HYBRID PHOTOCATALYST FOR SEAWATER PURIFICATION: CATALYST COMPOSITION

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ABSTRACT

Hybrid photocatalyst of Titanium Dioxide (TiO_2) catalyst become an attractive alternative promoter for seawater purification. The effect of catalyst composition in the seawater purification via photocatalytic reaction was investigated. Synthesis of a highly active solid catalyst is investigated by loading the different weight ratio of TiO_2 on activated palm oil fiber ash through wet impregnation technique. The prepared catalysts were characterized by X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Brunauer Emmett Teller (BET). The catalyst was tested with seawater (weight ratio of catalyst to seawater of 1:400). The experiment was conducted in a 1 L Borosilicate photoreactor and mercury light with 365 nm wavelength was used. The performance of the catalyst was tested for two hours. The Chemical Oxygen Demand (COD), pH, Conductivity, Turbidity, Biochemical Oxygen Demand (BOD), Total Dissolved Solid (TDS) and Dissolved Oxygen (DO) of the seawater was analysed prior and after the testing. Better quality of water was obtained. SEM images show that the fiber ash became a good supporter for $TiO_{2.}$ TiO_2 was well dispersed on fiber ash surface after the impregnation. BET indicates that the catalyst pore structure was mesoporous. The XRD result also indicates that the TiO_2 has anatase crystal while fiber ash has quartz crystal. The solid solution might form too. The weight ratio of fibre ash to TiO_2 of Ti:Ash 50:50 were found to be the most effective catalyst in purification of seawater by reducing 10.86% of salt concentration. In conclusion, the photocatalysis process is able to provide an alternative effective treatment for seawater purification.

Keywords: hybrid photocatalysis, Titanium Dioxide-; catalyst, palm oil fiber ash, mercury light, seawater purification

ABSTRAK

Fotopemangkin hibrid Titanium Dioksida (TiO_2) merupakan alternatif penggalakan yang menarik untuk penulenan air laut. Kesan komposisi pemangkin dalam penulenan air laut melalui tindak balas fotopemangkin telah dikaji. Sintesis aktif pepejal pemangkin telah disiasat dengan memuatkan nisbah berat antara TiO_2 ke atas abu gentian kelapa sawit melalui teknik impregnasi basah. Pemangkin tersedia telah disifatkan melalui Sinar-X Pembelauan (XRD), Imbasan Elektron Mikroscop (SEM) dan Brunauer Emmett Teller (BET). Pemangkin ini telah diuji dengan air laut (nisbah berat pemangkin kepada air laut 1:400). Eksperimen telah dijalankan dalam 1 L borosilikat fotoreaktor dan cahaya merkuri dengan 365 nm panjang gelombang telah digunakan. Prestasi pemangkin telah diuji selama dua jam. Keperluan Oksigen Kimia (COD), pH, konduktiviti, kekeruhan, Keperluan Oksigen Biokimia (BOD), Jumlah Pepejal Terlarut (TDS) dan Oksigen Terlarut (DO) air laut telah dianalisis sebelum dan selepas ujian. Kualiti air yang lebih baik diperolehi. Imej SEM menunjukkan bahawa abu gentian menjadi penyokong yang baik untuk TiO_2. TiO_2 telah tersebar di permukaan abu gentian selepas impregnasi basah. BET menunjukkan bahawa struktur pemangkin liang adalah mesoporous. Keputusan XRD juga menunjukkan bahawa TiO_2 mempunyai kristal anatase manakala abu gentian mempunyai kristal kuarza. Larutan pepejal juga mungkin membentuk. Nisbah berat abu gentian untuk TiO_2, Ti:Ash 50:50 didapati menjadi pemangkin yang paling berkesan dalam penulenan air laut dengan mengurangkan 10.86% daripada kepekatan garam. Kesimpulannya, proses fotopemangkinan mampu memberikan rawatan alternatif yang berkesan untuk penulenan air laut.

