

Supervisor : Assoc. Prof. Dr. Zainovia Lockman

Signature:

Date : 28 March 2020



ACKNOWLEDGEMENTS

In the name of Allah the most Gracious and Merciful. First and foremost, thank to Almighty Allah to give me patient to accomplish my PhD study. My sincere appreciation to Ministry of Higher Education (MoHE) under SLAB/SLAI 2015 Scholarship support throughout my doctorate study.

I would like to express my sincere gratitude to my supervisor, Assoc. Prof. Dr. Zainovia Lockman for her guidance, support, and encouragement and inspiration. Her guidance and advice has helped me in completing this thesis. I also would like to thank Assoc. Prof. Ir. Dr. Syed Fuad B. Saiyid Hashim (Dean), Profesor Ir. Dr. Mariatti Bt. Jaafar @ Mustapha and Profesor Dr. Zulkifli B. Mohamad Ariff (Deputy Deans), lecturers, technicians and administration staff of the School of Materials and Mineral Resources Engineering, USM. I am grateful to my GEMs (Mustaffa Ali Azhar Taib, Nurul Huda Bashirom, Nurul Izza Soaid and Subagja), JSG and SERG group members for friendship, moral supports, motivations and advice throughout my PhD journey. Acknowledgement also to all the funders for funding this work: 1001.PBAHAN.87004, 600RMI/RAGS 5/3 (20/2013) and 600-RMI/RACE 16/6/2 (5/2013). KPT-UiTM's SLAB Scholarship for postgraduate scholar is also acknowledged.

A special thanks to my loving and supportive husband, Nor Hisham Mohd Arshad, my wonderful children, Muhammad Aidil Wafiy, Ainul Wafa, Wardina Sofia and Ammar Wildan, who provide unending inspiration, my parents in law, my brothers and sister that are always there for the du'a and encouragement. I dedicate this thesis to my late parents, Hjh. Mah Senawi and Hj. Isa Salleh. Finally, thanks to all which are directly or indirectly contribute to the completion of this research and thesis.

TABLE OF CONTENTS

ACKNOWLEDGEMENTS	ii
TABLE OF CONTENTS	iii
LIST OF TABLES	vi
LIST OF FIGURES	viii
LIST OF SYMBOLS	xiv
LIST OF ABBREVIATIONS	xvi
ABSTRAK	xx
ABSTRACT	xxii
CHAPTER ONE: INTRODUCTION	
1.1 Introduction	1
1.2 Water Pollution	1
1.3 Reduction of MB by Catalysis Process using AgNPs	4
1.4 Problem Statement	7
1.5 Research Objectives	9
1.6 Thesis Outline	10
CHAPTER TWO: LITERATURE REVIEW	
2.1 Introduction	11
2.2 Water Pollution in Malaysia	11
2.3 Dye Pollutants	16
2.4 Nanomaterials	21
2.5 Nanoparticles in Catalysis	21
2.5.1 Synthesis of AgNPs	22
2.6 Dye Removal by Colloidal AgNPs	38
2.6.1 Reduction of MB by NaBH ₄	40
2.7 Catalyst Support for AgNPs	41
2.7.1 Synthesis of TiO ₂ Nanotube (TNTs) Array as Catalyst Support	42
2.7.2 Mechanistic Aspect in the Fabrication of TNTs as Catalyst Support	48
2.8 TNTs as Catalyst Support for AgNPs	52
2.8.1 Immobilisation of AgNPs on Catalyst Support TNTs	53
CHAPTER THREE: METHODOLOGY	
3.1 Introduction	58

