SYNTHESIS AND CHARACTERIZATION OF $MgFe_2O_4$ FOR PHOTO-CATALYTIC DEGRADATION OF PRE-TREATED POME

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ABSTRACT

Edible oil production from Malaysia currently accounts for 12% and 27% of the world's total production and exports of oils and fats. Consequently, the palm oil industry also discharges substantial waste during the oil processing in the form of oil palm trunks, oil palm fronds (OPF), empty fruit bunches, palm kernel shells and palm oil mill effluent (POME). The current work reports the use of ferrite based photocatalyst for the photodegradation of POME that was collected from Felda Lepar Hilir 3. X-ray diffraction pattern confirmed the presence of $MgFe_2O_4$ with crystalline size ranged from 25.4 to 50.5 nm estimated using Scherrer's formula. Significantly, N_2 physisorption isotherm revealed a BET specific surface area of 4.87 m^2/g and pore diameter of 205.23 nm. Transmission Electron Micrograph (TEM) showed d-spacing for $MgFe_2O_4$ atomic lattice which was 0.298 nm. FESEM-EDX analysis indicated that $MgFe_2O_4$ nano-particles were comprised of Mg, Fe and O elements with compositions of 22.5, 43.04 and 34.7 wt%, respectively. For the photoreaction study, before the POME photodecomposition investigation, the photoactivity of catalysts was tested with methylene blue (MB). MB that initially showed a concentration of 20 ppm exhibited significant photodegradation (%) after 90 min of light irradiation, attaining approximately 20% conversion. For POME, the degradation of POME was circa 9% after 4 h employing catalyst loading of 1.0 g/L, which was superior to 5.0, 2.0 and 0.5 g/L. As a conclusion, phototreatment for POME showed positive results, and may be feasible for POME treatment eventually.

Key words: Magnesium ferrite; Palm Oil Mill Effluent; Photocatalysis; Visible Light

ABSTRAK

Pengeluaran minyak dari Malaysia kini menyumbang 12% dan 27% daripada jumlah pengeluaran dunia dan eksport minyak dan lemak. Akibatnya, industri minyak sawit melepaskan sisa-sisa seperti bentuk batang kelapa sawit, pelepah kelapa sawit (OPF), tandan buah kosong, tempurung isirong sawit dan cecair buangan kilang minyak sawit pelepasan (POME) semasa pemprosesan minyak. Projek ini melaporkan penggunaan fotomangkin mengandungi ferit bagi pemfotorosotaan POME yang dikumpulkan dari Felda Lepar Hilir 3. X-ray diffraction mengesahkan bahawa $MgFe_2O_4$ dengan saiz kristal antara 25.4-50.5 nm yang dianggar mengikut formula Scherrer. Dengan ketara, N_2 physisorption isoterma mendedahkan kawasan permukaan tertentu BET adalah 4.87 m^2/g dan diameter liang bersama 205.23 nm. Transmission Electron Micrograph (TEM) menunjukkan d-jarak bagi $MgFe_2O_4$ kekisi atom adalah 0.298 nm. Analisis FESEM-EDX pula menunjukkan bahawa $MgFe_2O_4$ nano-zarah ini terdiri daripada Mg, Fe dan O elemen dengan komposisi masing-masing dengan 22.5, 43,04 dan 34.7 wt%. Bagi kajian photoreaction, sebelum penyiasatan photodecomposition POME, fotoaktiviti pemangkin diuji dengan metilena biru (MB). MB yang pada mulanya menunjukkan kepekatan 20 ppm mempamerkan pemfotorosotaan yang penting (%) selepas 90 min sinaran cahaya, mencapai kira-kira 20% penukaran. Untuk POME, degradasi POME adalah sekitar 9% selepas 4 h menggunakan pemangkin pemuatan 1.0 g / L, yang lebih unggul berbanding dengan 5.0, 2.0 dan 0.5 g / L. Kesimpulannya, phototreatment bagi POME menunjukkan hasil yang positif, dan mungkin boleh dilaksanakan bagi rawatan POME kemudiannya.

