UNIVERSITI PUTRA MALAYSIA

TREATMENT OF PALM OIL MILL EFFLUENT BY USING 2-STAGE PHOTO FERRIOXALATE/TiO2/OZONE SYSTEM

NOR AQILAH BINTI MOHD FADZIL

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MASTER OF SCIENCE

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2013

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By

NOR AQILAH BINTI MOHD FADZIL

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Master of Science (Catalysis)

May and 2013

DEDICATIONS

- IN THE NAME OF ALLAH-

I dedicated this thesis to my parents;

Mr. Mohd Fadzil bin Mohd Nor and Mdm. Khairiyah Binti Jaafar

Thank you for giving me a chance to improve my life and giving me a full support during my studies.

May ALLAH bless both of you

Amiiin.

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of athe requirement for the degree of Master of Science (Catalysis)

TREATMENT OF PALM OIL MILL EFFLUENT BY USING 2-STAGE PHOTO FERRIOXALATE/TiO_2/OZONE SYSTEM

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May, 2013

Chair : Zulkarnain Zainal, PhD

Faculty: Faculty of Science

The feasibility of advanced oxidation processes (AOPs) named photo Ferrioxalate/TiO_2/Ozone system in degrading Palm Oil Mill Secondary Effluent (POMSE) was investigated. The investigation was divided into two major parts; first was the degradation of POMSE by using single (photo Fenton, Ferrioxalate, TiO_2 and Ozone) and combined system of AOPs (photo Ferrioxalate/TiO_2 and photo Ferrioxalate/TiO_2/Ozone) and second was the degradation of POMSE by two stages treatment system. As expected combined processes showed better performance than single systems with the COD removal recorded for photo/Ferrioxalate, photo TiO_2 and photo Ferrioxalate/TiO_2 were 49 %, 57 % and 65 %, respectively. In addition, two stages treatment system of photo Ferrioxalate/TiO_2/Ozone system (photo Ferrioxalate/TiO_2 for the first two hours followed by ozonation for another two hours) shows total removal of color and COD. Moreover, more than 85 % removal was recorded for the TOC. On the other hand, single stage treatment process gave only 54 %, 69 % and 61 % removal of COD, TOC and color, respectively. Besides, the effect of H_2O_2 concentration, TiO_2

loading and pH were also studied to determine optimum condition for the removal. The reaction mechanism was illustrated to explained the chemical process occur in all system. First order kinetic model was applied to explain the relationship between initial POMSE concentration and its initial degradation rate. The optimization of single stage treatment process was conducted by using Response Surface Methodology (RSM) and it gave 20 % increment in four hours reaction time with optimum parameters as follow: $[H_2O_2:Fe^{3+}]$ = 5.5 :1.0; [oxalate: Fe^{3+}] = 5.5 : 1.0 and TiO_2 = 225 mg. The optimization was verified by using analysis of variance (ANOVA). Methyl Orange (MO) had been used as colored organic pollutant to observe the feasibility of photo Ferrioxalate/TiO_2/Ozone system in treating simple colored wastewater. The results gave total decolorization for 20, 100 and 200 ppm of MO. Meanwhile, almost 90 % decolorization recorded at 500 ppm.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Sarjana Sains (Pemangkin)

RAWATAN SISA SEKUNDER KILANG MINYAK KELAPA SAWIT MENGGUNAKAN SISTEM FOTO FERRIOXALAT/TiO_2/OZON SECARA DUA PERINGKAT

Oleh

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Kemampuan proses pengoksidaan termaju (AOPs) iaitu foto Ferioxalat/TiO_2/Ozon telah dikaji untuk degradasi efluen sisa sekunder kilang minyak kelapa sawit (POMSE). Proses degradasi terbahagi kepada dua bahagian utama; pertama melalui degradasi sistem tunggal (Foto Fenton, Ferioxalat, TiO_2 dan Ozon) dan sistem kombinasi AOPs (Foto Ferrioxalate/TiO_2 dan foto Ferioxalat/TiO_2/Ozon) dan kedua melalui degradasi POMSE secara dua peringkat. Sistem kombinasi menunjukkan prestasi degradasi yang lebih baik berbanding sistem tunggal AOPs. Penyingkiran COD untuk proses Foto/Ferioxalat, Foto/TiO_2 dan Foto/Feriolezalat/TiO_2 adalah masing-masing sebanyak 49 %, 57 % dan 65 %. Manakala, kaedah dua peringkat (Foto Ferioxalat/TiO_2 pada dua jam pertama diikuti pengozonan untuk dua jam berikutnya) pula mencatatkan keputusan penyingkiran sepenuhnya bagi COD dan warna. Tambahan pula, 85 % penurunan TOC turut dicatatkan. Sebaliknya, sistem satu peringkat hanya mencatatkan penyingkiran