Kata kunci: fotopemangkin hibrid, Titanium Dioksida-; pemangkin, abu gentian kelapa sawit, cahaya merkuri, penulenan air laut

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LIST OF SYMBOLS

nm	Nanometer
%	Percentage
µm	Micrometre
^{o}C	Degree Celsius
ml	Milliliter
L	Liter
g	Gram
min	Minute
cm	Centimetre
eV	Electron volt
~	Approximately
IV	Four
kV	Kilovolts
rpm	Revolutions per minute
NTU	Nephelometric Turbidity Units
m^2/g	Meter square per gram
cm^3/g	Centimeter cubed per gram
2θ	2-theta
^{o}	Degree
mS/cm	Microsiemens per centimetre
g/L	Gram per liter
mg/L	Milligram per liter
Ca^{2+}	Calcium ion
Mg^{2+}	Magnesium ion
Na^{2+}	Sodium ion
K^+	Potassium ion
CO_3^{2-}	Carbonate ion
SO_4^{2-}	Sulfate ion
$<$	Lower than

LIST OF ABBREVIATIONS

TiO_2	Titanium Dioxide
COD	Chemical Oxygen Demand
TDS	Total Dissolved Solid
DO	Dissolved Oxygen
BOD	Biochemical Oxygen Demand
BOD_5	Biochemical Oxygen Demand for five days
pH	Potential Hydrogen
SEM	Scanning Electron Microscopy
BET	Brunauer Emmett Teller
XRD	X-ray Diffraction
AOP	Advanced oxidation processes
UV	Ultraviolet
H_2O	Water
CO_2	Carbon dioxide
Eg	Band gap energy
SiO_2	Silicon dioxide
WHO	World Health Organization
UNICEF	United Nations International Children's Emergency Fund
OH•	Hydroxyl radicals
$ZnTiO_3$	Zinc titanate
$ZrTiO_4$	Zirconium titanate
hv	Photon energy
e^-	Negative – electron
h^+	Positive – holes
Cb	Conduction band
Vb	Valence band
O_2	Oxygen
$O_2•^-$	Superoxide radical anions
H^+	Hydrogen ion
Ca	Calcium
Si	Silicon
Al	Aluminium
Ti	Titanium
Fe	Iron
Mg	Magnesium
Na	Sodium
K	Potassium
S	Sulphur
P	Phosphorus
FIST	Faculty of Industrial Sciences & Technology
UMP	Universiti Malaysia Pahang
FKKSA	Faculty of Chemical & Natural Resources Engineering
Ti:Ash	Titanium Dioxide : fiber ash
NaCl	Sodium chloride

1 INTRODUCTION

1.1 Research background

Access to safe water is essential to sustain the human life and must be satisfactory in the part of adequate, safe and accessibility. By improving the access of safe water can provide significant benefits to health. Seawater is conquering the world for 97.5 % and remain is the freshwater where 1.75% had locked up in the ice caps. This will prove the fact that almost half of the globe's land surface is lies within international watersheds which is land contributes to the world's 261 transboundary waterways affect increasing of scarcity (Wolf, 1999). Seawater becoming the major topic because it will be the main role of water source worldwide. This study purposes to examine the efficiency decomposition of high salt concentrations containing in seawater or extract fresh water from salty water by adapting the application of photochemical reaction. In fact, Middle East and North Africa have relied on desalted of seawater as their viable solutions in restrain the water shortage (Ghaffour et. al., 2011). Thus, the innovative methods for seawater are needed urgently to improve the quality of drinking water and to reduce water contamination.

Seawater has become the vital sources for safe drinking water in the last two decades. In the northern Chile, the production processes in the mining industries using the seawater as their raw materials (Pia et. al., 2012). The processing or desalination of natural seawater converted to be drinking water by using various methods is increasing throughout the world (Radwan and David, 2003). Many researchers such as Ghaffour et. al. (2001), Francois et. al. (2008) and Akili et. al. (2008) has implemented the centralization of the distillation, electrodialysis, and reverse osmosis for seawater treatment. The advance methods ought to develop regarding to desalination water requires high energy (Shakhashiri, 2011). The updated technologies for the sea water purification have been studies to receive the sign of inadequate water in the future. The cost reduction can be decreased through design improvement, innovation of cheaper and more efficient chemicals and utilization of low- grade energy.