3.2	Raw Materials	58
3.3	Synthesis AgNPs Catalyst	62
3.3.1	Preparation <i>Kyllinga Brevifolia</i> Extract (KBE)	62
3.3.2	Identification of Phytoconstituents in KBE	62
3.3.3	Synthesis of AgNPs: Optimisation Studies	65
3.3.4	Synthesis AgNPs using Commercial Plant Sterol	68
3.3.5	Characterization of AgNPs	68
3.4	Catalytic Study of Degradation of MB by KBE-Driven AgNPs	70
3.4.1	System 1	71
3.4.2	System 2	71
3.4.3	System 3	74
3.4.4	Kinetic studies	75
3.5	Synthesis TNTs as Catalyst Support	75
3.5.1	Optimisation Studies	76
3.6	Immobilised AgNPs Catalyst on TNTs Catalyst Support (TNTs/AgNPs)	77
3.6.1	Characterization of TNTs Catalyst Support and TNTs/AgNPs	77
3.6.2	Catalytic Study of System 4	79
CHAPTER FOUR: RESULTS AND DISCUSSION		
4.1	Introduction	80
4.2	Synthesis of AgNPs Catalyst	80
4.2.1	Identification of Phytoconstituents in KBE	80
4.2.2	Synthesis of AgNPs using KBE as the Reducing Agent	84
4.2.3	Synthesis of AgNPs using Stigmasterol and Campesterol as the Reducing Agents	93
4.2.4	Characterization of AgNPs by KBE as Reducing Agent	94
4.2.5	AgNPs Formation by Stigmasterol and Campesterol as the Reducing Agents	99
4.2.6	Proposed Mechanism for the Synthesis of Mediated AgNPs	103
4.3	Catalytic Study of AgNPs for the Degradation of MB Dye	106
4.3.1	MB Removal Efficiency in System 1	106
4.3.2	MB Removal Efficiency in System 2	107
4.3.3	MB Removal Efficiency in System 3	124
4.3.4	Mechanistic Aspect of MB Removal in System 3	134

4.3.5	Mechanistic Aspect of MB Removal by Reducing Agent with AgNPs	135
4.3.6	Reusability of AgNPs Catalyst	136
4.4	Fabrication of TNTs as Catalyst Support for AgNPs	137
4.4.1	Effect of Different Water Contents on the Growth of TNTs	137
4.4.2	Effect of using Alkaline Electrolyte on the Growth of TNTs	142
4.4.3	Other Characterisations on TNTs as Support Material	146
4.5	Fabrication of AgNPs on TNTs Catalyst Support (TNTs/AgNPs)	149
4.5.1	MB Removal Efficiency in System 4	159
4.5.2	Mechanistic Aspect	163
4.5.3	Reusability Study	166
CHAPTER FIVE: CONCLUSION AND RECOMMENDATIONS		
5.1	Conclusions	168
5.2	Recommendations for Future Work	170
REFERENCES		171
APPENDICES		
APPENDICE		
LIST OF PUBLICATIONS		

LIST OF TABLES

	Page
Table 2.1 Selected standards parameters for textile industry effluent in Malaysia.	15
Table 2.2 Classification, characteristics, applications in textile industry and effect of dyes.	17
Table 2.3 Characteristics of textile effluent from selected areas in Malaysia.	20
Table 2.4 Reported preparation and characterization methods of AgNPs from literature surveys.	24
Table 2.5 Synthesis of AgNPs using plant extracts and their characteristics.	27
Table 2.6 Various removal conditions of MB dye using colloidal AgNPs.	39
Table 2.7 Fabrication of TNTs using different electrolytes via anodisation	44
Table 2.8 Anodisation of TNTs using different agitation methods.	47
Table 2.9 Summary of literature surveys on Ag/TiO ₂ for the removal of pollutants.	57
Table 3.1 Chemical reagents, apparatus and instruments used in this study.	60
Table 3.2 Screening test for identification of phytochemicals in KBE.	63
Table 3.3 Effect of different reaction times.	66
Table 3.4 Effect of initial concentration of metal precursor.	67
Table 3.5 Effect of concentration of KBE as reducing agent.	67
Table 3.6 Effect of temperature on formation AgNPs	68
Table 3.7 System 2 for MB removal	71
Table 3.8 Effect of initial MB concentration in System 2	72
Table 3.9 Effect of AgNPs dosage in System 2.	72
Table 3.10 Effect of pH solution in System 2.	73
Table 3.11 Effect of pH using NaBH ₄ without catalyst (control) for MB removal.	73
Table 3.12 Effect of reducing agent in System 3	74
Table 3.13 Effect of pH using KBE1 with AgNPs catalyst on MB removal.	75
Table 3.14 Effect of pH using KBE2 with AgNPs catalyst on MB removal.	75
Table 3.15 Synthesis parameters for the effect of water on fabrication TNTs.	76
Table 4.1 The observed colour and R _f value from TLC analysis	81

