PHOTODEGRADATION AND ADSORPTION PROCESSES IN TREATMENT OF METHYL ORANGE DYE AND PALM OIL MILL EFFLUENT BY TITANIUM DIOXIDE-IMPREGNATED CHITOSAN SYSTEMS

SITI NOR BINTI AB HAMID

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By

SITI NOR BINTI AB HAMID

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfillment of the Requirements for the Degree of Master of Science

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DEDICATION

-IN THE NAME OF ALLAH, the most merciful-

I dedicated this thesis to:

My late father;

Ab Hamid bin Ab Samad

My beloved mother;

Zaradah bin Ibrahim

And my deareast husband;

Mohd Hafies bin Mohd Shahari

Thank you for giving me a full of support throughout my studies.

May Allah bless all of them in here and hereafter.

Amiiiinn

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Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

PHOTODEGRADATION AND ADSORPTION PROCESSES IN TREATMENT OF METHYL ORANGE DYE AND PALM OIL MILL EFFLUENT BY TITANIUM DIOXIDE-IMPREGNATED CHITOSAN SYSTEMS

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December 2018

Chairman : Professor Zulkarnain Zainal, PhD
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In this work, palm oil mill effluent (POME) was treated by using photodegradation and adsorption processes with the presence of titanium dioxide and chitosan catalyst. The titanium dioxide was combined chitosan (TiO_2-CS) through impregnation at varying conditions. At certain instances Methyl Orange (MO) dye, which served as a model pollutant was used as adsorbate. Parameters such as initial concentrations (20 to 100 ppm), pH (pH 3 to pH 9), contact time and TiO_2-CS loadings (0.10-1.00 g), and different catalytic systems were investigated. The optimum ratio of TiO_2-CS loadings used in this study was 2:1 (TiO_2:CS). Meanwhile, the optimum amount of TiO_2 and CS was 0.20 g and 0.10 g respectively at pH 4.5 for one hour of reaction with the total removal percentage of 20.0% and the colour removal of 70.0% POME by using TiO_2-CS. This prove that high colour removal is not an indicator for high COD removal. The TiO_2-CS catalyst could not be reused for further investigation after one hour of reaction, due to the instability of the materials. The problem was overcome by coating titanium dioxide and chitosan onto glass beads (TiO_2-CS/GB). The performance of the coated catalyst has been investigated in Methyl Orange (MO) removal. It was found that 20.00 g of glass beads was required for the optimum coating of titanium dioxide and chitosan. The maximum loading of TiO_2 and chitosan on the glass beads was approximately 1.0 g. The immobilised catalyst was tested for MO removal at concentration in range of 20 to 100 ppm. Photodegradation and adsorption of MO using TiO_2-CS/GB with the presence of light and in the dark have been proved to obey the first order kinetic model. The optimum pH of the solution with the highest removal percentage was 3.0, and the removal percentage increased with the increasing temperature. Besides, the coated catalyst was able to be reused for up to six cycles using 20 ppm of MO. The percentage COD removal for POME by using TiO_2-CS/GB was 40.0%, which was twice as much compared to unsupported TiO_2-CS and the colour removal achieved 100.0%.

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Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

PROSES FOTODEGRADASI DAN PENJERAPAN PEWARNA METIL JINGGA DAN RAWATAN SISA KILANG MINYAK KELAPA SAWIT MENGGUNAKAN SISTEM TITANIUM DIOKSIDA DILEKATKAN DENGAN KITOSAN