During the last decade, photocatalyst which is technique of advanced oxidation processes (AOP) have been one alternative to the water and wastewater treatment (Sylwia et. al., 2007). Hybrid photocatalyst can be an efficient methods used because this process is very simple and easily utilized. Photocatalyst are semiconductors that have capabilities to cause or accelerate the chemical reactions upon light absorption notably sunlight (Serpone and Emiline, 2002). UV light disinfection can be modified by replacing the light source to the mercury light 365 nm wave light to inactive the microorganisms. The development of using simple UV light such as generating device have been developed to be used for water treatment (Sherif et. al., 2013; Brownell et al., 2008). Based on the Yong-Suk et. al. (2000), an electron will be promoted from a valence band to a conduction band to give an electron or hole pair when the Titanium Dioxide (TiO_2) is illuminated with light of wavelength less than 400 nm.

Normally the disinfected of water has been done using several of methods which are physical and chemical treatment includes boiling, UV treatment, filtration, chlorination, iodine treatment, etc. (Shinde, 2011). Currently, many researches on water purification using the semiconductor photocatalyst by TiO_2 catalyst are carried out. The collected pollutant of the solution to the surface of TiO_2 catalyst improves the efficiency of photocatalyst (Ho et. al., 2007). TiO_2 catalyst or known as metal oxide have been choosen because its capability and efficiency in removing the wide range of pollutants. The advantages of using TiO_2 catalyst are inexpensive, non-toxic, have excellent in high production of hydroxyl radicals and stability in physical and chemical properties (Klankaw et. al., 2012; Yong-Suk et. al., 2000). Based on the Awal et. al., (1997), palm oil fiber ash contain high amount of silica which can be an alternative source to provide cheap of silica for industrial uses. Moreover, palm oil fiber ash also has some nutrient and can also be a good adsorbent on purifying water.

Photocatalytic oxidation is an efficient method because it can avoid sludge production problems. This method only allows the complete degradation of organic pollutants without using the chemical into harmless species such H_2O and CO_2 (Shon et. al., 2007). According to Shon et. al. (2007), the organic matter mixing in water in the system can be removed by utilizing these methods which is interfacial effect of particles enhancing adsorption on TiO_2 particle surface and the photo oxidation of organic matter due to TiO_2 in presence of UV light. But, in this investigation, we only pay attention to the photo oxidation of organic matter due to the effect of hybrid TiO_2 in presence of UV light. The effectiveness of hybrid TiO_2 catalyst by using the palm oil fibre ash as a supporter for the TiO_2, on the organic pollutants and desalination of seawater was studied in this investigation.

1.2 Problem statement

The demand of water supply according to the growing of global population has become a serious problem nowadays. The population rising and economic growth around the world is driving higher water demands for production of energy, manufacturing households, agriculture and others. Urbanization, industrialization, increasing populations, consumerism and irrigated agriculture is resulting due to arise of demand in industry, agriculture and domestics utilize (Undala, 1998) and it turns to affect the water quality (Nash, 1993). Based on the WHO and UNICEF, (2012) report, 2.5 billion people are still not attach to improve sanitation facility and over 900 million people worldwide still do not have access to safe water. This problem becomes a huge problem because health hazards are the major restriction for the clean water quality requirement.

Besides that, the oil and gas industry face the problem in managing the water management offshore. It will be more critical notably in deeper waters; the water treatment can be extremely expensive due to footprint and platform weight requirement. As a non-core capability for oil producers, water treatment is often considered the weak link in oil production. Rather than that, the shipping industries also required the water. Distilling plants cannot be utilized because of short stays in the areas even though seawater is fit for distillation. In addition, the demand of clean water is necessary as ships will stay at sea for a prolonged period of time (fishing, hydrographic and research vessels or tramps) (Sobol, 1984). Furthermore, on the island, freshwater is becoming a scarce commodity, raising the spectre of shortages for the local population and for the all-important tourism industry.

TiO_2 is belongs to the family of transition metal oxides (Shon et. al., 2007). The TiO_2 catalyst is expensive but is relatively cheap when compared to membrane. Fiber ash from palm oil mill effluent is highly dispersive. Research is in progress to find out the various ways to utilize the large quantities of palm oil fiber ash to prevent any environmental problems as well as effectively use them. Palm oil fibre ash is also very cheap and can be used as a support for TiO_2 photocatalyst for purifying pollutants in air and wastewater. TiO_2 catalyst is inertness to chemical environment and its long term photo stability has made TiO_2 catalyst become the vital materials in many applications (Alex and Paul, 2013). The reason why the application of TiO_2 is important because it is environmental friendly, easy to handle and cheap as only using sunlight or artificial source light to purify the seawater is needed.