Table 4.2	Phytochemical compounds from screening test	82
Table 4.3	GCMS results of KBE (based on more than 90% match to Wiley and NIST libraries)	83
Table 4.4	Observation of the solution at different reaction times	87
Table 4.5	ANOVA results of AgNPs formed using different reducing agents	102
Table 4.6	Scheffe' test method for post hoc comparison analysis	102
Table 4.7	Removal efficiency (% RE) and pseudo-first order kinetics for catalysed and uncatalysed samples in System 2	111
Table 4.8	Comparative analysis of reduction of MB by AgNPs	112
Table 4.9	% RE, pseudo-first and pseudo-second order kinetics for different dosages of AgNPs	118
Table 4.10	Removal efficiency and kinetics data for degradation of MB at different amounts of KBE as coagulant	133
Table 4.11	Comparison of length and diameter of TNTs prepared using different water contents	140
Table 4.12	Comparison of dimensions of TNTs formed by various alkaline solution	146
Table 4.13	Pseudo-first and pseudo-second order kinetics, and % RE for TNTs/AgNPs, TNTs, and AgNPs under lab light condition in the presence of NaBH ₄	162

LIST OF FIGURES

	Page
Figure 1.1	Gibbs energy and activation energy of catalysed and uncatalysed reaction. 4
Figure 1.2	The number of publications using keywords “silver nanoparticles” and “catalyst”. (Data obtained from ScienceDirect) 8
Figure 2.1	(a) Craft sales value (percentage, %) and (b) number of craft entrepreneurs for different industries according to segmentation year 2016 (Yearly performance report by Malaysian Handicraft Corporation). 13
Figure 2.2	Processes involved in batik manufacturing. 14
Figure 2.3	Shapes of AgNPs: (a) TEM image of Ag pyramid (Wiley et al., 2006), (b) TEM image of Ag bars (Wiley et al., 2007), (c) TEM image of Ag wire (Murphy and Jana, 2002), (d) TEM image of mixed shape Ag (Darmanin et al., 2012), (e) TEM image of spherical shaped Ag and (f) pie chart of different shapes of AgNPs prepared using plant extract as the reducing agent. 29
Figure 2.4	(a) Percentages of different size ranges of AgNPs synthesised from plant extracts as the reducing agent (data from publications in 2015-2019), (b) example of a TEM image of AgNPs and (c) histogram of size distribution of AgNPs synthesised using <i>Ceratostigma minus</i> extract (the TEM image and histogram were retrieved from a work by Ahn et al., (2019)). (Ahn et al., 2019). 30
Figure 2.5	(a) Agglomeration of AgNPs, (b) Highly dispersed AgNPs after the addition of cationic surfactant (the TEM images of (a) and (b) were retrieved from the work of Sharma and Tapadia (2016) and (c) pie chart of the dispersion of AgNPs. 32
Figure 2.6	(a) Percentages of AgNPs formation using different parts of plant extract as reducing agent. Examples of different parts of plants: (b) flowers (Vidhu and Philip, 2014b), (c) fruits (Kaviya et al., 2011), (d) roots (Alsammarraie et al., 2018), (e) stem (Ahn et al., 2019) and (f) aerial parts of plants (Ahn et al., 2019). 33