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A	The absorbance of the sample incubated
Å	The angstrom or ångström is a unit of length equal to 10^{-10} m
A_o	Absorbance of the phosphate buffer
C	A characteristic constant of the adsorbate
C_{eq}	Equilibrium concentration
C_F	Formate concentration
$C_{OH^\bullet}$	Hydroxyl and super oxide radical concentrations
C_R	Concentration of organic pollutant
d	Distance between atomic layers in crystal
E_b	Binding energy of photoelectron with respect to the Fermi level of the sample
E_k	kinetic energy of the photoelectron
K	Adsorption constant onto the catalyst surface
k_r	Intrinsic reaction rate constant
k_R	The second-order rate constant
k'_R	Pseudo-first-order rate constant
n	An integer
P	Gas pressure
P_s	Saturation pressure of the adsorbate gas
r_o	Initial reaction rate
V	Volume of gas adsorbed
V_m	Oolume of gas adsorbed corresponding to monolayer coverage

Greek

λ	Wavelength of incident X-ray beam
h	Planck’s constan
v	Frequency of the exciting radiation
φ	Work function of the spectrometer

Subscripts

ads	adsorption
g	gas
l	liquid

LIST OF ABBREVIATIONS

BET	Brunauer, Emmett and Teller theory
BOD	Biochemical oxygen demand
CB	Conducting band
CDM	Clean development mechanisms
COD	Chemical oxygen demand
DOE	Department of Environmental
EDX	Energy dispersive X-ray
FESEM	Field emission scanning electron microscopy
CPO	Crude palm oil
FFB	Fresh fruit brunches
GHG	Greenhouse gas
MB	Methylene blue
N/A	Not applicable
POME	Palm oil mills effluent
PPF	Palm pressed fibres
ppm	Part per million
TEM	Transmission Electron Micrographs
UV	Ultraviolet light
VB	Valence band
XRD	X-ray diffraction

1 INTRODUCTION

1.1 Background

Palm oil is one of the world's most rapidly expanding equatorial crops. Indonesia and Malaysia are the two largest oil palm producing countries in the world. This is due to the availability of fertile arable land and suitable climate. As of today, oil palm cultivation currently occupies the largest farmed land bank in Malaysia. In year 2011, the total planted area was 4.917 million hectares while Malaysia produces 19.2 million tonnes of the global oils and fats trade in 2013.

Although palm oil industry generates a lucrative recurring income, it also emits highly polluting waste-water that is widely known as Palm Oil Mill Effluent (POME). POME is an oily wastewater generated by palm oil processing mills and consists of various suspended components. This liquid waste combined with the wastes from steriliser condensate and cooling water is called palm oil mill effluent (POME). On average, for each ton of fresh fruit bunches (FFB) processed, a standard palm oil mill generate about 1 tonne of liquid waste with biochemical oxygen demand (BOD) 27 kg, chemical oxygen demand (COD) 62 kg, suspended solids (SS) 35 kg and oil and grease 6 kg (Zafar, 2011). The suspended solids in the POME are mainly oil-bearing cellulosic materials from the fruits. This liquor is often discarded in disposal pond that risks leachate leaking that can potentially pollute the groundwater and soil. Moreover, POME when naturally degraded also releases CH_4, a greenhouse gas agent capable of wreaking havoc to the global weather pattern.

POME poses detrimental effects to aquatic life as it has very high Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) values, topping more than 100 times of the municipal sewage. Although POME can be classified as a non-toxic waste in the absence of chemical additions during oil extraction, it will still pose serious environmental issues due to large oxygen depleting capability, organic and nutrient contents in aquatic system. The high organic matter is due to the presence of different sugars such as arabinose, xylose, glucose, galactose and manose.

Several treatment technologies have been employed for POME treatment, since the direct discharge of POME adversely affects the environment. These treatment processes include bioreactor system, membrane technology and anaerobic biodegradation to convert waste into valuable products such as feed stock and organic fertilizer (Singh et al., 2010). As an alternative, the current research proposed the photocatalysis pathway as another promising technology for the treatment of POME. The advantage of photocatalysis in water purification is the complete mineralization of organics. This ensures the effectiveness of POME treatment as the main purpose for the treatment is to degrade the organic contents. Besides, in terms of energy consumption, ultimately the sun would be a continuous and readily available power supply for photocatalysis as the activator needed for this process is visible light or UV radiation (Kondarides, 2001). Thus, the operating costs would be greatly reduced and the cost efficiency guaranteed.

