DEVELOPMENT OF MESOPOROUS AND ADSORPTION PHOTOCATALYSIS HYBRID SYSTEM FOR WASTEWATER TREATMENT

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ABSTRACT

In this work, vetiver adsorbent was synthesized by calcining the leaves of vetiver grass at 600°C in ambient condition. The physico-chemical characteristics of the vetiver adsorbent was investigated using X-Ray Fluorescence (XRF) and X-ray Diffraction (XRD) while the adsorption ability was tested using Methylene blue (MB) adsorption. The synthesized vetiver adsorbent was found to be able to adsorb MB with the removal efficiency of 95% at a loading of 3 g/L. Moreover, the vetiver adsorbent were proven to be reusable.

In order to improve the photocatalytic activity of Titanium Dioxide (TiO_2) using enhanced adorption-photocatalysis bi-mechanism, TiO_2-vetiver catalyst was synthesized by sol-gel method. The physico-chemical characteristics of the TiO_2-vetiver catalyst were characterized using X-ray Diffraction (XRD), Brunauer–Emmett–Teller (BET) method, Transmission Electron Microscopy (TEM), UV-Vis Diffuse Reflection Spectroscopy (DRS), and Photoluminescence (PL) spectra. The photocatalytic activity of TiO_2-vetiver catalyst and pure TiO_2 was investigated via the degradation of methylene blue (MB) under UV-A irradiation. The results indicates that the TiO_2-vetiver catalyst showed the higher MB degradation thanks to the bi-mechanisms of photocatalytic and adsorption.

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ABBREVIATION

AOPs = Advanced Oxidation Processes
VG = Vetiver Adsorbent
MB = Methylene Blue
XRF = X-Ray Fluorescence
XRD = X-Ray Diffraction
BET = Brunauer–Emmett–Teller
SEM = Scanning Electron Microscopy
TEM = Transmission Electron Microscopy
PL = Photoluminescence

CHAPTER I

INTRODUCTION

Background

Water is indispensable for human life. In addition to be required as the unique drinking supply to all living things, water is necessary for various human activities. However, according to UN-Water (Vol.1, 2012) freshwater resources are currently diminishing mainly due to effects of global warming, over-exploitation of the resources and water pollution. With the increasing growth of global population, water demand is predicted to increase significantly. The current global population (2013) is estimated to continue increasing from 7.2 billion to 9.3 billion in 2050. It means an additional 2 billion people is supposed to share a diminishing water resource in the next 40 years. As estimates, over 40% of global population has to suffer water stress during 2050.

In order to deal with water scarcity, wastewater treatment and reclamation is a promising solution. Treated wastewater not only provides benefits in term of preventing water pollution, guaranteeing water supply quality, and protecting public health, but also can be introduced as a water source for various purposes depending on the quality of treated wastewater, thus reducing water exploitation and consumption (Hochstrata, et al., 2006). The key criterion in wastewater treatment and reclamation is the quality of treated water so that the treated water is determined to be safe for use. The currently common technologies used in wastewater treatment include physical processes such as sedimentation, flocculation and coagulation, filtration, and carbon adsorption, chemical oxidation processes such as chlorination, and ozonation, and biological processes such as activated sludge, nitrification and denitrification, and phosphorus removal. These wastewater treatment technologies have a long history in large scale application and show effectiveness in removal of conventional pollutants such as solids, biodegradable organic compounds, nutrients, pathogen, and heavy metals to some extent. However, these technologies are still unable to deal effectively with refractory and toxic organic compounds as well as emerging organic compounds to produce effluents with an expected quality to meet increasingly stringent requirements for wastewater discharge and water supply (CDM Smith Inc., 2012).