Figure 2.7	Crystallinity analysis of AgNPs (XRD and SAED): (a) <i>Selaginella</i> -AgNPs (Dakshayani et al., 2019) and (b) <i>Euphrasia officinalis</i> -AgNPs (Singh et al., 2018).	35
Figure 2.8	Phytochemicals responsible as reductant in AgNPs formation.	36
Figure 2.9	Schematic reduction mechanism of dye via electron relay effect (Mallick et al., 2006).	40
Figure 2.10	Schematic illustration of anodic oxidation set-up for TNTs formation (Taib et al., 2017).	43
Figure 2.11	FESEM images of (a) TNTs with: (i) no water content, (ii) 0.18% of water in electrolyte (Raja et al., 2007); (b) TNTs with: (i) rough surface at high water content, (ii) smooth surface at low water content (Regonini et al., 2015); and (c) well-aligned TNTs with 2 vol% of water in electrolyte: (i) surface, (ii) cross section (Sun et al., 2017).	46
Figure 2.12	Schematic illustration of the mechanistic formation of TNTs by anodisation	51
Figure 2.13	(a) Preparation of silver nanoparticle immobilisation on titanium dioxide-tungsten trioxide (Ag/WTNTs) via electrodeposition method, (b) FESEM image of Ag/WTNTs and (c) EDX results of Ag/WTNTs (retrieved from the works by Momeni et al., (2017)).	55
Figure 2.14	(a) FESEM and (b) TEM images of Ag/TiO ₂ nanotubes, and (c) XRD patterns and (d) Raman spectroscopy results of as-made TNTs, annealed-TNTs and Ag/TNTs (Retrieved from the works by Nyein et al., (2016)).	56
Figure 3.1	Experimental work in this study.	59
Figure 3.2	Schematic picture on experimental and catalytic activity of System 3 (TNTs/AgNPs) and TNTs catalyst support.	78
Figure 4.1	(a) Real TLC results and (b) Drawn sample from TLC: The colour and the R _f value from TLC analysis for crude and EF5 samples	82
Figure 4.2	Effect of reaction time on the AgNPs SPR peak by UV-vis.	85
Figure 4.3	SPR plot on the stability of AgNPs after 90 min and 12 months	86
Figure 4.4	Digital photographs displaying the colour change of solution reacted at different reaction times from 10 min to 120 min	86
Figure 4.5	Effect of pH on the AgNPs SPR	88

Figure 4.6	SPR plot on the effect of precursor concentration on the formation of AgNPs	89
Figure 4.7	SPR peak on the effect of KBE concentration on the formation of AgNPs	90
Figure 4.8	SPR plot of AgNPs formed in solution at varying temperatures	92
Figure 4.9	(a) TEM image and (b) histogram of size distribution of AgNPs for HT sample	92
Figure 4.10	UV-vis spectra for AgNPs _{stigma} , AgNPs _{campes} and AgNPs _{KBE}	94
Figure 4.11	(a) TEM image, (b) histogram of size distribution and (c) HRTEM image of AgNPs	95
Figure 4.12	XRD pattern of KBE-driven AgNPs	96
Figure 4.13	Results of (a) Particle size analysis and (b) Zeta potential of synthesised AgNPs	97
Figure 4.14	FTIR analysis results for KBE, AgNO ₃ , and AgNPs	99
Figure 4.15	TEM images and histograms of size distribution of (a) AgNPs _{stigma} and (b) AgNPs _{campes}	100
Figure 4.16	HRTEM images of (a) AgNP _{stigma} and (b) AgNP _{campes}	101
Figure 4.17	Mean particle size of AgNPs from the applications of stigmasterol, campesterol, and KBE as reducing agents (from TEM images)	102
Figure 4.18	Structure of reduced AgNPs by stigmasterol and campesterol in KBE	106
Figure 4.19	Removal of MB in System 1 (only AgNPs)	107
Figure 4.20	MB removal in NaBH ₄ solution without AgNPs	107
Figure 4.21	RE (%) of MB at different initial MB concentrations for catalysed and uncatalysed samples in System 2	110
Figure 4.22	Pseudo-first order kinetic plots for 30 to 100 ppm MB in AgNPs catalysed and uncatalysed samples in System 2	113
Figure 4.23	Pseudo-second order kinetic plots for 30 to 100 ppm MB in AgNPs catalysed and uncatalysed samples in System 2	114
Figure 4.24	Time resolved UV-vis measurements of AgNPs during their catalytic degradation of MB in System 2	116
Figure 4.25	Removal efficiency (% RE) of MB at different AgNPs dosages for catalysed and uncatalysed samples in System 2	117

