PHOTOCATALYTIC DEGRADATION OF OILY WASTEWATER: EFFECT OF CATALYST CONCENTRATION LOAD, IRRADIATION TIME AND TEMPERATURE

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I declare that this thesis entitled "Photocatalytic Degradation of Oily Wastewater: Effect of Catalyst Concentration Load, Irradiation Time and Temperature" is the result of my own research except as cited in references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree."

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Special Dedication of This Grateful Feeling to My…

Beloved father and mother;
Mr. Mok Bin Saliman and Mrs. Roslinda Bt Katan

Loving brothers;
Khairul Azahari and Kamarul Azizi

Supportive families;
Uncles and Aunties

For Their Love, Support and Best Wishes.

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ABSTRACT

The photocatalytic degradation of an oily wastewater over titanium dioxide, TiO_2 suspensions was investigated. The study focused on the effects of various operating parameters on the treatment efficiency which include catalyst concentration load, irradiation time and reaction temperature. Catalyst concentration load was studied in the range 0.5-2.5 g/L, irradiation time between 0-150 min and the reaction temperature in the range 30-60 ^{o}C. The regression and graphical analysis with statistical significance for this researched were done using Design Expert 7 software. In order to visualize the relationship between the experimental variables and responses, the response surface was generated from the model. Treatment efficiency, which was expressed in terms of chemical oxygen demand (COD), generally increased with decreasing initial COD. Higher treatment efficiency involved the increasing of irradiation time with temperature. The percent of degradation nearly achieved 51% depending on the conditions employed. The optimum conditions for this research work can be acquired at catalyst concentration of 0.5 g/L while the effect of temperature and reaction time were conducted at 60 ^{o}C and 150 min respectively.

ABSTRAK

Degradasi cahaya bermangkin ke atas air buangan berminyak bergantung kepada titanium dioxide katalis telah dijalankan. Kajian ini tertumpu pada kesan pelbagai operasi parameter ke atas efisiensi rawatan air buangan termasuk kadar katalis yang digunakan, masa penyinaran dan juga suhu tindak balas. Kadar pemangkin yang telah dikaji adalah di dalam lingkungan 0.5-2.5 g/L, masa penyinaran diantara 0-150 minit dan suhu tindak balas dalam lingkungan 30-60 ^{o}C. Regresi dan analisa grafik dengan signifikasi statistik di dalam kajian ini telah dilakukan dengan menggunakan “Design Expert 7 software”.Untuk menggambarkan hubungan di antara faktor dan reaksi eksperimen, reaksi permukaan telah terhasil daripada model tersebut. Efisiensi rawatan air buangan, yang mana dinyatakan dalam istilah “COD”, biasanya meningkat dengan penurunan nilai COD asal. Efisiensi rawatan air buangan yang tinggi melibatkan pertambahan masa penyinaran bersama pertambahan suhu tindak balas. Peratus penguraian yang dicapai dalam kajian ini hampir 51% bergantung kepada keadaan dimana tindak balas dijalankan. Keadaan yang maksimum diperolehi untuk mencapai peratus penguraian yang tertinggi di dalam kajian ini adalah pada 0.5 g/L kadar katalis sementara suhu tindak balas dan masa penyinaran dijalankan pada 60 ^{o}C dan 150 minit berturut-turut.

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CHAPTER 1

INTRODUCTION

1.1 Overview of Research

Palm oil industry currently viewed as the most important agro-industry in Malaysia (Bhatia *et al*., 2007; Zhang *et al*., 2007; Kathuria, 2006). Malaysian Palm Oil Board (MPOB) has been recorded that the production of Crude Palm Oil (CPO) increased 12.1% in 2008. The statistics from MPOB proved that the production of CPO increased annually as the result of expansion of the Malaysian palm oil industry (http://econ.mpob.gov.my/economy/Overview2008-latest130109.htm).

However, the rapid growth of the palm oil industry in Malaysia has invited serious water pollution in the rivers. Increased the production of CPO resulted the increased of Palm Oil Mill Effluent (POME) produced from the CPO process. This in turn results on the increase of discharges of untreated wastewater into water bodies. As the consequence of this situation, the waters are harmed and the aquatic life especially freshwater fish could not survive in them. Palm oil industry in Malaysia was identified as the industry that produces the ever largest pollution load into the rivers of Malaysia (Kathuria, 2006).

In the past decades, there were various treatment and disposal methods have been proposed, investigated and commercialized to eliminate and reduce POME pollution. The treatment processes included crop irrigation, animal fodder, decanting and drying, evaporation, simple skimming, coagulation, adsorption, flotation, membrane technology, various aerobic and anaerobic biodegradation (Zhang *et al.*, 2007). Overall, the conventional biological treatments of anaerobic or facultative digestion are the most commonly used, although it requires high maintenance and monitoring (Ahmad *et al.*, 2003).

