



Solar- Photocatalytic of Zinc Oxide for Mineralization of Phenol

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DEDICATION

This dissertation is dedicated to my parents Nik Yusoff and Zaripah Hamzah and as an inspiration for my younger brother Nik Muzakkir and Nik Amer Aziden.

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LIST OF ABBREVIATIONS

AOPs	Advanced Oxidation Processes
CB	Conductance Band
COD	Chemical Oxygen Demand
CO ₂	Carbon Dioxide
CO ₃ ²⁻	Carbonate Ion
CuO	Copper Oxide
D	Crystallite Sizes
Eg	Energy Band Gap
Fe ₂ O ₃	Iron (III) oxide
Fe ₂ O ₃ /UV	Iron oxide / Ultraviolet
FWHM	Full Width at Half Maximum
GAC	Granular Activated Carbon
H ₂ O	Water
H ₂ O ₂	Hydrogen peroxide
H ₂ O ₂ /UV	Hydrogen peroxide / Ultraviolet
H ₂ SO ₄	Acid sulphuric
IR	Infrared
NaOH	Sodium hydroxide
NaHCO ₃	Sodium Bicarbonate
O ₂	Oxygen
O ₃	Ozone
O ₃ /H ₂ O ₂ /UV	Ozone / Hydrogen peroxide / Ultraviolet
O ₃ /UV	Ozone / Ultraviolet
OH ⁻	Hydroxide anion
PAC	Powdered Activated Carbon
SEM	Scanning Electron Microscope
TGA	Thermogravimetric Analysis
TiO ₂	Titanium (IV) dioxide
UV	Ultraviolet
UV-Vis	Ultraviolet-Visible
VB	Valance Band
XRD	X-Ray Diffraction
Zn(CH ₃ CO ₂) ₂ .2H ₂ O	Zinc Acetate
ZnO	Zinc oxide
ZnO-C	Commercial Zinc Oxide
ZnO-H	Hydrothermal Synthesized Zinc Oxide
ZnO-P	Precipitation Synthesized Zinc Oxide
ZnO-S	Sol-gel Synthesized Zinc Oxide

LIST OF SYMBOLS

β	Broadening Diffraction Peak
θ	Bragg Diffraction Angle
λ	X-Ray Wavelength
%	Percent
$^{\circ}\text{C}$	Degree Celcius
C	Concentration
C_0	Concentration at time = 0
C_t	Concentration at time = t
e^-	Excited Electron
h	Hour
h^+	Electron Hole
H^+	Hydrogen
$\bullet\text{HO}_2^-$	Hydroperoxyl Radical
k	Reaction Rate Constant
k	Scherrer Constant
mg/l	Miligram per litre
mM	Milimolar
nm	Nanometer
$\bullet\text{O}_2^-$	Superoxide radical anion
OH \bullet	Hydroxyl radical
t	Time
μm	Micrometer

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Fotopemangkin Zink Oksida Untuk Penguraian Fenol