1.3 Research objectives

The objectives of this research are:

1) to synthesize and characterize the hybrid TiO_2 catalyst.
2) to investigate the effect of catalyst composition via photocatalytic reactor in purifying the seawater.

1.4 Scopes of study

To achieve the outlined of this investigation, the following scopes of research have been identified.

1) The rig set up for photocatalytic reactor was designed and fabricated.
2) The catalyst with different weight ratio of TiO_2 to palm oil fiber ash was prepared via wet impregnation. The catalyst performance was tested in the photocatalytic reactor with the weight ratio of the catalyst to seawater of 1:400 for two hours.
3) Characterization of the fresh and used catalyst using X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Brunauer Emmett Teller (BET) was done.
4) The feed and product of this investigation was analyzed. The pH, Conductivity, Chemical Oxygen Demand (COD), Total Dissolve Solid (TDS), Dissolved Oxygen (DO), Biochemical Oxygen Demand (BOD) and Turbidity of the water was determined prior and after the experiment.

1.5 Significance of study

Palm oil fiber ash from biomass palm oil becomes a new material to be used in the application of seawater purification via photoreaction. The significant of this research is to reduce overall cost to produce clean water since palm oil fiber ash is residue where it can be found easily at the palm oil mill. This research is also to prepare various composition of TiO_2 catalyst and fiber ash which effectively for purifying the seawater. If the TiO_2 fiber ash catalyst can completely absorb the pollutants by using this photochemical reaction, alternative safe and clean water technology is produced and thus reducing the impact of water shortage.

1.6 Organisation of this thesis

The structure of the reminder of the thesis is outlined as follow:

Chapter 2 provides a description of the photocatalyst concept in purifying the water. Some of the related researches according to the photocatalyst and photocatalytic reactor will be discussed. Rather than that, this chapter also provides a brief discussion of the TiO_2 catalyst notably its crystal structure and properties, application of TiO_2 and the mechanism on how TiO_2 catalyst by photocatalyst working on to purify the seawater also will be studied. The advantages of palm oil fiber ash are also presented. A brief discussion on the advantages of photocatalyst technology is also provided.

Chapter 3 gives a review of the photocatalyst approach applied for purifying the seawater. The seawater sample will be analysed by pH, Conductivity, COD, DO, BOD, TDS and Turbidity to compare its quality before and after the experiment. This paper will be review the hybrid catalyst preparation via wet impregnation technique. The hybrid catalyst will be characterized by XRD, SEM and BET. The effectiveness of hybrid catalyst will be tested on the seawater sample for 2 hours in the photocatalytic reactor.

Chapter 4 is devoted to a result and discussion after the experiment has been done. The hybrid catalyst is characterized via SEM to analyse the surface area of the catalyst produced, BET to analyse the specific surface area, pore area and pore volume of the catalyst and XRD to analyse the crystal structure of the catalyst. The characterization of catalyst is done before and after testifies. Besides, the seawater sample is tested by pH, Conductivity, COD, DO, BOD, TDS and Turbidity before and after the experiment. The result is tabulated in the data to compare its quality according to the catalyst used perform.

Chapter 5 draws together a summary of the thesis and outlines the recommendations which might be applied on the future research and can develop the system in purifying the water.

2 LITERATURE REVIEW

2.1 Overview

This paper presents the experimental studies by applying the photocatalyst in the wide range of field in purifying the water. The efficient photocatalyst reactor used to purify the water was established. The TiO_2 was found to be an efficient catalyst because it is the most efficiency photoactivity, the highest stability and the lowest cost. In this study, palm oil biomass which is fiber ash will be used as supporter for TiO_2 photocatalyst for purifying the water. The fiber ash was selected because it contains some minerals and nutrient.

