THE SIMULTANEOUS ADSORPTION AND PHOTOCATALYTIC DEGRADATION OF PHENOL USING ELECTROSPUN P(3HB)-TiO_2 NANOCOMPOSITE FIBERS

AINIL HAWA BINTI JASNI

MASTER OF SCIENCE

UNIVERSITI PERTAHANAN

NASIONAL MALAYSIA

JANUARY 2017

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Thesis Submitted to the Centre for Graduate Studies, Universiti Pertahanan Nasional Malaysia, in Fulfilment of the Requirements for Master of Science (Biology)

January 2017

ABSTRACT

Introduction: Photocatalytic degradation and adsorption of crude oil on poly-3-hydroxybutyrate P(3HB) electrospun nanofiber immobilized with nanosized titanium dioxide (TiO_2) for phenol cleanup was evaluated in this study. The P(3HB) used in this study which is made from renewable sources is cost effective and biodegradable. It is hydrophobic and thus was proven to show simultaneous adsorption of phenol while TiO_2 photocatalytically degrades the adsorbed phenol molecules. **Objectives**: This study aims to develop a nanocomposite fibrous material using the environmentally friendly PHA and inert TiO_2 to simultaneously adsorb and degrade phenol. **Methodology**: Palm oil based sources of palm olein (PO), crude palm kernel oil (CPKO), waste cooking oil (WCO) had been used in this study to produce poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate) [P(3HB-*co*-3HHx) bioplastics from wild type *Cupriavidus necator* and recombinant *Cupriavidus necator* Re2058/pCB113. Meanwhile, P(3HB) homopolymer was extracted from mice pellets (mice fed with lyophilized cells of *C. necator* H16 containing 39 wt% PHB). Kaneka Commercial P(3HB-*co*-3HHx) with 11.8% and 8.4% of 3HHx monomer composition were used as comparison. Different applied voltages, polymer concentrations and mixed solvent ratios were tested and optimized for the fabrication of electrospun nanofiber. Electrospun P(3HB)-TiO_2 films were successfully fabricated and were used in adsorption studies. Phenol was used as crude oil model as it is organic and stable. The fabricated nanofibers were characterized by FESEM, EDX, DSC, GPC and TGA and used for degradation of phenol under different parameters of contact time, pH, initial concentration, temperature and light condition. **Results**: It is apparent that high electrospinning voltage of 25kV produced homogenous strands and better fibrous networks of the nanocomposite films. The intrusion rate of electrospinning was found to be optimum at 40 μL/min, meanwhile the concentration of polymer solution for electrospinning was set at 10 wt. % for all sample types. The maximum adsorption capacities was 59.047 mg/g. Langmuir and Freundlich isotherm models had been generated to provide reasonable fittings for this sorption data of oil and the sorbent. The trend of adsorptions were in a good agreement with Freundlich which R^2= 0.99. The optimal contact time was 270 minutes of nearly 99.9% phenol removal. The equilibrium time was 10 minutes. The effects of photocatalyst-TiO_2 loading on the rates of photocatalytic degradation of phenol had increased in four different light conditions: solar>UV>fluorescent>dark. The experimental results illustrate that the kinetics of degradation of phenol are pseudo-2nd order. Phenol was effectively removed at pH 4 and at 60 ^{0}C and higher. **Conclusion**: In view of the results, the P(3HB)-TiO_2 nanocomposite films were proven to act as an effective material to simultaneously adsorb and degrade phenol in aquatic environment.