Magnesium ferrite ($MgFe_2O_4$) is a catalyst that has been employed in a number of prior studies to degrade organic compounds. Therefore, in principle, it can also be used for POME treatment. The $MgFe_2O_4$ has a cubic structure of normal spinel-type which finds a number of applications in heterogeneous catalysis, adsorption, sensors, and in magnetic technologies (Maensiri, 2008). These structures of magnetic materials have received more and more attention due to their novel material properties that are significantly different from those of their bulk counterparts. In addition, it also possesses low toxicity, low resistance towards corrosion and contain magnetic property.

1.2 Problem Statement

In Malaysia, the wastes from palm oil industry has created an environmental hazard and entailed high disposal costs every year (Nour, 2012) due to its sheer volume of 12.48 million tonnes POME annually. Therefore, it needs to be treating treated before being discharged. The commonly used conventional treatment facilities such as holding ponds, decanters, anaerobic digesters and aerated lagoons, are unable to meet the emission limits set by the Department of Environment (DOE), which has decreed BOD_3 as a controlling parameter with a limit of 100 mg/L, and to some extent and most cases, $BOD_3 < 20$ mg/L is imposed. Therefore, high rate treatment systems are necessary to treat POME and protect the river system from water pollution.

In the past, photocatalysis process has been found as an alternative technology and widely investigated for treating organic contents in water. Photocatalysis applies the concept of photoreaction acceleration over a catalyst irradiated by UV or visible light (Singh, 2007). It has been touted as one of the most effective clean technology for waste water treatment via removal of organic contaminants. During photoreaction, the photocatalyst will absorb the UV or visible light-energy and attract electrons across the energy gap into the conduction band. This electron will change into hydroxyl radicals which can decompose organic compounds. Most of the previous works in this area uses titanium oxide TiO_2 (Amadelli et al., 2005), based photocatalysts. However, this type of photocatalyst is only effective under the UV-light source and not efficient for visible light application (Fujishima et al., 2000). To solve this problem, in the current work, ferrite-based photocatalysts will be prepared with magnesium (Mg) as an active metal. Subsequently, the effectiveness of synthesized catalyst and photoreaction result will be determined from the work. With this photocatalyst, the performance of photocatalysis of POME will be greatly enhanced and photo-degradation of POME will be successfully implemented.

1.3 Objective

This study is to synthesize and characterize magnesium Ferrite ($MgFe_2O_4$) for photocatalytic degradation of pre-treated POME.

1.4 Scope of Study

To achieve the objective of current work, several scopes have been identified:

1. To synthesize ferrite-based photocatalyst magnesium as active metal employing wet-impregnation technique (stoichiometric ratio Magnesium to Iron (III)oxide 1:2)
2. To characterize the physiochemical properties of photocatalysts via:
   i. Liquid N_2 physisorption for surface area and pore size distribution measurement
   ii. X-ray diffraction (XRD) for crystalline structure scanning
   iii. Transmission Electron Micrographs (TEM) for atomic lattice imaging and *d*-spacing measurement
   iv. UV-Vis for band gap energy characterization

v. Field Emission Scanning Electron Microscopy-Energy Dispersive X-ray (FESEM-EDX) for surface morphology capturing

3. Analyse the chemical oxygen demand (COD) of pre-treated POME before and post photoreaction by 1g/L photocatalyst loading with different time.

1.5 Rational and Significance

Palm oil and its industry is a significant contributor to the Malaysian economy with a production of 19.2 million tonnes of global oils and fat trade in 2013. Nutrients contain in POME according to are nitrogen, phosphorus, potassium, magnesium and calcium. If the effluent is discharged untreated, it can cause significant environmental impact due to its high biochemical oxygen demand (BOD), chemical oxygen demand (COD), oil and grease, and total solids (Mohammed, 2014). Therefore, in the current work, photocatalysis as another pathway for treatment of POME will be tested. With a better treatment process, POME's organic compound can be reduced. In addition, this will maintain the ecological balance preserve the environment. Secondly, although biological treatment is the most favoured POME treatment in Malaysia, an anaerobic biological system has difficulties of start-up procedure, which can be time-consuming and unproductive. The ponding system, extended aerobic system and anaerobic digestion normally require long retention time (Cail & Barford, 1985). This work is believed to reduce the time for treatment process.