2.2 Introduction

In this chapter, basically describes on the photocatalyst definition and previous or recent development of photocatalysis processes by some researcher. Other than that, it will discussed regarding to Titanium Dioxide (TiO_2) catalyst especially its crystal structure and properties and application of TiO_2. Besides, the mechanism on how TiO_2 catalyst by photocatalyst working on to purify the seawater also will be studied. Rather than that, palm oil fiber ash and the advantages of photocatalyst technology also will be discussed in this part.

2.3 Introduction of photocatalyst

Photocatalyst is a light-activated catalyst agent when detects or exposes to light, it absorbs photon energy and causes various chemical reactions. Photocatalyst specifically an energetic light source of TiO_2 catalyst and oxygen or air such as an oxidizing agent will destroy the organic pollutants in the photocatalytic oxidation process (Ahmed et. al., 2011). In photocatalysis, metal oxide catalysts used such as titanium dioxide (TiO_2) generate hydroxyl radicals in the presence of ultraviolet (UV) light (photons) which in turn can attack organic matter present as pollutants in water and wastewater (Shon et. al., 2007). Thus, the main mechanism of photodegradation is the reaction of holes with surface hydroxyls or water will generate the hydroxyl radicals and it will attack the organic compounds. Hydroxyl radicals (OH•) are very reactive species because it can react rapidly, non-selectivity with organic compounds and the common oxidizing agent (Xekoukoulotakis et. al., 2007). Investigation on the seawater purification has also been done by some researchers. The Table 2-1 shows the some major cornerstones in the development of TiO_2 in photoactivated processes are:

Table 2-1: The development of TiO_2 based on photocatalysis process

Title	Researcher
Photocatalytic Degradation of Humic Acid in Saline Waters: Part 1. Artificial seawater: influence of TiO_2, temperature, pH, and air-flow. It has been proved that the Humic acid can be effectively demineralized by using the photocatalyst and TiO_2.	Radwan and David (2003)
Photoinduced reactivity of titanium dioxide. This investigation describes a new process used on the surface of TiO_2 films which is trapping of holes at the TiO_2 surface causes a high wettability namely photoinduced superhydrophilicity.	Carp et. al. (2004)
Preparation of nanocrystalline TiO_2-coated coal fly ash and effect of iron oxides in coal fly ash on photocatalytic activity. TiO_2 photocatalyst was immobilized on coal fly ash by a precipitation method in order to separate more easily TiO_2 photocatalyst from treated wastewater.	Yeon (2004)
Photocatalytic activity of sea water using TiO_2 catalyst under solar light. This paper describes the photocatalytic degradation of the seawater using approach of photoelectrochemical (PEC) reactor module equipped with spray deposited TiO_2 catalyst under solar light.	Shinde et. al. (2011)
TiO_2 photocatalysis: Design and applications. This paper was summarized the recent development of	Kazuya and Akira (2012)

TiO_2 photocatalysis research, according to new materials from a structural design perspective.	
Improving UV seawater disinfection with immobilized TiO_2: Study of the viability of photocatalysis (UV254/TiO_2) as seawater disinfection technology. This study purposes the photocatalyst with immobilized TiO_2 as a disinfection treatment for seawater and investigates its efficiency by comparing with UV254 radiation treatment.	Rubio et. al. (2013)

2.4 Photocatalytic reactor

An ideal photocatalyst should be stable, inexpensive, non-toxic and highly photoactive (Beydoun et.al., 2000). The design of photocatalytic reactor is a vital to perform the experimental work. The reactors can be divided into two types, reactors that using catalyst as suspension form and reactors that used a thin film catalyst. The reactor can be design as an immersion well or flat well. Immersion well photoreactors are normally used at laboratory scale for evaluation purposes. The catalyst can be used as thin film or as suspension form, but the most preferable is in suspension and the light source can be single or multiple with or without reflectors. The suspension form reactors are normally more efficient that thin film reactors and that are due to the large surface area in contact with the substrates (Radwan and David, 2003). Therefore, in this investigation the photocatalytic reactor will be rig set up according to suspension form reactor based on the catalyst used is in powder form.