COD, TOC dan warna masing-masing sebanyak, 54 %, 69 % dan 61 %. Selain itu, kajian berkaitan parameter lain seperti kepekatan optima bagi H_2O_2 dan TiO_2 dan pH turut dijalankan. Mekanisma tindak balas bagi setiap proses telah ditunjukkan. Selain itu, model kinetik turutan pertama telah digunapakai bagi menjelaskan hubungan antara kepekatan POMSE dan kadar degradasinya. Pengoptimum sistem satu peringkat menggunakan metodologi permukaan tindakbalas (RSM) turut dijalankan dan berjaya memberi peningkatan penurunan COD sebanyak 20 %. Parameter optimum yang telah diberikan adalah seperti berikut [H_2O_2:Fe^{3+}] = 5.5 :1.0; [oxalate: Fe^{3+}] = 5.5 : 1.0 dan TiO_2 = 225 mg. Penyahwarnaan Metil Oren (MO) juga telah dilaksanakan bagi memerhati kebolehupayaan sistem Foto/Ferioxalat/TiO_2/Ozon dalam merawat sistem sisa air berwarn. Keputusan menunjukkan sepenuh penyahwarna berjaya dicapai pada kepekatan 20, 100 dan 200 ppm. Manakala, hampir 90 % penurunan warna berjaya direkodkan pada kepekatan 500 ppm MO.

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I certify that a Thesis Examination Committee has met on **(20/05/2013)** to conduct the final examination of Nor Aqilah Binti Mohd Fadzil on her thesis entitled "**Treatment of Palm Oil Mill Effluent by 2-Stage Photo Ferrioxalate/TiO_2/Ozone System**" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Master of Science (Catalysis).

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DECLARATION

I declare that the thesis is my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously, and is not concurrently, submitted for any other degree at Universiti Putra Malaysia or at any other institution.

_____

NOR AQILAH BINTI MOHD FADZIL

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(c) and [H_2O_2: Fe^{3+}]

LIST OF ABBREVIATIONS

MPOB	:	Malaysia Palm Oil Board
USD	:	United States Dollar
POME	:	Palm Oil Mill Effluent
POMSE	:	Palm Oil Mill Secondary Effluent
BOD	:	Biological Oxygen Demand
AOPs	:	Advanced Oxidation Processes
TiO_2	:	Titanium dioxide
UV	:	Ultra violet
UV-C	:	Ultra violet C
H_2O_2	:	Hydrogen peroxide
•OH	:	Hydroxyl radical
•OOH	:	Hydroperoxyl radical
O_3	:	Ozone
$•O_3$	:	Ozonide radical
$K_2C_2O_7$	:	Potassium dichromate
CIO_2	:	Chlorine dioxide
COD	:	Chemical Oxygen Demand
Fe^{3+}	:	Ferric ion
Fe^{2+}	:	Ferrous ion
RSM	:	Response Surface Methodology
CPO	:	Crude Palm Oil
UASFF	:	Up-flow anaerobic sludge fixed
UASB	:	Up-flow anaerobic sludge blanket
OLR	:	Organic loading rate
$[COD]_0$	:	Initial COD reading
UF	:	Ultrafiltration
RO	:	Reverse osmosis
MWCO	:	Molecular weight cut-off
hν	:	Energy from UV light

TOC	:	Total Organic Carbon
X_0	:	Initial weight
X_i	:	Weight at second time
PZC	:	Point of Zero Charge
e^-	:	Photogenerated electron
h^+	:	Photogenerated holes
C	:	Concentration
C_0	:	Initial concentration
ANOVA	:	Analysis of Variance

CHAPTER 1

INTRODUCTION

1.1 Background

In recent years, oil palm plantation has been receiving national attention in Malaysia. Almost 5 million hectares of cultivation area are planted with oil palm trees, compared to only 54 000 hectares in 1960 as shown in Table 1.1. This was attributed to the opening up of many virgin jungles for oil palm plantation. At the same time, many estates converted its crops plantation from rubber to oil palm due to the high demand for oil palm fruits. In addition, oil palm is an efficient oil crops and can produce 10 times higher yield than soy bean oil with the same plantation hectares requirements.

Table 1.1. Total planted area of oil palm in Malaysia in 2012 (source: MPOB, 2012)

Region	Oil palm planted area, hectares
Peninsular Malaysia	2 546 760
Sabah	1 431 762
Sarawak	1 021 587
Total	5 000 109

The benefits plantations of oil palm are their high yield and high demand for palm oil; palm oil is defined as the product from oil palm fruits. This resulted in high numbers of palm oil mills operated to fulfill the high demand for palm oil. In 2006, Yacob et al. (2006) identified 381 active palm oil mills in Malaysia. As mentioned earlier, the rapid growth of oil palm plantation was due to the high world demand for oil and fats that could be produced from palm oil. These oil and fats are the main ingredients in the

making of shortening, margarines and others food preparation (Low et al., 1998). It has been estimated that 75 % of the Malaysia's palm oil product was exported to many countries (Table 1.2) (MPOB, 2012) (Yusoff, 2006). Due to this reason, palm oil industry has become as the major player for oil and fats trading (MPOB, 2012).