This project helps in exploring the application potential of photocatalysis process in POME treatment. The best composition of photocatalyst to get an excellent result will be determined in this work. Besides that, this method not just in POME treatment, it also can use for other industry wastewater. Then, this technology has potential to be commercialized for industrial application due to low cost and significantly low energy consumption.

2 LITERATURE REVIEW

2.1 Overview

The oil palm industry is one of the leading agricultural industries in Malaysia with an average crude oil production of more than 13 million tons per year. The original plant was introduced from West Africa to the Bogor Botanical Gardens, Indonesia in 1848. Introduced as an ornamental in 1871 in Malaya at that time, the oil palm was commercially exploited as an oil crop only from 1911 onwards when the first oil palm estate was established (Basiron, 2004). Much has been written about the crop, its products and commercial trade. However, the production of crude palm oil has resulted in large amount of palm oil mill effluent (POME) that contains high chemical oxygen demand (COD) and biochemical oxygen demand (BOD) values. In particular, a direct POME discharge will cause a disastrous ecological wipe out to the aquatic organisms and plants. Therefore, POME needs further treatment before discharged into waterway.

Normal treatment methods viz. anaerobic digestion, extended aerobic process, ponding system, bioreactor system as well as composting system have different drawbacks i.e. long retention time for ponding system and high operating cost for aerobic digestion. Hence, the specific objective of this work employs a green photo-catalytic pathway to degrade organic compounds of the POME. Towards this end, magnesium ferrite, ($MgFe_2O_4$) photocatalyst will be synthesized by wet-impregnation technique for the phototreatment.

In a brief for this chapter, palm oil and its sustainability, palm oil production process, palm oil mill effluent (POME), photocatalysis reaction, application of photocatalysis, environmental regulations of effluent discharge is presented. Besides, previous research that related to the topic will be taken as references and review especially in photoreaction that varies with time in a photocatalyst loading of 1 g/L.

2.2 Palm Oil Production Process

Figure 2.1 presents typical process flow diagram for the extraction of crude palm oil. Post-harvesting, the fresh fruit bunches (FFB) will be transported to the mills for processing. Each FFB consists of hundreds of fruits, each of which containing a nut surrounded by a bright orange pericarp containing the oil. These FFBs will be sterilized with steam at a pressure of 3 bars and a temperature of 140 ℃ for 75-90 min. The objectives of this process are to prevent further formation of free fatty acids due to enzyme action, to facilitate stripping and to prepare the fruit mesocarp for subsequent processing. The steam condensate coming out of the sterilizer constitutes as one of major sources of liquid effluent.

After sterilization, the FFBs are fed to a rotary drum-stripper where the fruits are stripped from the bunch. The detached fruits are passed through the bar screen of the stripper and are collected below by a bucket conveyor and discharged into a digester. In the digester, the fruits are mashed by the rotating arms. In this stage, the mashing of the fruits under heating breaks the oil-bearing cells of the mesocarp. Twin screw presses are generally used to press out the oil from the digested mash of fruit under high pressure. Hot water is added to enhance the flow of the oils. The crude oil slurry is then fed to a clarification system for oil separation and purification. The fibre and nut (press cake) are conveyed to a depericarper for separation.

The crude palm oil (CPO) from the screw presses consists of a mixture of palm oil (35-45 %), water (45-55 %) and fibrous materials in varying proportion. It is then pumped to a horizontal or vertical clarification tank for oil separation. In this unit, the clarified oil is continuously skimmed-off from the top of the clarification tank. It is then passed through a high speed centrifuge and a vacuum dryer before sent for the storage tanks.