2.5 Titanium Dioxide (TiO_2) catalyst

TiO_2 catalysts with chemical formula of TiO_2 are naturally occurring oxide of titanium. TiO_2 is belongs to the family of transition metal oxides (Shon et. al., 2007). TiO_2 also can be known as titania. TiO_2 is commonly used and suitable for industrial at present and in the future because it is the most efficiency photoactivity, the highest stability and the lowest cost. There are two types of photochemical reaction proceeding on a TiO_2 surface when it exposed to light which are the photo-induced redox reactions of adsorbed substances and photo-induced hydrophilic conversion of TiO_2 itself (Kazuhito et. al., 2005). Titanium is the world‘s fourth most abundant metal (exceeded by aluminium, iron and magnesium) and the ninth most abundant element which is constituting about 0.63% of Earth’s crust. TiO_2 was discovered by Reverend William Gregor in England on 1791 that has recognized the presence of a new element ilmenite. The element then was rediscovered in the several years then by Heinrich Klaporth (German chemist) in rutile ore who named it after Titans, mythological first sons of the goddess Ge (Earth in Greek mythology) (Carp et. al, 2004).

In the beginning, Fujishima and Honda succeed in their research about possibility of hydrogen production through water decomposition by photocatalyst and solar energy (Fujishima and Honda, 1972). Afterwards, the TiO_2 photocatalyst has become well-known in the research field and industrial field. TiO_2 is the most common catalyst used in photocatalytic reaction compared to the research has been done on zinc oxide which could be a viable alternative for some applications. Research also has been done by Yong-Suk et. al. (2000) has investigated the photocatalytic disinfection of E. coli in a suspended TiO_2/UV reactor. The TiO_2 is cheaper and has explored for the photocatalytic degradation of phenol (Ahmed et. al., 2011) and humic acid (Radwan and David, 2003). Recently, the improvement have been done for degrading of methyl orange and methylene blue dyes (Simmamora et. al., 2012) by utilizing the most active form TiO_2 which is anatase. In addition, Klankaw et. al. (2012) studied about the hybrid photocatalyst of TiO_2–SiO_2 thin film prepared from rice husk silica by the decolorization of Methylene Blue dye under UV irradiation.

2.6 TiO_2 crystal structure and properties

The main three crystalline forms of TiO_2 are brookite (orthorhombic), rutile (tetragonal) and anatase (tetragonal). The modifications have slighltly varied the band gap energies and the photocatalytic activities (Winzenburg and Faust, 2012). Based on the crystalline forms, anatase (Eg = 3.2 eV) is known to be highly active, brookite (Eg = 3.13 eV) and rutile (Eg = 3.0 eV) are generally not efficient photocatalysts (Chatterjee and Dasgupta, 2005). Thus, the oxidation reduction potentials are slightly less for the rutile phase and thermodynamically, some reaction may not be favored with rutile.

Increasing in surface area of TiO_2 will enhance the photocatalytic activity due to increase adsorption of H_2O and OH• (Yong-Suk et. al., 2000).

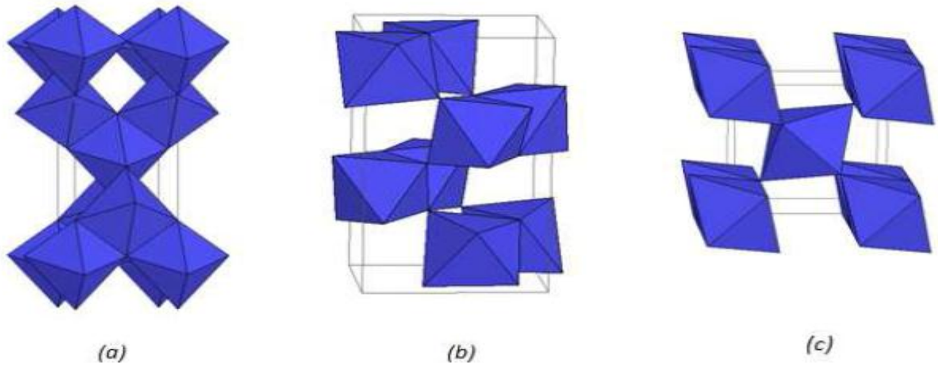

Figure 2-1: Crystal structure of anatase (a), brookite (b) and rutile (c) (Carp et. al., 2004)