ABSTRAK

Keprihatinan terhadap kesan fenol sebagai bahan pencemar organik daripada air sisa industri seperti industri racun serangga, penukaran arang, resin polimer, petrokimia, farmasi dan penapisan minyak adalah semakin meningkat. Fenol berpontensi untuk memberi ancaman terhadap manusia dan ekosistem disebabkan sifat kuat ketahanan biologi dan toksik akut. Terdapat beberapa faktor yang menghadkan rawatan fenol melalui kaedah rawatan konvensional seperti rawatan biological memerlukan masa yang panjang; rawatan membran adalah berkos tinggi dan bahan pencemar lain boleh dihasilkan melalui rawatan karbon aktif. Penggunaan Zink Oksida (ZnO) dalam Proses Pengoksidaan Lanjutan (PPL) melalui proses sinaran suria fotopemangkin merupakan satu kaedah rawatan air buangan mengandungi fenol yang menjaminkan. Penguraian fotopemangkin oleh fenol dikaji dengan menggunakan zink oksida sebagai pemangkin dibawah sinaran suria. Parameter operasi seperti kepekatan awal fenol, jumlah pemangkin, pH, kesan pengudaraan, dos H_2O_2 dan kesan sinaran suria dikaji. Kepekatan awal fenol yang rendah menunjukkan penguraian yang lebih efisien. Jumlah pemangkin optimum untuk menyediakan permukaan aktif yang mencukupi untuk tindak balas fotopemangkin ialah 0.6 g. Sementara itu, keadaan pH optimum adalah di dalam keadaan berasid kerana ia menunjukkan prestasi yang lebih baik daripada keadaan berkalkali. Tindak balas fotopemangkin lebih memberangsangkan dalam pengudaraan dengan kadar penguraian $14.325 \text{ mg L}^{-1} \text{ h}^{-1}$. Selain itu, penambahan 0.1 M H_2O_2 juga meningkatkan penguraian fenol. Keputusan yang diperoleh mematuhi model kinetic Langmuir-Hinshelwood. Analisis UV-VIS dan keperluan oksigen kimia (COD) menunjukkan penguraian lengkap fenol dan kebolehan untuk penguraian sepenuhnya. Pemangkin bersifat mesra alam ZnO semikonduktor di sintesis melalui kaedah *precipitation* (ZnO-P), *hydrothermal* (ZnO-H) dan *sol-gel* (ZnO-S). Bentuk permukaan pemangkin di analisis melalui SEM menunjukkan bentuk ZnO-P dan ZnO-H adalah sfera tidak lengkap dengan bersaiz 20 nm hingga 130 nm. Sementara itu, bentuk yang tidak teratur dengan permukaan tepi yang tajam diperhatikan untuk ZnO-S. Selain itu, bentuk prisma besar dengan saiz zarah 110- 400 nm diperoleh oleh ZnO-S. Keputusan analisis XRD menunjukkan kesemua ciri puncak ZnO sintesis adalah selaras dengan corak standard yang diambil daripada *Joint Committee of Powder Diffraction Standard (JCPDS)* kad bernombor No. 36-1451. Corak XRD untuk kesemua pemangkin adalah sama dengan kelainan kelangsingan menunjukkan saiz kristal yang berbeza. Puncak tertinggi berada di 2θ 36.24° , 36.31° , dan 36.32° untuk ZnO-P, ZnO-H dan ZnO-S yang disesuaikan dengan satah (1 0 1). Indeks puncak ialah hexagonal dalam kumpulan P63mc (186). Analisis haba mencadangkan suhu pembakaran yang sesuai adalah diantara 350°C sehingga 400°C . Pemusnahan *hydrocarbonate* (OH^- and CO_3^{2-}) berlaku pada suhu 370°C dan 73.08 % berat daripada ZnO-P, 74.52 % ZnO-H dan 72.41 % ZnO-S tinggal. Penguraian ZnO pelopor lengkap pada suhu ini dan dianggap sebagai suhu pengkalsian yang optimum untuk proses sintesis. Tiada sebarang kehilangan berat diperhatikan pada suhu 430°C sehingga 800°C . Satah mendatar menunjukkan pembentukan ZnO sebagai hasil penguraian. Perbandingan diantara fotopenguraian menunjukkan keupayaan fotopemangkin boleh disusun seperti berikut $\text{ZnO-C} > \text{ZnO-S} > \text{ZnO-P} > \text{ZnO-H} > \text{TiO}_2$. Hasil kajian ini dijelaskan dalam model kinetic Langmuir-Hinshelwood. Nilai tetap k adalah berkadaran terus dengan keberkesanan pemangkin. Kajian lanjutan untuk menilai fotopemangkin ZnO boleh membantu dalam membangunkan kaedah rawatan semikonduktor suria-pemangkin

yang masih pada peringkat kajian di seluruh dunia. Oleh itu, rekaan kilang perintis adalah permulaan yang baik untuk mengkaji aplikasi ZnO sebagai fotopemagkin dalam rawatan air sisa yang sebenar.