An ideal wastewater and water treatment process should be cost effective and most importantly, the process do not leave behind any hazardous residues. In the past two decades, photocatalytic degradation has been found as an alternative technology and widely investigated to be applied in solving environmental problems. It is useful for the removal of organic pollutant and microorganisms (Saquib *et al.*, 2007; Josef *et al.*, 2006). Using titanium dioxide, TiO_2 as photocatalyst, the process has been successfully degraded and reduces the organic pollutant and microorganisms in wastewater (Chen *et al.*, 2007; Josef *et al.*, 2006).

There are two catalyst configuration of photoreactor used which are slurry and immobilized. In a slurry photoreactor, the catalyst particles will be freely dispersed throughout the reactor. On the other hand, for immobilize photoreactor, the catalyst will be anchored to a fixed support such as fiberglass, activated carbon, fiber optic cables, glass, glass beads, glass wool, membranes, quart sand, zeolites, silica gel, stainless steel and Teflon (Hugo *et al.*, 2005).

Many parameters have been investigated to identify the effectiveness of photocatalytic degradation treatment. The parameters that have been studied are the effects of irradiation time, solution pH, temperature, initial concentration of substrate, catalyst concentration, photoreactor design and light intensity (Huang *et al.*, 2007; Fotiadis *et al.*, 2007; Chen *et al.*, 2007; Saquib *et al.*, 2007; Tang *et al.*, 2007). For example, the degradation efficiency of the substrate decreases with the increases of substrate concentration (Saquib *et al.*, 2007). The result for the effects in the catalyst concentration loading found that the initial reaction rates directly proportional to the catalyst concentration (Huang *et al.*, 2007). Besides that, the degradation efficiency enhanced with increasing incident light intensity as the result effect of light intensity (Huang *et al.*, 2007).

1.2 Statement of Problem

As mentioned earlier, large quantities of oily wastewater are produced from the crude oil extraction process known as Palm Oil Mill Effluent (POME). The effluent contains high biochemical oxygen demand (BOD) liquid waste and chemical oxygen demand (COD) (Bhatia *et al.*, 2007; Okwute *et al.*, 2007; Zhang *et al.*, 2007; Kathuria, 2006; Ahmad *et al.*, 2003; Borja *et al.*, 1996). Based on the statistics of total CPO production in May 2001, for 985, 063 tonnes of CPO produced will use 1,477,595 m^3 of water and 738,797 m^3 will end up as POME. In the year 2005, the production of CPO resulted in 44.88 million tonnes of POME. Abundance of effluent will pollute the watercourses if the POME discharged without proper treatment (Bhatia *et al.*, 2007; Ahmad *et al.*, 2003).

Currently, the majority of palm oil mills have adopted conventional biological treatment. In conventional biological treatment, vast amount of biogas were generated. The biogas contains methane, carbon dioxide and hydrogen sulphide which some of the gas are corrosive and odorous. Besides that, the treated water produced also cannot be recycled back to the plant (Bhatia *et al.*, 2007).

However, innovative treatment technologies have been developed and applied to compliments primary treatment and secondary treatment for further improvement of wastewater quality. Therefore, tertiary treatment process in particular photodegradation will be applied as a new and improved POME treatment technology in order to meet Zero Discharge Approach and achieved standards of pollution control.

1.3 Objectives of the Study

This research aims to study the effectiveness of photocatalytic degradation treatment on oily wastewater. There are two specific objectives:

i) To study the effect of catalyst concentration, temperature and irradiation time under the UV lamp sources on the treatment efficiency.

ii) To study the degradation activity of oily wastewater.

1.4 Scope of the Study

The scopes of study for this research are:

i) The treatment efficiency of the degradation is measure in terms of dissolved oxygen (DO) and chemical oxygen demand (COD) by using the DO meter and COD analyzer before and after the treatment.

In this research, the degradation process will be conducted at constant oil concentration (4 wt%). The catalyst concentration range within 0.5 g/L to 2.5 g/L. the temperature condition will be in the range of 30 ^{o}C to 60 ^{o}C. The irradiation process will be conducted from 0 min to 150 min.

1.5 Rational and Significance

The photocatalytic degradation is an alternative technology that has been investigated during the past two decades by many researchers. This technology widely investigated for the degradation of organic pollutants in the treatment of wastewater without leaving behind any hazardous residues and should also be cost effective. The potential in successfully degraded pollutant bring this method useful and advantageous to improve wastewater effluent. Photocatalytic degradation will help to achieve standards of pollution control and to prevent environmental pollution such as river and soil pollution. This technology can be commercialized for industrial application due to low operation temperature, low cost and significantly low energy consumption.