Based on the Figure 2-1, the three structures differ according to the distortion of each octahedral and by the assembly patterns of the octahedral chains. The structures of these crystal structures can be reviewed in terms of octahedrals (TiO_2^{6-}) (Carp et. al., 2004). Anatase can be explained to be built up from octahedrals that are connected by their vertices. While rutile is connected via edges and brookite are connected in both vertices and edges. The different crystalline structures of TiO_2 will represent the different material properties which are density, index of refraction and catalytic properties. The investigation has been done on the anatase and it also become the common product in the sulphate process industrial (Sascha et. al., 2003). Anatase requires photo excitation of light at wavelength < 387 nm exceeding the band gap of the active phase of 3.2 eV in order to activate the degradation process (Alex and Paul, 2013). If the particles sizes of the three crystalline phases are equal, compared to another two crystal structures, anatase is the most thermodynamically stable in the sizes less than 11 nm, while brookite is most stable between 11 and 35 nm and, rutile is most stable at sizes greater than 35 nm (Zhang and Banfield, 2000).

2.7 Application of TiO_2

Nowadays, the production of TiO_2 catalysts have exceeds 4 million tons per year (Natara et. al., 1998). TiO_2 catalysts have been used in paints (51% of total production), plastic (19%), and paper (17%) as a white pigment. Other than that, it is also used in textiles, leather, food (it is approved in food –contact applications and as food colouring (E-171) under a EU legislation on the safety of the food additives (Philips and Barbano, 1997), pharmaceuticals (toothpastes, tablet coatings and other cosmetic products) and various titanate pigments (mixed oxides such as $ZnTiO_3$ (Cord and Saunder, 1971)), $ZrTiO_4$ (Hund and Anorg, 1985 and etc.). TiO_2 catalyst also becomes the important materials in many practical applications and will be used as a desiccant, brightener or reactive radiator (Alex and Paul, 2013) and also can be applied in energy catalyst (in water splitting to produce hydrogen fuel), an environmental catalyst (in water and air purification) or an electron transport medium (in dye-sensitized solar cells) (Manoj et. al., 2012).

2.8 Mechanism of TiO_2 – based photocatalysis

Photocatalytic process begins when the TiO_2 is exposed to the photon (hv) with equal or higher energy than the band gap energy of the photocatalysis (Ahmed et. al., 2011). After TiO_2 absorbing enough energy from a photon light, negative-electron (e^-) of TiO_2 is promoted to conduction band from the absorption of energy promotes the electron to the conduction band of TiO_2 therefore creating the negative-electron (e^-) and positive-hole (h^+) pair as illustrated in Figure 2-2 (Alex and Paul, 2013) and reaction (1) until reaction (5), (Ahmed et. al., 2011).

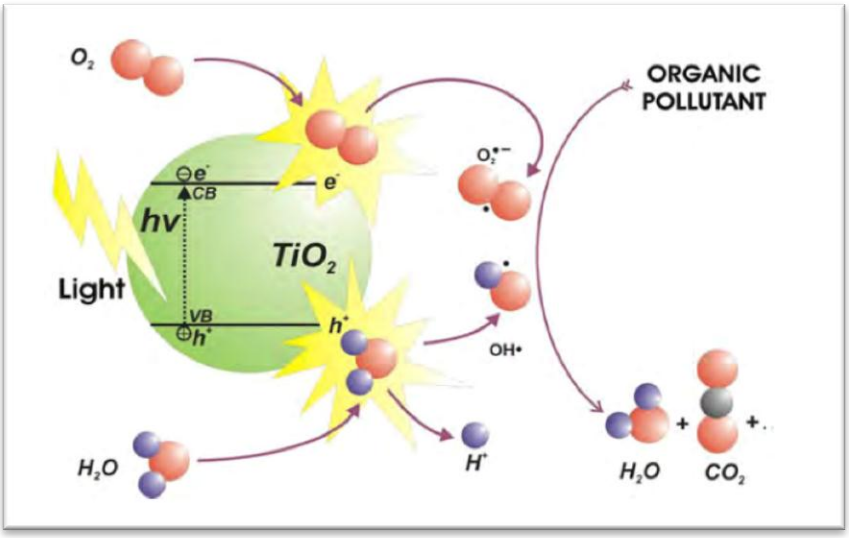

Figure 2-2: Schematic of semiconductor excitation by band gap illumination leading to the creation of "electrons" in the conduction band and "holes" in the valance band (Alex and Paul, 2013).