Figure 4.26	Pseudo-first and pseudo-second order kinetics regression plots for MB reduction using synthesised AgNPs at different dosages	120
Figure 4.27	Digital photographs displaying the solution colour changes upon degradation of MB at different pH by NaBH ₄ (a) with and (b) without AgNPs as catalyst	123
Figure 4.28	UV-vis absorption spectra of MB at different solution pH by NaBH ₄ (a) with and (b) without AgNPs as catalyst	124
Figure 4.29	MB removal efficiency in System 3	125
Figure 4.30	UV-vis absorption spectra of MB in System 3: (a) at 1 mL KBE and (b) at 2 mL KBE	127
Figure 4.31	Digital photographs of solution colour change evaluation upon degradation of MB at different pH using 1 mL KBE at different reaction times: (a) 0 min and (b) 60 mins with AgNPs as catalyst in System 3	128
Figure 4.32	Digital photographs of solution colour change evaluation upon degradation of MB at different pH using 2 mL KBE at different reaction times: (a) 0 min and (b) 60 mins with AgNPs as catalyst in System 3	129
Figure 4.33	UV-vis absorption spectra of KBE without AgNPs at different pH values and reaction times of (a) 60 mins and (b) 20 mins	130
Figure 4.34	Digital photographs of solution colour change evaluation upon degradation of MB at different pH using 2 mL KBE at different reaction times: (a) 0 min, (b) 60 min, and (c) 20 hrs, without AgNPs	130
Figure 4.35	Pseudo-first and pseudo-second order kinetics plots for different amounts of KBE as coagulant: (a) 1 mL and (b) 2 mL	132
Figure 4.36	Reaction mechanism in the degradation of MB in System 3 by CFS technique	135
Figure 4.37	Reductive-removal of MB in System 2 and System 3	136
Figure 4.38	Cross-section and surface FESEM images of (a) TW0, (b) TW1, (c) TW3, and (d) TW5 samples, with HRTEM images (inset) of TNTs samples anodised in EG/NH ₄ F with air bubbles	139
Figure 4.39	Low magnification FESEM images of anodised Ti wires for (a) TW0, (b) TW1, (c) TW3, and (d) TW5 samples	142

Figure 4.40	FESEM images of Ti wires: (a) when K_2CO_3 was added at the beginning of anodizing process, (b) low magnification image at surface of TNTs, (c) high magnification image at surface of TNTs and (d) Low magnification image at cross sections; and HRTEM images of (e) TNTs at high magnification and (f) Low magnification TNTs catalyst support	145
Figure 4.41	(a) FTIR spectra of as-made and annealed TNTs catalyst support, (b) HRTEM image displaying fringes, and (c) SAED image of TNTs	147
Figure 4.42	XRD pattern of TNTs annealed at 400 °C	148
Figure 4.43	EDX spectrum of annealed TNTs	148
Figure 4.44	Raman spectra of annealed TNTs and Ti substrate	149
Figure 4.45	FESEM images of (a) surface and (b) cross section of TNTs/AgNPs	150
Figure 4.46	Images of TNTs/AgNPs from (a) HRTEM analysis and (b) SAED analysis	150
Figure 4.47	EDX spectrum with element wt % and at % count for TNTs/AgNPs	151
Figure 4.48	XRD patterns of (a) AgNPs, (b) TNTs, and (c) TNTs/AgNPs	152
Figure 4.49	Raman spectra of TNTs and TNTs/AgNPs samples	153
Figure 4.50	FTIR spectra of TNTs/AgNPs and TNTs samples	154
Figure 4.51	(a) XPS survey spectra of TNTs and TNTs/AgNPs; and high resolution peaks of (b) Ti 2p, (c) F 1s, (d) Ag 3d, (e) C 1s, and (f) O 1s	158
Figure 4.52	(a) UV spectrum of TNTs/AgNPs and (b) % RE of MB dye by TNTs/AgNPs, TNTs (control), and colloidal AgNPs under lab light condition	162
Figure 4.53	Kinetics data on the degradation of MB under lab light condition using TNTs/AgNPs and TNTs	163
Figure 4.54	Schematic diagram of possible process mechanisms of MB removal by TNTs/AgNPs in the presence of $NaBH_4$ under lab light condition	164