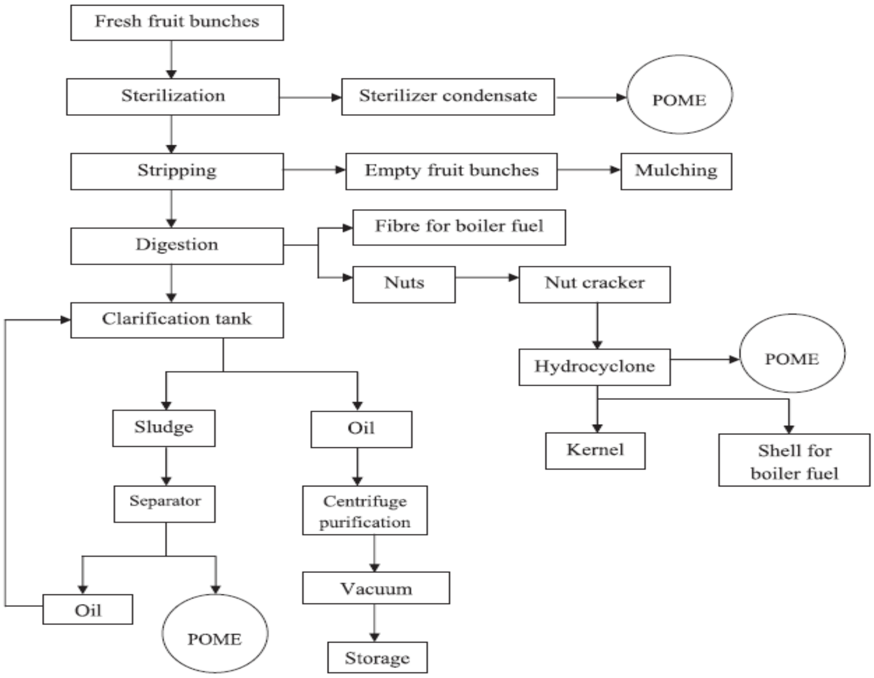

Figure 2-1: Process involved in milling palm oil

The press cake discharged from the screw press consists of moisture, oily fibre and nuts, and the cake is conveyed to a depericarper for nuts and fibres separation. The fibre and nuts are separated by strong air current induced by a suction fan. The fibre is usually sent to boiler house and is used as boiler fuel. Meanwhile, the nuts are sent to a rotating drum where any remaining fibre is removed before they are sent to a nut cracker. Hydrocyclone is commonly used to separate the kernels and shells. The discharge from this process constitutes the last source of wastewater stream.

Sterilization of FFB, clarification of the extracted CPO, hydrocyclone separation of cracked mixture of kernel and shell hydrocyclone are the three major processing operations contributing to the POME generation (Othman et al., 2008). POME is also generated from oil extraction, washing and cleaning processes in the mill and these wastes contains cellulosic material, fat, oil, grease suspended solids and total dissolved solids in the range of 18000 to 40000 ppm respectively (Agamuthu, 1995). Moreover, milling of every tonne FFB is estimated to discharge about 0.5- 0.75 tonne of POME.

2.3 Pail Oil Mills Effluent (POME)

Palm oil industry has been recognized for its contribution towards economic growth and rapid development in Malaysia. Nevertheless, it also has caused major environmental pollution (Nour, 2011). The waste products consist of oil palm trunks, oil palm fronds (OPF), empty fruit bunches and palm pressed fibres (PPF), palm kernel shells and liquid discharge palm oil mill effluent or also known as POME (Rupani, 2010). The most significant pollutant is POME (Poh & Chong, 2009), which is a brownish colloidal suspension with high organic content. This waste is hot and acidic in nature and comprised of oil, plant debris and nutrients. Table 2.1 shows the general properties of POME.

Table 2-1: The characteristics of untreated palm oil mill effluent (POME).

Parameter	**Concentration**
pH	4.7
Temperature(K)	353-363
BOD (3 days, 303 K)	25000
COD	50000
Total Solids	40500
Total Suspended Solids	18000
Total Volatile Solids	34000

*All parameters in mg/l except pH and temperature (Ma, 2000)

From the Table 2.1, it can be seen that the COD and BOD of POME are relatively high. When it is discharged into water resources, it can contaminate the drinking water supply. BOD produced in year 2009 was about 1095 million kg if discharged without prior purification. In other words, if each human being is assumed to produce 14.6 kg annually, this BOD value is equivalent to the waste generated by 75 million people which is nearly thrice the current population in Malaysia (Ahmad & Chan, 2009). Furthermore, high value of total suspended solid will make unpleasant smell and may cause disease (S.Peavy, 1985).