Oleh

SITI NOR BINTI AB HAMID

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Dalam penyelidikan ini, sisa kilang minyak kelapa sawit telah dirawat dengan menggunakan proses fotodegradasi dan penjerapan dengan kehadiran pemangkin titanium dioksida dan kitosan. Eksperimen telah dijalankan dengan menggunakan pelbagai kepekatan awal larutan (20 to 100 ppm), nilai pH POME (pH 3 to pH 9), tempoh tindak balas, muatan titanium dioksida dan kitosan (0.10-5.0 g), dan sistem mangkin. Nisbah muatan titanium dioksida dan kitosan (TiO_2-CS) terbaik yang digunakan adalah 2:1 (TiO_2:CS). Manakala sebanyak 20.0% penyingkiran COD dan 70.0% penyahwarnaan telah diperoleh dalam larutan sisa dengan pH 4.5 selama 1 jam tempoh tindak balas dengan menggunakan 0.20 g titanium dioksida dan 0.10 g kitosan. Keadaan ini membuktikan bahawa walaupun penyahwarnaan yang tinggi, tidak semestinya menunjukkan penyingkiran COD juga tertinggi. Walaubagaimanapun, sistem titanium dioksida dan kitosan didapati tidak stabil selepas satu jam di dalam larutan. Untuk mengatasi masalah tersebut, kaedah penyalutan titanium dioksida dan kitosan ke atas manik kaca telah dijalankan (TiO_2-CS/GB). Dalam sistem ini, eksperimen lanjutan telah dijalankan dengan menggunakan 20.0 g manik kaca bagi penyalutan optimum titanium dioksida dan kitosan. Muatan maksimum dalam lingkungan 1.0 g titanium dioksida dan kitosan dapat disalutkan ke atas manik kaca. Eksperimen telah dijalankan dengan menggunakan Metil Jingga (MO) sebagai model bahan pencemar dengan julat kepekatan 20 hingga 100 ppm. Proses fotodegradasi dan penjerapan MO telah dibuktikan mematuhi model tindak balas kinetik tertib pertama. Nilai optimum pH larutan MO adalah pH 3 dan peratus penyingkiran MO bertambah apabila suhu larutan bertambah. Di samping itu, kajian bagi penggunaan semula mangkin terpegun ini telah di jalankan sehingga enam kitaran bagi 20 ppm larutan MO. Peratus penyingkiran COD menunjukkan peningkatan sebanyak dua kali ganda iaitu 40.0% apabila dibandingkan dengan sistem pemangkin TiO_2-CS dan peratus penyahwarnaan mencapai 100.0%.

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This thesis was submitted to the Senate Universiti Putra Malaysia and has been accepted in fulfilment of requirement for the degree of Master of Science. The members of the supervisory committee were as follows:

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This is to confirm that:

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LIST OF ABBREVIATIONS

e^-	:	Photogenerated electron
h^+		Photogenerated holes
AOPs		Advanced Oxidation Processes
BOD		Biological Oxygen Demand
C		Concentration
C_o		Initial Concentration
COD		Chemical Oxygen Demand
CPO		Crude Palm Oil
CS		Chitosan
FFB		Fresh fruit bunch
GB		Glass Bead
MO		Methyl Orange
MPOB		Malaysia Palm Oil Board
POME		Palm Oil Mill Effluent
PPM		Part per million
PZC		Point of Zero Charge
UV		Ultra violet

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CHAPTER 1

INTRODUCTION

1.1 Background

The development of the palm industry has been phenomenal. The industry has been growing rapidly in Malaysia. From 2007 until 2017, Malaysia was the second largest manufacturer of palm oil in the world. It was estimated that 18.7 million tonnes crude palm oil (CPO) were manufactured from 429 mills (Taha and Ibrahim, 2014). From 2015 to 2017, the plantation of palm trees increased from 5.642 to 5.811 million hectares (MPOB, 2017). Many areas have been used to cultivate the oil palm including the virgin jungle and conversion of plantations originally for rubber or other crops.