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Solar-Photocatalytic of Zinc Oxide for Mineralization of Phenol

ABSTRACT

There are increasing concerns on the significant of phenols as an organic contaminant from industrial wastewater such as pesticides, coal conversion, polymeric resin, petrochemical industry, pharmaceutical and oil refinery industries. Phenols can be threatening to human being and ecosystems due to its biorecalcitrant and acute toxicity behavior. There are some limitations for phenols treatment via conventional wastewater treatment such as in biological treatment, a longer time which is required; membrane treatment is expensive and another pollutant are generated via activated carbon treatment. Zinc oxide (ZnO) utilization in Advanced Oxidation Process (AOP) via solar-photocatalytic process was a promising method for treating wastewater containing phenol. The photocatalytic degradation of phenol was investigated with zinc oxide (ZnO) as photocatalyst under solar light irradiation. Operating parameters such as initial phenol concentration, catalyst loading, pH, effect of aeration, H_2O_2 dosage and effect of solar light irradiation were investigated. The low initial concentration of phenol indicates more efficient photocatalytic degradation. The optimum catalyst loading to provide sufficient active site for the photocatalytic activity is 0.6 g. While, the optimum pH condition is in acidic condition as it show a better performances than in alkaline condition. The photocatalytic activity improved with aeration and the photodegradation rate is $14.325 \text{ mg L}^{-1} \text{ h}^{-1}$. Besides that, the addition of 0.1 M H_2O_2 also enhanced the degradation of phenol. The results obtained fitted well with Langmuir-Hinshelwood kinetic model. Analysis of UV-VIS and chemical oxygen demand (COD) attested the complete degradation of phenol concentration and possibility for mineralization. The environmental friendly ZnO photocatalyst semiconductor was synthesis by precipitation (ZnO-P), hydrothermal (ZnO-H) and sol-gel (ZnO-S) method. The morphologies of the photocatalyst were observed by SEM showed the morphology of ZnO-P and ZnO-H are pseudo-spherical shape with sizes of 20 nm until 130 nm. While, an irregular shape with sharp edges was observed for ZnO-S. The particles sizes of 110-400 nm were obtained for ZnO-S. The results from XRD analysis interestingly indicate all the characteristic peaks observed in synthesized ZnO are in a good agreement with the pure ZnO standard pattern taken from the Joint Committee of Powder Diffraction Standard (JCPDS) card No. 36-1451. The XRD patterns of all photocatalyst are the same with different intensity indicates different crystallite sizes. Particularly, the strongest characteristic peaks were described at 2θ 36.24° , 36.31° , and 36.32° for ZnO-P, ZnO-H and ZnO-S, which correspond to plane (1 0 1). The peak indexed as hexagonal with space group P63mc (186). Thermal analysis suggested the ideal calcinations temperatures are within range of 350°C until 400°C . The destruction of hydrocarbonate (OH and CO_3^{2-}) takes place at temperature 370°C and 73.08 % of ZnO-P, 74.52 % ZnO-H and 72. 41 % ZnO-S weight left. The decomposition of the ZnO precursor was complete at this temperature and can be considered as the optimum calcinations temperature for synthesized process. No further weight loss was observed from 430°C until 800°C . This plateau indicates the formation of the ZnO as a decomposition product. The comparison of photodegradation showed that the photocatalytic performances of all five tested photocatalyst could be arranged as $\text{ZnO-C} > \text{ZnO-S} > \text{ZnO-P} > \text{ZnO-H} > \text{TiO}_2$. The finding of this study was described in Langmuir-Hinshelwood model. The apparent rate constant is proportional to the efficiency of the photocatalyst. Further research to evaluate ZnO photocatalyst would be of great help in developing the semiconductor solar-photocatalytic treatment which are currently still in an experimental phase

worldwide. Hence, pilot plant design can be a good start to study the application of ZnO as photocatalyst in real wastewater treatment.

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CHAPTER 1

INTRODUCTION

1.1 Introduction

Rivers, lakes, wells, springs as well as seas acted as the main sources of drinking water to humans, animals and plants irrigation. Nowadays, most of the water exist in this world is much-reused water that being cycled from billions of years before. The treatments are crucially needed for the water to become acceptable for benefits of mankind. Maintaining the needs of high quality becomes the primary concern as the water sources are threatened by different types of pollutants. Sources of water pollution can be classified into two, which are natural sources and human-caused sources. Natural sources are mostly originated from surface runoff of atmospheric precipitation (rain, snow, etc) that carried out all types of mineral, organic and biological substances. The runoff also able to carry suspended soiled due to the high density of water. Consequently, those substances will enter water bodies and cause the pollution.