Studies on the effects of POME on soil showed that raw POME is acidic and alters microbiological and physicochemical properties of soil, which ultimately affects soil fertility (Wu et al., 2009). In addition, POME is one of the sources of greenhouse gas (GHG) emissions (Lim et al., 2012). It is well known that POME from the mill site is directly released into open-air holding ponds for remediation and eventually greenhouse gases such as carbon dioxide, methane, and hydrogen sulphide will be released to the air. These gases are one of the main causes of global warming, contributing to the climate change all over the world (Yoshihito, 2003). Several measures under the Kyoto Protocol 1997 have been drawn up to reduce the greenhouse gases emission. One of the measures is Clean Development Mechanisms (CDM).

Significantly, nutrient contents in POME comprised of nitrogen, phosphorus, potassium, magnesium and calcium, which are the vital elements for plant growth (Habib, 1997). Therefore in theory, POME can be utilized for producing value-added chemicals in line with cradle-to-grave concept. According to America Palm Oil Council (2003), POME is an excellent substitute for inorganic fertilizer. Upon treatment, the pH of POME can be raised from 4.0 to 8.0. Moreover, the BOD is also significantly lower whilst at the same time maintaining the plant nutrients. In terms of fertilizer value, 500 litres of treated POME is equivalent to 1.96 kg of urea (America Palm Oil Council, 2003).

Alternatively, hydrogen gas could be extracted from POME as a potential source of renewable energy. Hydrogen is considered as a clean energy as no carbon will be emitted when oxidized (Atif et al., 2005), therefore reducing dependency on the dwindling fossil fuel (Lee, 2012).

2.4 Conventional POME Treatment

Palm oil mill effluent (POME) treatment plants cater for all raw effluent produced. An approximately 0.65 tonnes of raw POME is produced for every ton of fresh fruit bunches (FFB) processed. In 2003, a total of 2,106,956 tonnes of FFB were processed, resulting in 1,369,521 tonnes of POME being produced (Yusoff, 2006).

In Malaysia, most of palm oil mills adopt anaerobic digestion for the primary treatment (Tay, 1991). This two-phase anaerobic process gives excellent pollutant destruction efficiency of above 95%. Anaerobic digestion system offers advantages such as (i) two phase system allows greater control of digester environmental conditions, (ii) long solid retention times allows better biodegradation efficiencies and also (iii) capability to cope with full effluent load, regardless of fluctuation.

Extended aerobic system is also used in POME treatment. In this system, the anaerobic liquor is aerated to further reduce the BOD content. Besides providing O_2, the floating aerators also ensure complete mixing is achieved and the pod contents are always in suspension. In this process, levels of beneficial micro-organisms are increased which in turn hasten the conversion of pollutants into carbon dioxide, water and energy. The aerobic suspension is allowed to settle in a settling tank to ensure production of a fairly clean supernatant. The main advantages of extended aerobics systems are its high BOD removal efficiency and low solid yield.

Both the aforementioned processes however represent slow routes as both are bio-based pathways. As an alternative, photocatalysis process has been touted as green treatment for photodegrading organic matters. The advantage of photocatalysis is the process is chemical-based and utilizes the energy of light to degrade the organic contents of POME. Moreover, in terms of energy consumption, ultimately the sun would provide a continuous and readily available power supply for photocatalysis as the activator needed for this process is visible light or UV radiation (Kondarides, 2001).

For extra information, Karim and Kamil (1989) found that by using aerobic treatment with mixed culture, the COD of POME has recorded more than 95% reduction after 7 days. Besides, Oswal et al. (2002) mentioned that treating POME with a type of yeast, Yarrowia lipolytica NCIM 3589 provided 97% of COD reduction in 2 days. Researcher Vijayaraghavan and his team (2007) reported that POME treatment by employing aerobic oxidation based on sludge process was able to remove about 10% COD value in 2.5 days. Borja & Banks (1995) recorded that the anaerobic fluidized bed reactor method is shorter retention time compare to others by employing 0.25 days to reduce 78% COD. The other methods are summarized in Table 2.3, together with their retention time and COD reduction percentage.

Table 2-2: Conventional POME Treatments.