ABSTRAK

Pengenalan: Penjerapan fotokatalisis minyak mentah oleh poli-3-hydroksibutirate P(3HB) gentian pemintalan elektro digabung dengan titanium dioksida (TiO_2) bersaiz nano bagi penjerapan minyak telah dikaji dalam kajian ini. P(3HB) yang digunakan di dalam kajian ini disintesis daripada sumber yang boleh diperbaharui yang murah dan terbiodegradasi. Sifatnya yang hidrofobik telah membuktikan bahawa penjerapan dan degradasi fotokatalis minyak mentah secara serentak adalah berkesan. **Objektif:** Kajian ini bertujuan membangunkan sebuah bahan berfiber nanokomposit menggunakan PHA yang mesra alam dan TiO_2 yang stabil untuk menjerap sekaligus mendegradasi minyak mentah. **Kaedah:** Minyak kelapa sawit daripada sumber olein sawit (PO), isirung kelapa sawit mentah (CPKO), minyak masak terpakai (WCO) telah digunakan untuk menghasilkan bioplastik poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate) [P(3HB-*co*-3HHx) daripada *strain* liar *Cupriavidus necator* dan *Cupriavidus necator* Re2058/pCB113 rekombinan. Homopolimer P(3HB) pula telah diekstrak daripada tinja tikus (tikus yang diberi makan dengan sel *C. necator* H16 yang mengandungi 39% kandungan PHB). Komersial Kaneka P(3HB-*co*-3HHx) dengan kepekatan 11.8% and 8.4% monomer 3HHx komposisinya telah digunakan sebagai kajian komparatif. Penggunaan kadar voltan yang berlainan, kepekatan polimer dan nisbah campuran pelarut telah dijalankan dan dioptimumkan. Gentian pemintalan elektro P(3HB)-TiO_2 telah berjaya difabrikasi and digunakan di dalam kajian penjerapan. Fenol telah digunakan sebagai model minyak mentah kerana sifatnya yang organik dan stabil. Gentian-gentian pemintalan elektro telah dikaji sifatnya dengan analisa FESEM, EDX, DSC, GPC dan TGA dan digunakan untuk penjerapan fenol di bawah parameter berlainan seperti; masa penjerapan, pH, kepekatan asal, suhu dan sumber cahaya. **Keputusan**: Kajian membuktikan bahawa pada voltan tinggi iaitu 25kV telah menghasilkan jalinan gentian yang berluas permukaan tinggi pada gentian nanokomposit. Kadar penyemperitan telah dioptimumkan dan ditetapkan pada 40 μL/min, selain itu kepekatan polimer telah diformulasi sebanyak 10 wt. % untuk semua jenis sampel. Kapasiti penjerapan maksima adalah 59.047 mg/g. Model isoterma Langmuir dan Freundlich telah dijana untuk menyediakan penanda yang sesuai untuk data minyak dan penjerap. Corak penjerapannya mempunyai korelasi baik dengan Freundlich iaitu R^2= 0.99. Tempoh penjerapan optimum adalah selama 270 minit iaitu sebanyak 99.9% penyingkiran fenol. Manakala masa ekuilibrium adalah 10 minit. Efek integrasi fotokatalisis-TiO_2 terhadap kadar degradasi fotokatalisis fenol telah meningkat di bawah pencahayaan 4 jenis keadaan sumber cahaya: solar>UV>kalimantan>gelap. Keputusan eksperimen menyatakan degradasi kinetik fenol adalah bersamaan dengan perintah pseudo-kedua. Fenol telah disingkirkan secara efektif di dalam pH 4 dan pada suhu 60 ^{0}C dan ke atas. **Kesimpulan**: Keputusan menunjukkan P (3HB) filem-TiO_2 nanokomposit telah terbukti bertindak sebagai bahan yang berkesan pada masa yang sama menjerap dan mendegradasi fenol di persekitaran akuatik.

ACKNOWLEDGEMENTS

First of all, I would like to express my utmost gratitude to my supervisor Dr. Nanthini Sridewi a/p Appan for her kind guidance and supervision during the preparation of this report. Her encouragement, guidance, and support enabled me to develop a very detailed understanding of the subject thus ensured the success of all the work involved. I have achieved a lot of positive personal growth during my master's degree period. In addition, I would also like to take this opportunity to thank those who have made this report possible. Special thanks to my parents and spouse who provide me with valuable moral supports during the course of completing this report. I really appreciate the facilities support, advices and guidance from my co-supervisor, Prof. Dr. K. Sudesh Kumar (Professor of Microbiology and Biotechnology at the School of Biological Sciences, Universiti Sains Malaysia (USM) from 2013- 2015. I learned a lot and develop new skills in his facilities. I am also very grateful to the helpful Ecobiomaterial Lab 409 members in USM Penang Campus for their willingness to assist me theoretically and practically in the lab and guide me in the way to use all the valuable equipment. Thanks to my colleague in USM, Dr. Hanisah Kamilah Razak for the accommodation and tremendous assistance during my stay there. Thanks to Ms. Kasturi from Nottingham University, Semenyih for the high tech analysis and financial support. A warm thanks to my colleagues Ms. Filzah, Mdm. Khairani Hasuna Jaapar and Ms. Fatihah Suhaimi (lab technicians) from Nottingham University for the assistance in running my samples for characterization tests of FESEM and TGA. Thanks also to Madam Jamilah Afandi of Electron Microscopy Unit, School of Biological Sciences, USM for technical assistance during SEM analyses. This study had been presented in ICMSM 2015 in poster exhibition. Last but not least, million thanks to my National Defence University of Malaysia peers for the moral supports and concern. The process of completing this report would not be so smooth and inspiring without their cooperation and encouragement from everybody around me. This work has been funded by Ministry of Higher Education (MOHE) Malaysia under the Research Grant of FRGS/1/2013/SG05/UPNM/03/1.