Impurities or pollutants give major negative effect toward ecosystems, animals and human. The formation of eutrophication phenomena is one of the significant examples. Organic waste and plant nutrient in polluted water will be decomposed. This condition promotes algal bloom especially blue-green algae which grows in a fast rate and consumes all the dissolved oxygen. As a result, all aquatic animals will die. While, mass destruction of aquatic life occurred due to discharge of non-biodegradable pesticides and chemical in water bodies. Biomagnification is another effect of water pollution. The process initiated when the pollutant move up to the food chain through consumption by fish or other aquatic organisms which later consumed by birds, animals

or humans. These harmful substances become concentrated in tissues and internal organs and consequently cause serious damage to human health.

In the global scope, water pollution become a threaten issue both in developed and developing countries. However, the focus on water pollution is different between these countries. The treatments for contaminated drinking water become dominated issues in developing countries. They tend to focus on reducing the incidence disease caused by consuming contaminated drinking water. While, in developed countries, large scale of water treatment and sanitation was invested. Thus, the water quality concerns are mainly in terms of environmental impact from both point source (industrial and urban) and non-point source contamination, primarily from agriculture.

In other words, it can be concluded that human activities are the leading cause to water impurities worldwide. Some important sources are from construction, mining, petroleum discharges and spills, leachate from landfills, septic tanks, treatment lagoons and mine tailings, agricultural application of chemical fertilizers, herbicides and pesticides, effluents from industries and waste treatment. From the above human-caused sources, it can be summarized that wastewater effluent is the main cause for water pollution. Wastewater pollutant mostly being classified into two major types: organic pollutant and inorganic pollutant. Inorganic pollutant consists of heavy metals, phosphorus, nitrogen, chlorides, sulfur etc.

Organic pollutants are widely being found in wastewater due to the ability to form straight, branched and cyclic chains. Organic pollutant can be divided into biodegradable and non-biodegradable. Biodegradable organic pollutant such as proteins, carbohydrates and fats can be easily removed through physical and biological treatment. However, the non-biodegradable organic pollutants are difficult to be treated. One of the

refractory organic pollutants that have high ability to give a negative effect towards water consumers is phenol.

Phenol is widely being used in industrial and others application. Phenol is being utilized in the drugs production industries especially in producing aspirin. Besides, herbicides, pesticides and synthetic resins industries also consume phenol. In medical application, phenol is used for aseptic techniques in surgery due to its antiseptic properties. Phenol is commonly mixed with chloroform for DNA and RNA purification from proteins in molecular biology. Moreover, in production of cosmetic products such as sunscreens, hair dyes and skin lightening, phenol are being used (Bahera, 2009).

Phenol can be threatening to human being and ecosystems due to its biorecalcitrant and acute toxicity behavior (Ahmed et al., 2010). The effluent wastewater that contains phenol compound need to be treated until fulfilling the requirement enacted by Malaysia Department of Environmental Quality Act 1974 (Sewage and Industrial Effluent), which is 0.001mg/l for Standard A and 1.0 mg/l for Standard B. Despite the low concentration, phenol treatment has become issue due to its toxicity, genotoxicity and extremely high potency of endocrine disrupting (Ahmed et al., 2010).

There are some limitations for phenol treatment via conventional wastewater treatment. For instance, research by Prieto et al, (2002) in biological treatment, a longer time which was 40 hour required to degrade 200 mg/l of phenol (Prieto et al., 2002). Previous studies have also shown the limitation of biochemical treatment which required suitable temperature and pH to produce an activated sludge at the end of treatment (Krumme and Boyd, 1988). While, other pollution are tended to occur after

treatment by activated carbon as it only involves pollutant phase transfer (Pardeshi and Patil, 2008).

Thus, an initiative method for phenol degradation in wastewater was discovered which was through the Advanced Oxidation Process (AOP) as suggested by Alnaizy and Akgerman, (2000). AOP are the aqueous phase oxidation process which involves the generation and use of hydroxyl free radical ($\text{OH}\cdot$) as a strong oxidant to destroy compounds that cannot be oxidized by other conventional oxidants (Quiroz et al., 2011). Among various processes in AOP, photocatalytic process showed a great potential. Previous study by Fujishima et al., (2000) has reported photocatalytic process occurs when there is an interaction between the solid semiconductor and photons having the appropriate wavelength. Teh and Mohamed, (2011) reviewed that photocatalytic only involves a low operation temperature, low operation cost, and low energy consumption.