Treatment Process	Retention Time (day)	Reduction in COD (%)	References
Semi-Continuous Digester	5.6	75	(Cail & Barford,1985)
Anaerobic Filter	1	99	(Borja & Banks,1995)
Anaerobic Digester	15-16	91	(Ma & Ong, 1986)
Modified Anaerobic Baffled Reactor	10	95	(Faisal & Unno, 2001)
Membrane Anaerobic System	3.15	92	(Fakhrul'l-Razi & Noor, 1999)
Completely Mixed Reactors	50	83	(Borja et al., 1995)
Tank Digester	30	98	(Edewor, 1986)
Aerobic Treatment with Mixed Culture	7	>95	(Karim & Kamil, 1989)
Activated Sludge Reactor	2.5	10	(Vijayaraghaven et al., 2007)
Aerobic Treatment with Yarrowia Lipolytica	2	97	(Oswal et al., 2002)
Pressurized Activated Sludge Process	0.42	98	(Ho & Tan, 1988)

2.5 Environmental Regulations of Palm Oil Mill Effluent (POME) Discharge

To ensure that there will be a safe and clean environment, policy has been draft to effectively control palm oil industry’s pollution. The Environmental Quality (prescribed Premises) (Crude Palm Oil) Regulations 1977, promulgated under the enabling powers of Section 51 of the EQA, are the governing regulations and contain the effluent discharge standards. Other regulatory requirements are to be imposed on individual palm oil mills through conditions of license according to Environmental Quality Act 1974 (Pierzynski et al., 2005). The limits of the POME are presented in Table 2.3.

Table 2-3: Effluent discharge standards for crude palm oil mill.

Parameter	Limit
BOD(3 days 303 K)	100
COD	-
Total Solids	-
Suspended Solids	400
Oil and Grease	50
Ammoniacal Nitrogen	150
Total Nitrogen	200
pH	5-9
Temperature(K)	318

*All parameters in mg/l except pH and temperature

2.6 Photocatalysis Reaction

In recent years, photocatalytic technology has attracted a lot of attention due to its versatility and mild reaction conditions (Wang, 2014). The word photocatalysis is a composite word which is composed of two parts, “photo” and “catalysis”. “Photo” means light and catalysis is the process where a substance participates in modifying the rate of a chemical transformation of the reactants without being altered or consumed in the end. A substance is known as photocatalyst which adds into photoreaction and increases the rate of a reaction by reducing the activation energy (Inagaki, 2014). Photocatalysis is based on the double aptitude of the photocatalyst to simultaneously adsorb both reactants and to absorb efficient photons. The basic fundamental principles are described as well as the influence of the main parameters governing the kinetics, such as: mass of catalyst, wavelength, initial concentration, temperature and radiant flux (Herrmann, 1999). The photocatalytic activity (PCA) depends on the ability of the photocatalyst to create electron–hole pairs, which generate free radicals (e.g. hydroxyl radicals: $OH^{\bullet}$) able to undergo secondary reactions.

For example, chlorophyll of plants is a typical natural photocatalyst. Usually chlorophyll captures sunlight to turn water and carbon dioxide into oxygen and glucose. Photocatalysis can be divided into two different systems viz. homogeneous as well as heterogeneous photocatalysis.

2.6.1 Heterogeneous Photocatalysis

Heterogeneous photocatalysis is one of the advanced oxidation processes that couples light activation with photocatalysts. It can be carried out in various media: gas phase, pure organic liquid phases or aqueous solutions. The use of heterogeneous photocatalysis to solve global pollution problems has been increasing in the last decades owing to its great potential to remove pollutants (Valencia et al., 2011). As for classical heterogeneous catalysis, the overall process can be decomposed into five independent steps:

1. Transfer of the reactants in the fluid phase to the surface
2. Adsorption of a least one of the reactants
3. Reaction in the adsorbed phase

4. Desorption of the product(s)

5. Removal of the products from the interface region

In the field of photocatalysis, most applications are concerned with water and air purification or self-cleaning coatings materials for outdoor and indoor uses (Simonsen, 2014).