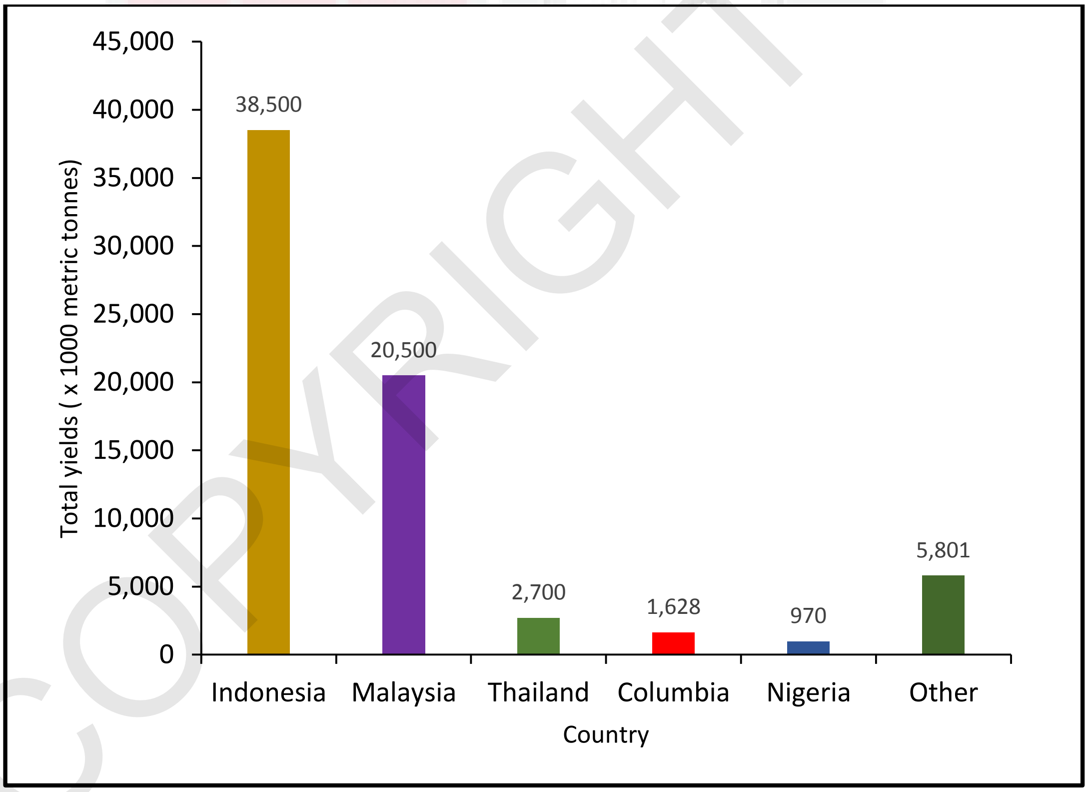

Figure 1.1 : Production of palm oil worldwide
(Source: MPOB, 2017)

The oil palm mills grow accordingly due to increasing of planted area by palm trees in all over Malaysia and corresponding to increasing of capacity of fresh fruit bunch (FFB) production. The research and development has been strengthened by adhering to the outcomes of the annually held United Nations Framework Convention on Climate Change (UNFCCC) negotiations, which requires the palm oil industry to tackle the challenges in meeting the growing worldwide demand. Figure 1.2 depicts

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that Malaysia oil palm industry showed steady increased in planted area between 2014 and 2017. Crude palm oil (CPO) production and FFB yield also witnessed significant increases over these years (MPOB, 2017).

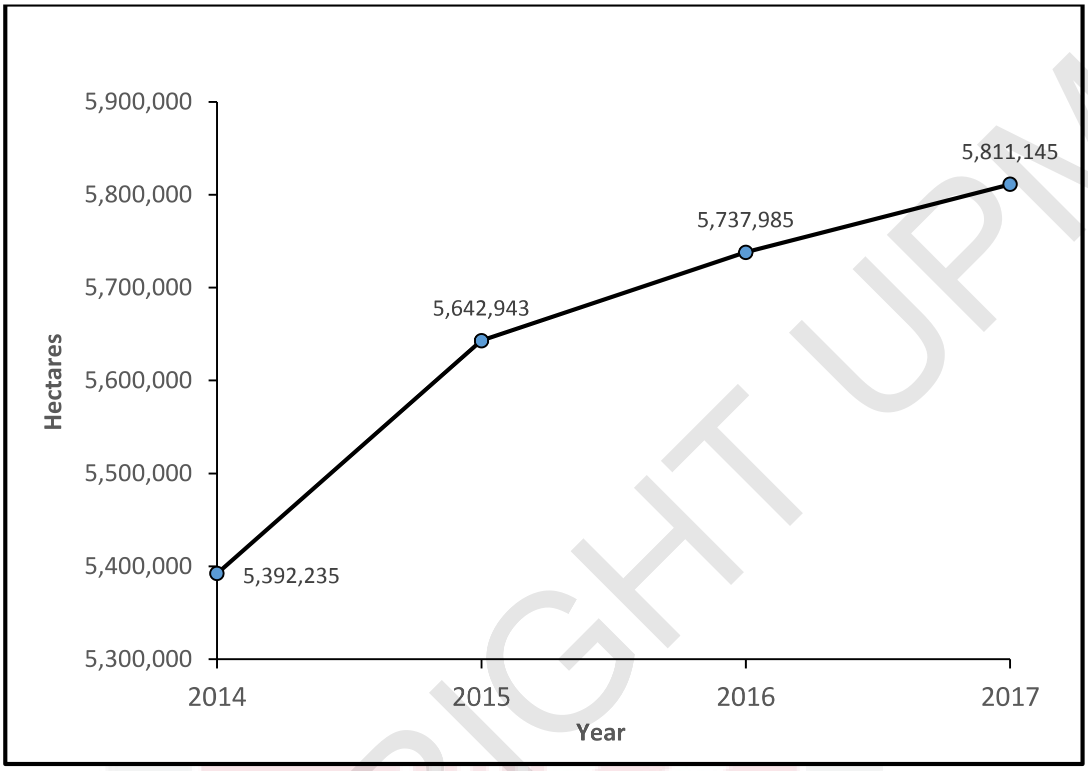

Figure 1.2 : Planted area of oil palm in Malaysia
(Source: MPOB 2017)

Palm oil mill effluent is the waste generated during the processing FFB. It is the most expensive and difficult waste to manage by mill operators. This is because large volumes in tonnes are generated at a time. The palm oil industry still considers POME treatment a burden rather than as part of the production process. For these obvious reasons, raw POME or partially treated POME is still being discharged into nearby rivers or land, as this is the easiest and cheapest method for disposal. However, excessive quantities of untreated POME deplete a water body of its oxygen and suffocate aquatic life. Many small and big rivers have been devastated by such discharge and people living downstream are the worst affected (Madaki and Lau, 2013).