- Figure 4.55 Schematic diagram of possible process mechanisms for photocatalytic degradation of MB by TNTs/AgNPs under visible light irradiation 165
- Figure 4.56 (a) Reusability analysis on AgNPs, TNTs/AgNPs, and TNTs under lab light condition, and (b) FESEM image of TNTs/AgNPs after the 3rd cycle of reusability under lab light condition 167

LIST OF SYMBOLS

%	Percentage
°C	Degree Celsius
°	Degree
>	More than
<	Less than
[]	Concentration
$h\nu$	Photon energy
m	Meter
cm	Centimeter
cm^{-1}	Per centimetre
mm	Milimeter
nm	Nanometer
mg	Miligram
μm	Microgram
V	Voltage
mV	Milivolt
wt %	Weight percent
vol %	Volume percent
At %	Atomic percent
L	Liter
mL	Mililiter

μL	Microliter
s	Second
min	Minute
min^{-1}	Per minute
$\text{Lmg}^{-1}\text{min}^{-1}$	Liter per milligram per minute
h	Hour
T	Temperature
M	Molar
ppm	Part per million
k	Kinetic rate
R^2	Regression squared
λ	Wavelength
θ	Bragg angle
\AA	Angstrom
h^+	Holes
h^+_{VB}	Valence band holes
VB	Valence band
e^-	Electrons
e^-_{CB}	Conduction band electrons
E_g	Bandgap energy
$\text{O}_2^{\bullet-}$	Superoxide radical
OH^\bullet	Hydroxyls radical

LIST OF ABBREVIATIONS

2-CP	2-Chlorophenol Dye
4-NP	4-Nitrophenol Dye
2,4-DCP	2,4-Dicholophenol Dye
ADMI	American Dye Manufacturers Institute
AFM	Atomic Force Microscopy
AgNPs	Silver Nanoparticles
AgNPs _{Scampes}	Silver Nanoparticles using Campesterol as Reducing Agent
AgNPs _{KBE}	Silver Nanoparticles using KBE as Reducing Agent
AgNPs _{stigma}	Silver Nanoparticles using Stigmasterol as Reducing Agent
Ag-N-TiO ₂	Silver-Nitrogen-TiO ₂ Composite
a.u	Arbitrary Unit
ANOVA	Analysis of Variance
AOP	Advanced Oxidation Process
BOD	Biological Oxygen Demand
BSA	Bovine Serum Albumin
COD	Chemical Oxygen Demand
CP	Crude Protein
CR	Congo Red Dye
CV	Crystal Violet Dye
df	Degree of Freedom
DOE	Department of Environment
DLS	Dynamic Light Scattering