2.6.2 Mechanism of Photocatalysis

The acceleration of a chemical transformation by the presence of a catalyst with light is called photocatalysis. The catalyst may accelerate the photoreaction by interaction with the substrate in its ground or excited state and/or with a primary photoproduct. This depends upon the mechanism of the photoreaction and itself remaining unaltered at the end of each catalytic cycle. Heterogeneous photocatalysis is a process in which two active phases, solid and liquid are present. The solid phase is a catalyst, usually a semiconductor while the liquid phase is the reactant. The molecular orbital of semiconductors has a band structure (Tieng et al., 2011). The bands of interest in photocatalysis are the populated valence band (VB) and it's largely vacant conduction band (CB), which is commonly characterized by band gap energy (E_{bg}). The semiconductors may be photoexcited to form electron-donor sites (reducing sites) and electron-acceptor sites (oxidising sites), providing sites for redox reaction (Haque, 2012). When the semiconductor is illuminated with light (h*v*) of greater energy than the band gap, an electron is promoted from the VB to the CB leaving a positive hole in the valence band and an electron in the conduction band as illustrated in Figure 2.2.

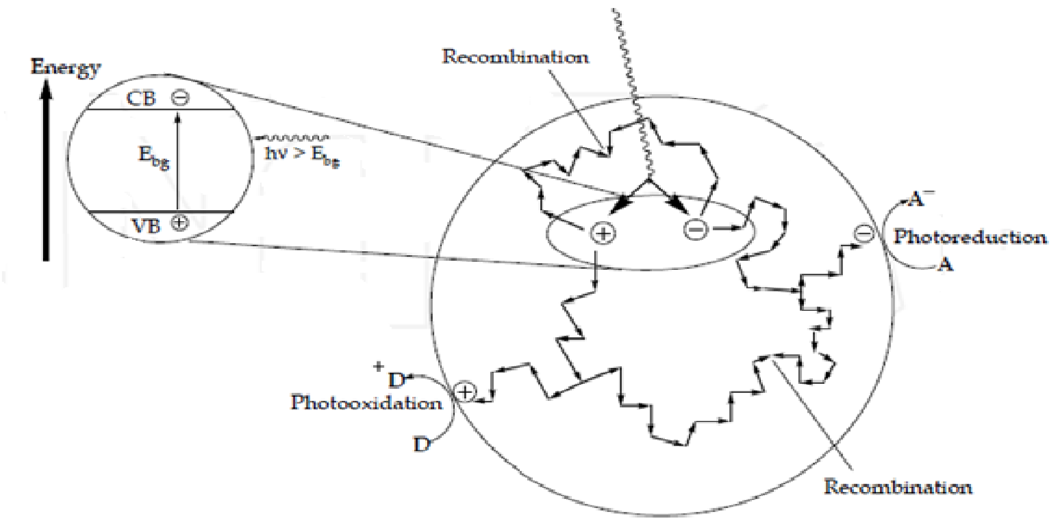

Figure 2-2: Photoexcitation of semiconductor.

If charge separation is maintained, the electron and hole may migrate to the catalyst surface where they participate in redox reactions with sorbed species. Specially, h_{vb}^{+} may react with surface-bound H_2O or OH^- to produce the hydroxyl radical and e_{cb}^{-} is picked up by oxygen to generate superoxide radical anion ($O_2^{\bullet -}$), as indicated in the following Eq. (1) to (3):

- Absorption of efficient photons by titania ($h\nu \geq E_{bg} = 3.2eV$)

$$TiO_2 + hv \rightarrow e_{cb}^{-} + h^{+}{}_{cb} \qquad (1)$$

- Formation of superoxide radical anion

$$O_2 + e^{-}{}_{cb} \rightarrow O_2^{\bullet -} \qquad (2)$$

- Neutralization of OH^- group into $^{\bullet}OH$ by the hole

$$(H_2O \Leftrightarrow H^+ + OH^-)_{ads} + h_{vb+} \rightarrow OH^{\bullet} + H^+ \qquad (3)$$

It has been suggested that the hydroxyl radical ($OH^{\bullet}$) and superoxide radical anions ($O_2^{\bullet -}$) are the primary oxidizing species in the photocatalytic oxidation processes. These oxidative reactions would result in the degradation of the pollutants as shown in the following equations (4)-(5);

- Oxidation of the organic pollutants via successive attack by $^{\bullet}OH$ radicals

$$R + OH^{\bullet} \rightarrow R^{'\bullet} + H_2O \quad ` \qquad (4)$$

- or by direct reaction with holes

$$R + h^{+} \rightarrow R^{\bullet +} \rightarrow \text{Degradation products} \qquad (5)$$