Photocatalyst is defined as the catalyst that inactive during normal conditions, but only activated when being irradiated by UV light. Photocatalyst are semiconductor metal oxides such as TiO_2 , ZnO and CuO that are safe to be used in environment during photocatalytic process. These semiconductors are able to utilize sunlight to initiate the photocatalytic reaction and consequently degrade the pollutant (Karunakaran and Dhanalakshimi, 2008). The reaction is initiated when there is sufficient energy source radiated on the semiconductor, and produces an electron-holes pair. Series of chemical reactions will occur and produce hydroxyl radical, superoxide ion and hydroperoxyl radical which able to destroyed the contaminants. ZnO has gained attention due to its suitability in environmental detoxification. ZnO which is also known as II-IV semiconductor (Bahera, 2009), has a wide band energy bandgap (3.3 eV) (Tsay et al., 2010), high photosensitivity, and stability (Sakthivel et al., 2003).

Several studies have reported that the performances of ZnO as photocatalyst are more efficient compare to the commonly applied photocatalyst TiO₂ (Karunakaran and Dhanalakshmi, 2008; Sakthivel et al., 2003)

1.2 Problem statements

Rapid development in industries has heightened the need for appropriate treatment of the industrial effluent especially those containing toxic substances such as phenol. The permissible limit of phenol in water bodies is only less than 1.0 mg/l. Even though phenol is toxic and claimed to be threatening, the proper treatments of phenol are still neglected by some industries compare to other types of pollutant. The conventional treatment method for phenol can be classified into physical, chemical and biological method. The most common applied physical treatment such as air stripping and adsorption, are not reliable to be applied due to the production of extended pollutant from the treatment such as activated carbon. The spent activated carbon is usually disposed by incineration and eventually generated dioxin and furan which are severe to human health. Besides the behavior of the removal are non-destructive. Although some researchers have concluded that biological treatment is a safe and applicable treatment method, the rate of phenol degradation is low and time consuming.

Besides, the recalcitrant phenol compound has the potential to exert toxicity to microorganisms during biological treatment. Thus, it will lead to failure of whole wastewater treatment system. Nowadays, chemical oxidation treatment method is the most common chemical treatment applied. Unfortunately, most of the solvents such as chlorine dioxide are expensive and lead to the formation of by-products such as benzoquinone and organic acids. The debate over phenol treatment method is very complicated. However, it can be best explained by considering another promising

technology for organic pollutant remediation at ambient conditions known as solar photocatalytic. The main advantages of this method are the complete destruction of phenol and energy save as it utilized natural sunlight for the treatment. Expensive oxidizing chemicals are not consumed in this treatment. It only involves the non-hazardous photocatalyst and the oxidant is atmospheric oxidant. As solar-photocatalytic process contributes to phenol removal, photocatalyst played a key role in accomplishing this treatment. In this study zinc oxide (ZnO) was chosen as the photocatalyst.

1.3 Scope of study

Solar-photocatalytic has been found to be able to degrade phenol in wastewater. Among various metal oxides, particularly zinc oxide has become an interesting material to be studied. Most of the research has been carried out on the degradation of phenol using artificial UV light. To the best of our knowledge, the study of the degradation of phenol under solar light irradiation with various synthesized photocatalysts are least studied. Hence, in the present study, an attempt has been made to evaluate the degradation of phenol through solar-photocatalysis and compare the performances of various synthesized ZnO with the commercial ZnO and TiO₂.

The broad objective of this research is to study the degradation of phenol through solar-photocatalytic process. Specifically the objectives of this research are:

1. To investigate the effect of operating parameters for photocatalytic process.
2. To synthesize and characterize ZnO nanoparticles through various synthesis methods.
3. To compare the performances of phenol photodegradation between commercial and synthesized ZnO.

CHAPTER 2

LITERATURE REVIEWS

2.1 Treatment of Phenol

Phenol is one of the organic pollutants which continuously discharged into the environment without being removed in wastewater treatment systems. Some wastewater treatment plants are designed for carbon, nitrogen and phosphorus removal only (Auriol et al., 2006). To date, a variety of methods are used to degrade phenol. The removal of phenol basically can be dividing into three main categories; physical removal, biodegradation, and advanced oxidation process (AOP) (Liu et al., 2009).