Table 1.2. The importer countries of Malaysia oil palm products in 2012
(Source: MPOB, 2012)

Country	thousands tonnes
Egypt	386
India	1 524
Iran	302
Italy	112
Japan	364
Myanmar	228
Netherlands	889
Nigeria	99
Pakistan	918
Philippine	240
Singapore	390
South Korea	232
Spain	125
UAE	121
Ukraine	126
US	685

1.2 Problem Statement and Objectives

1.2.1 Research Problem

A large amount of waste including organic waste in effluent was generated from the palm oil mill. It has been estimated that about 140 thousands tonnes of POME are generated every day. Thus, every month about 4200 thousands tonnes of POME need to be properly managed. This effluent contains high amount of organic pollutant as it possesses high COD and BOD values (Ahmad et al., 2005). The BOD value of POME was almost 100 times more polluted compared to domestic sewage (Wu et al., 2010; Ma and Ong, 1985). Moreover, the fresh POME is thick brownish slurry with quite uncomfortable odor. However, it is non-toxic, due to no chemical added during oil extraction process (Zinatizadeh et al., 2005).

In order to control and eliminate the environmental pollution problem from palm oil industry, Malaysia government enforced an effluent discharge regulation under Environmental Quality (Prescribed Premises) (Crude Palm Oil) (Amendment) Regulations 1982. Therefore, each palm oil mill in Malaysia must treat their effluent before discharged. Most palm oil mills apply biological treatment such as aerobic and anaerobic treatment to treat POME before it is discharged (Wu et al., 2010).The discharged effluent that has been treated is called Palm Oil Mill Secondary Effluent (POMSE). Unfortunately, biological treatment did not enough to comply with the allowable limits for effluent discharge as stipulated by Malaysia government.

Therefore, the introduction of photo Ferrioxalate/TiO_2/Ozone system to treat POMSE was suitable, since this system provides a few advantages. Apart from this system

produce •OH to oxidize organic pollutant unselectively, this system also offer convenience and efficient performance at high pH condition. The application of modified photo Fenton process called photo Ferrioxalate process able to eliminate the major problems of photo Fenton that are inefficient at high pH (pH > 5) and need to remove iron residue by further treatment.

By the application of photo Ferrioxalate system, the treatment of POMSE degradation not only could be conducted at high pH but it also provides the simple way to remove iron residue without any further treatment. This is because POMSE degradation conducted at natural pH of POMSE (pH 9), therefore if any iron that not react in the reaction then it can be removed as $Fe(OH)_3$ precipitation as a result of the reaction between iron (Fe^{3+}) and OH^- ion.

The other reason that make photo Ferrioxalate/TiO_2/Ozone system as a good and reliable treatment system is the utilization of TiO_2 and ozone in one system. This combination can enhance the degradation performance since the presence of ozone can overcome TiO_2 photocatalyst limitation. As a result, more highly reactive radical could be produced and able to oxidize organic pollutant. Therefore, the application of photo Ferrioxalate/TiO_2/Ozone system able to treat POMSE through the oxidation of highly reactive radical produced without produce other sludge pollution.

1.2.2 Research Objectives

The objectives of this research are

i. To evaluate the feasibility of photo/Ferrioxalate/TiO_2/O_3 system in degrading POMSE at pH 9.

ii. To identify the optimum dosage of operating parameters such as TiO_2 amount, [Fe^{3+}], [H_2O_2] and [oxalate] in degrading POMSE at pH 9.

iii. To improve the degradation performance by optimizing the degradation condition by using Response Surface Methodology, RSM.

1.3 Scope of Research

The experiments in this study were conducted at laboratory scale. The sample studied that is POMSE was actual POMSE sample collected from palm oil mill in Dengkil, Selangor. Three major processes of AOPs were studied (i) photo Ferrioxalate; (ii) TiO_2 photocatalyst and (iii) ozonation process. All the processes were evaluated based on their performance in treating POMSE. This performance efficiency was monitored through COD, TOC, UV-Vis absorbance (λ=305 nm) and color removal. The high operating pH was applied to make the system become more convenience and simple, since no alteration of the pH condition was needed before start the experiments. The other parameters studied were pH, TiO_2 loading and optimum concentration ratio of Fe^{3+}: oxalate: H_2O_2.

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