1.2 Research Problem

Palm oil mill effluent (POME) is considered as harmful waste for the environment and aquatic life if discharged untreated (Rupani et al., 2010). This effluent contains high amount of organic pollutants as it possesses high Chemical Oxygen Demand (COD) and Biological Oxygen Demand (BOD) values (Ahmad et al., 2005). Most common

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treatment of POME by mills in Malaysia is biological treatment such as anaerobic and aerobic treatment before discharging the effluent. The biological treatment did not achieve the POME discharge standards of Environmental Quality Regulations (Wu et al., 2010). In addition, the eutrophication effect will occur when the high organic content of POME is being discharged into the river. This effect may cause the death of aquatic life due to the insufficient oxygen. Furthermore, the unpleasant smell of discharging POME is uncomfortable to the public. It affect the working environment and circumstances (Tan et al., 2014). However, it is non-toxic due to no addition of chemicals through the extraction process of palm oil.

In this study, the possibility of treating POME by using a combination of TiO_2 and chitosan (TiO_2/CS) systems were explored. The combined system is suitable because the incorporation of polyelectrolyte of chitosan polymer at the surface of the TiO_2 can induce synergistic effect (Zainal et al., 2009). Furthermore, the preparation of the catalyst is considered as a green process and low cost system with utilization of low amount of chemicals in the preparation of TiO_2/CS. Besides, chitosan is a natural, modified carbohydrate biopolymer produced by deacetylation of chitin obtained from shrimp shell wastes. Chitosan is considered as a versatile and an environmentally friendly raw material as it is non-toxic (Huang et al., 2017). It is recommended as a suitable resource material, because it has excellent properties, such as biodegradability, biocompability, adsorption property, flocculating ability, polyelectrolisity and its possibilities of regeneration in number of applications adsorption process (Ahmad et al., 2005).

The preparation of TiO_2 and chitosan, through immobilisation of the catalyst on the glass beads (GB). It is expected to be able to increase the photodegradation and adsorption processes in which GB will serve as a substrate to immobilise the TiO_2/CS during the treatment and enhanced the dispersion of TiO_2 in the solution as TiO_2 powder tends to agglomerate even under aeration during the photodegradation process. Besides, GB has tetrahedral units on glass surface interact with the protonated chitosan amino (NH^{3+}) during the coating process (Vieira et al., 2014). At this stage, during the initial study, Methyl Orange (MO) used as it is easy to vary the operating parameters in order to investigate the efficiency of the new modified system. MO is also considered as a model type of pollutant because they impart colour to the receiving water bodies as the MO used to substitute the POME in preliminary study. Besides, the aromatic compound of the MO structures existed as in the oil and grease of POME.

In addition that make this catalyst system suitable for treatment of POME due to the filtration steps by using micro membrane filter after experiment is not necessary compared to other methods. As a result, it produced low cost operation for this treatment. The reusability of catalyst is very important for industrial application, as this will also reduce the operation costs. Therefore, the modification of TiO_2 and CS is hopeful able to treat the POME efficiently with a green and low cost operations.

1.3 Research Objectives

The objectives of this research are:

1. To immobilised TiO2 and CS through Titanium Dioxide Impregnated Chitosan (TiO2-CS) for efficient treatment of POME.
2. To evaluate the performance of Titanium Dioxide Impregnated Chitosan (TiO2-CS) coated on glass beads system and optimise removal parameters by using a model dye, Methyl Orange.
3. To investigate the kinetic MO removal by using TiO2-CS coated on glass beads system.
4. To evaluate the feasibility of combination TiO2 and chitosan systems in the treatment of POME

1.4 Scope of Research

The experiments in this study were conducted at laboratory scale. The studied sample POME was collected from palm oil mill in Dengkil, Selangor. Three major systems were studied (i) TiO_2 photocatalyst; (ii) Chitosan adsorption, (iii) Titanium Dioxide Impregnated Chitosan (TiO_2-CS) photocatalyst and adsorption processes and (iv) Modification of Titanium Dioxide Impregnated Chitosan (TiO_2-CS/GB) photocatalyst and adsorption processes. All the processes were evaluated based on their performance in treating POME. The performance was analysed by using percentage COD and colour removal, UV-Vis absorbance (λ=287.0 nm for POME and λ=462.3 nm for MO) The parameters studied were pH, TiO_2 loading, chitosan loading, TiO_2-CS loading, glass beads loading and concentrations of Methyl Orange to obtain the optimum condition in treating POME.

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