CHAPTER 2

LITERATURE REVIEW

2.1 Photocatalytic Degradation

Over the past two decades, heterogeneous photocatalytic degradation has been widely investigated in the water and wastewater treatment. This treatment becomes an alternative technology for industrial applications (Josef *et al.*, 2006; Saquib *et al.*, 2007). This process involved the use of UV irradiation, solar irradiation, and titanium dioxide, TiO_2. Titanium dioxide, TiO_2 is widely used for photocatalytic degradation. It shows that photocatalytic degradation potentially advantageous, useful and successfully degraded organic pollutants and microorganisms in water (Chen *et al.*, 2007; Josef *et al.*, 2006). There are some reasons on increased interest research in photocatalytic degradation which this treatment takes place under ambient condition and no other chemicals are required. The previous research reported that photocatalytic degradation process yield almost complete mineralization of organic substrates to CO_2, H_2O and relevant inorganic ions (Huang *et al.*, 2007; Hugo *et al.*, 2005; Josef *et al.*, 2006; Zhao *et al.*, 2007).

2.2 Reaction Mechanism of Photocatalytic Degradation

Based on the previous research, when the TiO_2 semiconductor irradiated, a photo-excited TiO_2 will generate mobile electrons and electron-hole. It is happen when TiO_2 is irradiated with photons of energy equal to or higher than its band gap, an electron may be excited from the valence band to the conduction band (e-) and leaving a hole in the valence band ($h^{+)}$. Therefore, paired of e^- -h^+ are created. Oxidation and reduction reactions initiated at different sites by the subsequent reactions with O_2. The reactions formed several active oxygen species such as $HO^\bullet$ (hydroxyl radicals), $O^{2\bullet-}$ (superoxide radical anions), and $HO_2^\bullet$. $HO^\bullet$ radicals is the most important oxidizing agent which are very reactive and attack the pollutants molecule contributing to degrade the organic pollutants into mineral acids including CO_2 and H_2O (Huang *et al.*, 2007; Chen *et al.*, 2007; Zhao *et al.*, 2007; Saquib *et al.*, 2007; Josef *et al.*, 2006; Hugo *et al.*, 2005).

Equations below showed the photocatalytic degradation reaction mechanism. Overall reaction equation was indicated in Equation (2.1).

$$\text{Hydrocarbon} \xrightarrow{TiO_2,\ UV} CO_2 + H_2O \qquad (2.1)$$

$$TiO_2 \xrightarrow{hv} TiO_2\ (e^- + h^+) \qquad (2.2)$$

$$O_{2(ads)} + e^- \longrightarrow O_2\bullet^- \qquad (2.3)$$

$$O_2\bullet^- + H_2O \longrightarrow HO_2\bullet + OH^- \qquad (2.4)$$

$$2HO_2\bullet \longrightarrow H_2O_2 + O_2 \qquad (2.5)$$

$$H_2O_2 + hv \longrightarrow 2\bullet OH \qquad (2.6)$$

$$OH^- + h^+ \longrightarrow \bullet OH \qquad (2.7)$$

$$H_2O_{ads} + h^+ \longrightarrow OH + H^+ \qquad (2.8)$$

2.3 Titanium Dioxide, TiO_2 as Photocatalyst

Any semiconductors can be the catalyst of photocatalysis. But, photocatalysis on TiO_2 photocatalyst has been given attention in wastewater and water treatment. It is because lack of mass transfer limitations, the operation occurs under ambient conditions and the possible use under solar irradiation. TiO_2 reported as the best photocatalyst due to the particle characteristics such as non-toxicity, photochemically stable and high reactivity. Otherwise, the catalyst itself is inexpensive and commercially available in various crystalline forms (Tang *et al*., 2008; Zhao *et al*., 2007; Efthalia *et al.*, 2007; Fotiadis *et al*., 2007; Mohamed *et al*., 2004).

2.4 Reactors for Wastewater Treatment

Photocatalytic reactors for wastewater treatment can be classified according to their design characteristics such as state of the photocatalyst, type of illumination and position of the irradiation source.

2.4.1 State of the Photocatalyst

The photocatalyst can be either suspended or attached to a support:

i) Photocatalytic slurry reactors
ii) Photocatalytic reactors with immobilized photocatalyst.

The photocatalytic TiO_2 slurry reactors designed for the freely dispersed of catalyst particles in the solution while the photocatalytic immobilized TiO_2 reactors designed with the catalyst anchored to a fixed support and dispersed on the stationary phase (Hugo *et al.*, 2005).

2.4.2 Type of Illumination

The type of irradiation is a major design issue for photocatalytic reactors. Reactors can be irradiated using:

i) UV polychromatic lamps
ii) Solar light.