$$TiO_2 + hv \longrightarrow e^-_{cb} + h^+_{vb} \qquad (1)$$

$$e^- + O_2 \longrightarrow O_2\bullet^- \quad (2)$$

In this reaction, h^+ and e^- are powerful oxidizing and reductive agents, respectively. The oxidative and reductive reaction steps are expressed as,

Oxidative reaction:

$$h^+ + \text{Organic (R)} \longrightarrow \text{Intermediates} \longrightarrow CO_2 + H_2O \quad (3)$$

$$H_2O + h^+ \longrightarrow OH\bullet + H^+ \quad (4)$$

Reductive reaction:

$$OH\bullet + \text{Organic (R)} \longrightarrow \text{Intermediates} \longrightarrow CO_2 + H_2O \quad (5)$$

In the water photosplitting process, the positive-hole of TiO_2 breaks apart the water molecule to form hydrogen gas and hydroxyl radical. The negative-electron reacts with oxygen molecule to form super oxide anion. Organic compound in the water will be degraded through adsorption on the surface sites which was TiO_2 and by the chemical reaction it will convert into carbon dioxide (CO_2) and water (H_2O). However, the formations of CO_2 were not instantaneously but sometimes long-living intermediates and have been investigated as a limited extent (Carp O., et. al., 2004).

2.9 Palm oil fiber ash

Malaysia, Indonesia and Thailand were being the important country in the sector of palm oil plantation. Malaysia was being the world largest producer and exporter of the oil palm. In Malaysia, palm oil waste was being the higher and normally palm oil tree has an economic life span about 25 years. Malaysia produced over 11.9 million tons of oil and biomass was produces approximately 100 million tons by 6 million hectares of plantations in Malaysia (Abdul Khalil et. al., 2010). Other than that, the biomass ash was rich with Ca, Si, Al, Ti, Fe, Mg, Na, K, S and P (Olanders and Steenari, 1994) and some of this act as vital nutrient for the biomass. Based on the Ahmaruzzaman (2010), biomass such as rice husk had high silicon content while for the wood it had high alkali metal content.

Many researches have been done towards fly ash. According to Ahmaruzzaman, (2010), fly ash can be a promising adsorbent for the removal of various pollutants because the adsorption capacity of fly ash may be increased after chemical and physical activation. The study of using coal fly ash as a catalyst in the production of biodiesel has been done by Omotola et. al.,(2010). Furthermore, Yeon, (2004) also had studied concerning to prepare of nanocrystalline TiO_2-coated coal fly ash by precipitation method and effect of iron oxides in coal fly ash on photocatalytic activity. Another studied was done by Jian et.al. (2009) in investigating the favorable recycling photocatalyst TiO_2/coal fly ash: effects of loading method on the structural property and photocatalytic activity. Otherwise, in this paper, the new development will be done on palm oil fiber ash in purifying the seawater.

Fiber ash generates from palm oil mill effluent are highly dispersive. Normally, fiber ash is a major source of environment pollution because it will be generated in large quantities as a by-product of thermal power generation plants in dry form (Yeon, 2004). Thus, palm oil industries were generating large amount of biomass which when useful used will not harm the environment but can create value added products from this biomass. In this study, palm oil biomass which is fiber ash will be used as supported powder in a substrate for TiO_2 photocatalyst for purifying pollutants in water. This method provides a cheaper titania-immobilized photocatalyst according to TiO_2 catalyst was supported on a fiber ash. And, the feasibility of fiber ash as a supporter of TiO_2 photocatalyst was investigated. The combination of TiO_2 and fiber ash may degrade the contamination of present in sea water.

2.10 Advantages of photocatalyst

The processes that have been proposed are currently aimed to remove organic toxins from wastewater. Current treatment methods for these contaminants are adsorption by activated carbon and air stripping, merely concentrate the chemicals present by transferring them to the adsorption or air. This treatment is not effective because it do not convert contaminants non-toxic waste. Thus, photocatalytic processes have an advantage because it does not require any further requirement treatment for secondary disposal methods (Beydoun et.al., 2000). Rather than that, another advantage of photocatalytic process is when compared to other advanced technologies, notably