EDAX	Energy Dispersive Spectrometry
EDS	Energy Dispersive X-Ray Spectroscopy
EG	Ethylene Glycol
ETs	Electron Traps
FCC	Face Centre Cubic
FESEM	Field Emission Scanning Electron Microscopy
FTIR	Fourier Transform Infra-Red
FWHM	Full Width High Maximum
GCMS	Gas Chromatography Mass Spectroscopy
GO	Graphene Oxide
HSAB	Hard Soft Acid Bases
HRTEM	High Resolution Transmission Electron Microscopy
IC	Indigo Carmine Dye
ISO	International Organization for Standardization
KBE	<i>Kyllinga Brevifolia</i> Extract
LDE	Laser-Doppler Electrophoresis
LSPR	Local Surface Plasmon Resonance
MB	Methyl Blue Dye
MO	Methyl Orange Dye
MS	Mean Square
MSbg	Mean Square (Between Group)
MSwg	Mean Square (Within Group)
nd	No Data Provided
NIST	National Institute Of Standard Of Technology
NPs	Nanoparticles

NWQS	National Water Quality Standards
OAPs	Octahedral anatase particles
OER	Oxygen evolution reaction
OV	Oxygen Vacancy
PDI	Polidispersity Index
PMo12	Polyoxomelate
PP	Propyl paraben
PVA	Polyvinyl alcohol
PVP	Polyvinyl pyrrolidone
R6G	Rhodamine 6G
RB	Rhodamine B
RE	Removal Efficiency
R _f	Retention Factor
rGO	Reduced-Graphene Oxide
SAED	Selected Area Electron Diffraction
SEM	Scanning Electron Microscopy
SPR	Surface Plasmon Resonance
SS	Sum of Square
TEM	Transmission Electron Microscopy
TLC	Thin Layer Chromatography
TNSs	TiO ₂ Nanosheets
TNTs	TiO ₂ Nanotubes
TNTs/AgNPs	TiO ₂ Nanotube Immobilisation Silver Nanoparticles
Trp-AgNPs	Tryptophan-Silver Nanoparticles
TS	Technical Specification

TSS	Total Suspended Solids
UV-vis	Ultraviolet-Visible Spectrophotometer
VOCx	Volatile Organic Compounds
WQI	Water Quality Index
WSC	Water Soluble Carbohydrate
WTNTS	Tungsten Trioxide TiO ₂ Nanotubes
XPS	X-Ray Photoelectron Spectroscopy
XRD	X-Ray Diffraction

**SINTESIS NANOPARTIKEL PERAK DENGAN MENGGUNAKAN
EKSTRAK *KYLLINGA BREVIFOLIA* DAN IMOBILISASI PADA TIUBNANO
TiO₂ UNTUK MENYINGKIRKAN PEWARNA METIL BIRU**

ABSTRAK

Industri tekstil adalah penghasil air buangan yang banyak di mana jika ia tidak dirawat akan menghasilkan pewarna yang toxic dan merbahaya. Satu kaedah yang dapat membuang pewarna adalah melalui penurunan pada permukaan katalis yang diperbuat daripada nanopartikel perak (AgNPs) melalui kaedah penurunan garam. Bahagian pertama hasil kerja ini adalah fokus kepada penyediaan dan pencirian AgNPs dan kegunaannya dalam membuang pewarna metil biru (MB). Selain daripada agen penurun yang tipikal, AgNPs telah disintesis melalui kaedah kimia ‘hijau’ menggunakan ekstrak pokok *Kyllinga brevifolia* (KBE) sebagai agen penurun. KBE juga didapati dapat bertindak sebagai agen pelindung dan penstabil. AgNPs telah berjaya disintesis dengan mengawal suhu, kepekatan AgNO₃ sebagai bahan pemula, kepekatan KBE dan masa tindak balas. Analisa fitokimia KBE yang bertanggungjawab sebagai agen penurun telah dikenal pasti. Karbohidrat, protin dan sterol tumbuhan (stigmasterol dan campesterol) didapati mempunyai kepekatan yang tinggi dan dicadangkan sebagai bahan utama dalam penurunan Ag⁺ kepada Ag⁰. Partikel AgNPs daripada KBE ini didapati mempunyai kadar sebaran yang tinggi dengan purata diameter 17.64 nm dengan bentuk yang hampir bulat. Pembuangan MB menggunakan katalis AgNPs telah dikaji. Empat (4) sistem telah dibangunkan untuk mengukur pretasi AgNPs iaitu: Sistem 1 (AgNPs sahaja), Sistem 2 (AgNPs + NaBH₄), Sistem 3 (AgNPs