Two subcategories branch off from solar illuminated reactors which are non-concentrating reactors and concentrating reactors. Non-concentrating solar irradiated reactors employed intensities equal or lesser than natural solar irradiation while concentrating solar reactors used irradiation intensities that surpass irradiations equivalent to one sun (Hugo *et al.*, 2005).

Concentrating reactors is better than non-concentrating reactors because the degradation efficiency enhanced with increasing incident light intensity. The enhancement of degradation rate with increasing light intensity resulted there are being more light energy to be used for the photocatalytic degradation (Huang *et al.*, 2007).

The advantages of using UV polychromatic lamps are the photocatalytic degradation process was much faster and more complete (Zhao *et al.*, 2007). One of the disadvantages of UV polychromatic lamp the cost is expensive.

2.4.3 Position of the Irradiation Source

The position of the lamp or source of the irradiation is a distinguishing feature of a photocatalytic reactor. The lamp position determines different configurations:

i) Reactors with an immersed light source
ii) Reactors with an external light source
iii) Reactors with distributed light sources.

For immersed sources reactors, the lamp is placed inside the reactors while external source photocatalytic reactors have lamp located outside the reactor vessel. In distributed reactors design, irradiation is transported from the source to the reactor by optical mean such as reflectors or light guides (Hugo *et al*., 2005).

An immersed sources reactor is more efficient than external source and distributed reactors because the distance of lamp is one of the factors that influence the degradation rate. The lamp source placed inside the reactor is much closer to the wastewater resulted in higher degradation rate because greater increase in probability of absorption between photons and active sites on the TiO_2 surface (Zhao *et al*., 2007).

2.5 Types of Reactors for Photocatalytic Degradation

There are two types of photoreactors has been employed for water treatment before which are TiO_2 slurry reactors and immobilized TiO_2 photocatalytic reactors. The photocatalytic TiO_2 slurry reactors designed for the freely dispersed of catalyst particles in the solution while the photocatalytic immobilized TiO_2 reactors designed with the catalyst anchored to a fixed support and dispersed on the stationary phase. Currently, TiO_2 slurry reactors are majority used for water treatment. It showed that photocatalytic activity with TiO_2 slurry reactors is largest than immobilized TiO_2 reactors. The great advantage of TiO_2 slurry reactors is good mass transportation. But the main disadvantage is the catalyst requires long settlement times to be separated from the solution and have to be employed fine filters. So, the recently attention turned to use photocatalytic immobilized TiO_2 reactors. Table 2.1 shows the advantages and disadvantages between TiO_2 slurry reactors and photocatalytic immobilized TiO_2 reactors (Hugo *et al.*, 2005).

Table 2.1 : Suspended versus immobilized photocatalytic systems (Hugo *et al.*, 2005)

Slurry reactors	**Immobilized reactors**
Advantages • Fairly uniform catalyst distribution • High photocatalytic surface area to reactor volume ratio • Limited mass transfer • Minimum catalyst fouling effects due to the possible continuous removal and catalyst replacement • Well mixed particle suspension • Low pressure drop to the reactor	Advantages • Continuous operation • Improved removal of organic material from water phase while using a support with adsorption properties • No need for an additional catalyst separation operation
Disadvantages • Requires post-process filtration • Important light scattering and adsorption in the particle suspended medium	Disadvantages • Low light utilization efficiencies due to light scattering by immobilized photocatalyst • Restricted processing capacities due to possible mass transfer limitations • Possible catalyst deactivation and catalyst wash out.

2.6 Typical TiO_2 Supports

Previous studied shows that many typical TiO_2 supports are used. The supports which have been investigated are activated carbon, fiber optic cables, fiberglass, glass, glass beads, glass wool, membranes, quart sand, zeolites, silica gel, stainless steel and Teflon (Hugo *et al*., 2005).

2.7 Operating Parameters

Based on the previous investigations, several operating parameters were employed in the wastewater and water treatment. The parameters such as the effects of irradiation time, solution pH, temperature, initial concentration of substrate, catalyst concentration loading, photoreactor design and light intensity were investigated (Huang *et al*., 2007; Fotiadis *et al*., 2007; Chen *et al*., 2007; Saquib *et al*., 2007; Tang *et al*., 2007).

2.7.1 Effect of Initial Concentration of Substrate

The result for the effects of initial concentration of substrate is the degradation rate decreases with the increase in substrate concentration form 0.125 to 0.5 mM for photocatalytic degradation of disperse blue 1 using $UV/TiO_2/H_2O_2$ process. However, further increase in substrate concentration leads to increase in the degradation rate. Decreasing in degradation rate with the increasing of substrate concentration related to the fact as the initial concentration of substrate increases, the irradiating mixture color becomes more and more intense. This situation prevents the penetration of light to the surface of the catalyst. This can be conclude that the degradation efficiency of the substrate decreases with the increases of substrate concentration (Saquib *et al*., 2007).