APPROVAL

I certify that an Examination Committee has met on 2nd November 2016 to conduct the final examination of **Ainil Hawa Binti Jasni** on his degree thesis **The Simultaneous Adsorption And Photocatalytic Degradation Of Phenol Using Electrospun P(3HB)-TiO_2 Nanocomposite Fibers'**. The committee recommends that the student be awarded the **Master of Science (Biology)**.

Members of the Examination Committee were as follows.

Abdul Ghapor bin Hussin, PhD
Professor
Centre for Academic Development
Universiti Pertahanan Nasional Malaysia
(Chairman)

Wan Md Zin Bin Wan Yunus, PhD
Professor Emeritus Dato'
Centre for Tropicalization
Universiti Pertahanan Nasional Malaysia
(Internal Examiner)

Bassim H. Hameed, PhD
Professor
School of Chemical Engineering
Universiti Sains Malaysia
(External Examiner)

APPROVAL

This thesis was submitted to the Senate of Universiti Pertahanan Nasional Malaysia and has been accepted as fulfilment of the requirements for the degree of **Master of Science (Biology)**. The members of the Supervisory Committee were as follows.

Nanthini Sridewi Appan, PhD
Department of Science and Maritime Technology
Faculty of Defence Science and Technology
Universiti Pertahanan Nasional Malaysia
(Main Supervisor)

K. Sudesh Kumar, PhD
Professor Dato'
School of Biological Sciences
Universiti Sains Malaysia
(Co-Supervisor)

UNIVERSITI PERTAHANAN NASIONAL MALAYSIA

DECLARATION OF THESIS

Author's full name : Ainil Hawa Binti Jasni
Date of birth : 19th November 1988
Title : The Simultaneous Adsorption And Photocatalytic Degradation Of Phenol Using Electrospun P(3HB)-TiO_2 Nanocomposite Fibers
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LIST OF ABBREVIATIONS

a.m.	Ante meridiem
AOP	Advance Oxidation Process
cm	Centimeter
CME	Caprylate Methyl Ester
CPKO	Crude Palm Kernel Oil
CPO	Crude Palm Oil
DCM	Dichloromethane
DMF	Dimethylformamide
DSC	Differential Scanning Calorimetry
DOC	Dissolve Organic Carbon
ED	Oxidizing potential unit
EDX	Energy dispersive X-ray
eV	Electron Volt
FESEM	Field Emission Scanning Electron Microscope
GBP	Graphene + Bismuth Phosphate composite
GC	Gas Chromatography
GPa	Giga Pascal
GPC	Gel permeation chromatography
g	Gram
g / cm^3	Gram per centimeter cubic
HAs	Hydroxyalkanoates
HPLC	High performance liquid chromatography

ICI	Imperial Chemical Industries
kg	kilogram
kLux	kiloLux
kV	kiloVolt
L-H	Langmuir - Hinselwood
MCL	Medium chain-length
MPa	Mega Pascal
mg	Miligram
mg/g	Miligram per gram
mg/L	Miligram per litre
mg/mL	Miligram per mililitre
mL	Mililitre
mL/min	Mililitre per minute
mm	Millimetre
$mWcm^2$	Millwatt square centimeter
m^2/g	Square meter per gram
μg/L	microgram per Litre
µL	Microliter
µl/min	Microliter per minute
μM	Micro Molarity
M_n	Number -average molecular weight
M_w	Weight-average molecular weight
M_w/M_n	Polydispersity index
nm	Nanometer