+ KBE) dan Sistem 4 (AgNPs pada TNTs). Daripada pemerhatian, tiada penurunan MB diperhatikan pada Sistem 1 tetapi pada Sistem 2, menunjukkan prestasi yang terbaik. Kinetik pseudo-order satu dan pseudo-order dua telah digunakan untuk kajian kinetik. Sistem 2 menunjukkan pembuangan MB adalah 100% pada pH 8-10 dengan kadar kinetik tindak balas iaitu 2.515 min^{-1} untuk 30 ppm dan 1.4614 min^{-1} untuk 100 ppm. Ia mengambil masa kurang daripada 5 min untuk pembuangan 100% MB di mana tindak balas ini sangat pantas. Dalam Sistem 3, 93% MB telah dibuang dengan kadar tindak balas 0.2663 min^{-1} pada pH 2. Keberkesanan pmbuangan MB dalam Sistem 2, dipercayai adalah melalui proses penurunan dipanggil 'kesan elektron gantian' manakala dalam Sistem 3, mendakan berlaku bersama proses penurunan. Namun diakhir proses, didapati AgNPs sangat susah untuk diasingkan. Ia akan membawa kepada pencemaran sekunder. Untuk mengatasi masalah ini, AgNPs telah imobilisasi pada permukaan TiO_2 (Sistem 4) sebagai bahan pemegang katalis. TiO_2 adalah dalam bentuk nanotubes (TNTs). TNTs telah dibangunkan melalui proses penganodan dawai Ti. AgNPs kemudian disebarkan pada permukaan TNTs melalui kaedah rendaman impregnasi. Pencirian AgNPs pada TNTs dan kebolehan sebagai katalis telah diuji terhadap MB. Kajian ini mendapati peratusan pembuangan MB pada Sistem 4 agak lemah berbanding dalam Sistem 2. Ia mematuhi pseudo-order satu dengan kadar tindak balas $7.5 \times 10^{-3} \text{ min}^{-1}$.

**SYNTHESIS OF SILVER NANOPARTICLES USING *KYLLINGA*
BREVIFOLIA EXTRACT AND IMMOBILISATION ON TiO₂ NANOTUBES
FOR METHYL BLUE DYE REMOVAL**

ABSTRACT

The textile industry is an intensive producer of wastewater which unless treated may result in the discharge of toxic and harmful dyes to the environment. One method that can be used to remove dyes is by reduction on a surface of catalyst. The catalyst chosen in this work was silver nanoparticles (AgNPs) synthesised by salt reduction technique. The first part of this thesis focused on the synthesis process of AgNPs. However instead of using typical reductant, AgNPs were synthesised by green chemical route utilising *Kyllinga brevifolia* extract (KBE) as reducing agent. The KBE was also found to be a good capping as well as stabilizing agent. By controlling the temperature, concentration of AgNO₃ as the silver precursor, concentration of KBE and reaction time, the AgNPs were successfully synthesised. The phytochemical constituents in KBE responsible for Ag⁺ reduction were identified. Carbohydrate, protein, plant sterol (stigmasterol and campesterol) were found to have the highest concentration thus proposed as the main constituents that can reduce Ag⁺ ions to Ag⁰. KBE derived AgNPs are highly dispersed with ~ 17.64 nm diameter and have quasi-spherical shape. The catalytic removal of MB was then done to demonstrate the properties of AgNPs in removing MB. Four (4) systems were used to investigate the performance of AgNPs; System 1 (AgNPs alone), System 2 (AgNPs + NaBH₄), System 3 (AgNPs + KBE) and System 4 (AgNPs on TNTs). From the catalytic study on MB removal, no reduction was observed in System 1. Reduction was the highest in System 2. The pseudo first and