The physical removal through adsorption of activated carbon either powdered activated carbon (PAC) or granular activated carbon (GAC) was commonly utilized worldwide. However, Synder et al., (2007) reported its drawbacks, stated that the spent PAC and GAC must be disposed through land filling or in any other solids handling. Besides, GAC also required regenerations process to be re-used. The key problem with this treatment method is that another waste would be produce after treating another.

The membrane process is gaining attention due to its advantages in degraded an extremely low organic concentration including removal of microbes and viruses without chemical disinfection (Liu et al., 2009). Despite of all the advantages, it only can be applied in advanced water and wastewater treatment. Another option for phenol treatment is through activated sludge biodegradation. The activated sludge process is mostly concentrated in large cities wastewater treatment and mainly to degraded organic compounds present in sewage treatment plants influent (Auriol et al., 2006). This type of treatment is very applicable for lab-scale experiments as several parameters need to

be continuously controlled. Thus, it is a little bit unfeasible to be applied in conventional wastewater treatment and it is also highly in maintenance cost.

Furthermore, the pollutants adsorbed on activated sludge are potentially to contaminate the soil and groundwater as the digested sludge is usually being applied as fertilizer in agricultural (Auriol et al., 2006). Recently, one of the advanced oxidation process (AOP) which is photocatalytic has gain a main attention due to its effectiveness of degrade the persistent or bio-resistant organic contaminant.

2.2 Advances Oxidation Processes (AOPs)

Advances Oxidation Processes (AOPs) concept was primarily established by Glaze in 1987 (Quiroz et al., 2011). AOPs are defined as a process that generates highly reactive oxidizing species which has a strong ability to attack and degrade organic compounds (Quiroz et al., 2011). AOPs are very effective and have the capability to achieve total degradation for soluble organic contaminant either from water or soils in ambient temperature (Titus et al., 2003).

The highly oxidizing species, mainly hydroxyl radicals ($\bullet\text{OH}$) contribute to the high efficiency physical-chemical processes and consequently capable to cause change in the chemical structure of the organic compound (Quiroz et al., 2011). This is because hydroxyl radicals ($\bullet\text{OH}$) has high oxidation capability (Quiroz et al., 2011) due to its high standard reduction potential 2.8 V (Titus et al., 2004). Most of the organic compounds can be oxidized by these radicals except for simplest organic compounds such as acetic, maleic and oxalic acids, acetone and chloroform (Bigda, 1995).

There are two types of the possible initial attack, which is a hydrogen atom for alkenes and alcohols attached to the molecule for aromatic compounds (Titus et al., 2004). AOPs consist of various types of processes as classified below:

- 1) Photolysis (UV or VUV).
- 2) Hydrogen peroxide (H_2O_2):
 - $\text{H}_2\text{O}_2 + \text{UV}$
 - Fenton: $\text{H}_2\text{O}_2 + \text{Fe}^{2+}/\text{Fe}^{3+}$
 - Fenton-like reagents: $\text{H}_2\text{O}_2 + \text{Fe}^{2+}\text{-solid}/\text{Fe}^{3+}\text{-solid}$
 - photo-Fenton: $\text{H}_2\text{O}_2 + \text{Fe}^{2+}/\text{Fe}^{3+} + \text{UV}$
- 3) Ozone (O_3):
 - ozonation: O_3
 - photo-ozonation: $\text{O}_3 + \text{UV}$
 - ozonation + catalysis: $\text{O}_3 + \text{H}_2\text{O}_2$ and $\text{O}_3 + \text{Fe}^{2+}/\text{Fe}^{3+}$
- 4) Heterogeneous catalysis + UV and photocatalysis.

2.3 Principle of Photocatalytic

Among various processes in AOPs, photocatalytic process shows a great potential. Previous studies by Fujishima et al., (2000) have reported photocatalytic process occurs when there is an interaction between the solid semiconductor and photons having the appropriate wavelength. Heterogeneous photocatalytic is a new method for the removal of organic pollutant in water and wastewater. Photocatalytic treatment method also became as an alternative treatment method to fill up the void of the existing treatment method due to its high capability in removing bio-recalcitrant compound.

The photocatalytic reaction process is a combination of heterogeneous catalysis with UV radiation such as solar (Beydoun et al., 1999). There are three major components which are crucial for the photocatalytic reaction to occur; an emitted photon with appropriate wavelength, catalyst surface, and oxidizing agent such as