SYNTHESIS OF SILVER NANOPARTICLES USING *KYLLINGA BREVIFOLIA* EXTRACT AND IMMOBILISATION ON TiO_2 NANOTUBES FOR METHYL BLUE DYE REMOVAL

NORAIN ISA

UNIVERSITI SAINS MALAYSIA

2020

SYNTHESIS OF SILVER NANOPARTICLES USING *KYLLINGA BREVIFOLIA* EXTRACT AND IMMOBILISATION ON TiO_2 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 TiO_2 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

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

%	Percentage
^{o}C	Degree Celsius
^{o}	Degree
>	More than
<	Less than
[ ]	Concentration
hv	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
$Lmg^{-1}min^{-1}$	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
Å	Angstrom
h^+	Holes
h^+_{VB}	Valence band holes
VB	Valence band
e^-	Electrons
e^-_{CB}	Conduction band electrons
E_g	Bandgap energy
$O_2^{\bullet -}$	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
$AgNPs_{campes}$	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	*Kyllinga Brevifolia* 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	Trytophan-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 TiO_2 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 $AgNO_3$ 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 Ag^o. 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 + $NaBH_4$), 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 sekundari. Untuk mengatasi masalah ini, AgNPs telah imobilisasi pada permukaan TiO_2 (Sistem 4) sebagai bahan pemegang katalis. TiO_2 adalam 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 7.5×10^{-3} min^{-1}.

SYNTHESIS OF SILVER NANOPARTICLES USING *KYLLINGA BREVIFOLIA* EXTRACT AND IMMOBILISATION ON TiO_2 NANOTUBES FOR METHYL BLUE DYE REMOVAL

ABSTRACT

The textile industry is an intesive producer of wastewater which unless treated may result in the discharged 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 $AgNO_3$ as the silver precursor, concentration of KBE and reaction time, the AgNPs were sucsessfully 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 Ag^o. 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 + $NaBH_4$), 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