On the other hand, Advanced Oxidation Processes (AOPs) are in expectation to be able to remove effectively refractory organic compounds. AOPs are recognized as the processes that can produce hydroxyl radicals which is a very strong and non-selective oxidizing species to mineralize a wide range of organic compounds (Mascolo, et al., 2007). Compared to physical treatment processes, AOPs can mineralize organic pollutants rather than transferring them from one phase to another phase. Compared to other chemical oxidation processes, AOPs produce a more powerful oxidizing species (hydroxyl radicals) that can transform organic pollutants to carbon dioxide and water without secondary pollutants generation (Soon and Hameed, 2011). Among of AOPs, photocatalysis is a technology in interest that generates hydroxyl radicals by the activation of a semiconductor catalyst using photonic energy (Al-Baastaki, 2004). One of the most common used photocatalyst is titanium dioxide (TiO_2) due to its high photo-activity, photo-corrosive resistance, thermal resistance, nontoxicity, cost effective, and possible application under natural (solar) UV light having the wavelength range from 300 to 390 nm (Zhang et al., 2012; De la Cruz, et al., 2103). The main photocatalytic mechanism of TiO_2 is the formation of electron and hole pairs when TiO_2 is excited by a light source that has the energy equal to or greater than the band gap of the catalyst (3.0 – 3.2 eV). The generated holes then transfer to the surface of TiO_2 particles and react with water to form hydroxyl radicals ($^{\bullet}OH$). Other radical species such as $O_2^{\bullet -}$ and $^{\bullet}OOH$ are also generated through a set of reactions between free electrons and oxygen. In the presence of organic molecules in the medium, they can be oxidized directly by the generated holes or indirectly by the produced radicals to form simpler products, or even carbon dioxide and water (Pelaez, et al., 2012).

Despite the fantastic benefits of TiO_2 photocatalysis in wastewater treatment, the process has a big drawback that is the separation of TiO_2 particles after treatment. The small size of TiO_2 particles causes many difficulties for the conventional separation processes such as sedimentation with coagulation, cross-flow filtration, and membrane filtration. One of solutions for this problem is the immobilization of TiO_2 particles on an adsorbent. The introduction of an adsorbent into TiO_2 particles enhances not only the separation possibility of the particles due to the increase of particle size but also the pollutants removal efficiency thanks to the bi-mechanism of adsorption by adsorbents and photo-oxidation by titanium dioxide (Chong, et al., 2010).

In addition to common adsorbents used in wastewater treatment, typically activated carbon and zeolite, adsorbents derived from agricultural wastes are achieving many interests mainly due to cost effectiveness (Chen, et al., 2012; Ghorbani, et al., 2013). Among of agricultural wastes, vetiver grass is also a potential precursor. Vetiver grass that is a valuable plant for erosion control and oil extraction can be widely found throughout tropical and subtropical regions (Ye, et al., 2014). The fragrant and volatile oil extracted from the roots of **Vetiveria zizanioides L. Nash**, a species of vetiver grass, is commercially used in various industries including perfumery, cosmetics, soap, and pharmaceuticals (Paillat, et al., 2012). In environmental applications, vetiver grass has shown the ability to accumulate persistent organic pollutants (POPs), polycyclic aromatic hydrocarbons (PAHs), phenol, and a variety of heavy metals from contaminated soil and water (Paillat, et al., 2012; Singh et al., 2014; Yaseen, et al., 2014). Clearly a huge amount of vetiver grass is cultivated every year as the demand of oil extraction industry and erosion control purpose, which generates a large number of agricultural wastes because there is no point of use for vetiver leaves (Lal, et al., 2013). Therefore, in order to make full use of vetiver grass as well as contribute to solve the agricultural wastes discard, vetiver leaves can be considered as a precursor to synthesize adsorbents.

Objectives of research

This work is conducted with three main objectives that are:

1. To develop an adsorbent, of which the leaves of vetiver grass are used as the precursor.

2. To develop of a multifunctional nanomaterial that combines the photocatalytic activity of TiO_2 and adsorption ability of the adsorbent synthesized from vetiver leaves.

3. To apply the synthesized adsorbent and catalyst to wastewater treatment.

Scope of research

This work involves two major parts that are synthesis of adsorbent and catalyst, and application of synthesized materials to wastewater treatment. The detailed work includes:

1. To synthesize and characterize the adsorbent from vetiver leaves those are collected from the field in Phitsanulok province, Thailand.

2. To immobilize TiO_2 on the synthesized vetiver adsorbent and characterize the synthesized catalyst.

3. To evaluate the adsorption capacity and adsorption isotherms of vetiver adsorbent via batch experiment, in which Methylene Blue (MB) is used as a contaminant to be removed.

4. To evaluate the photocatalytic activity of synthesized TiO_2-vetiver catalyst via batch experiment, in which MB is used as a contaminant to be removed.

CHAPTER II

REVIEW OF RELATED LITERATURE AND RESEARCH

Water resources

Water demand is expected to increase greatly with the world's population growth. More strikingly, the availability of freshwater resources is becoming scarce due to the depletion of both water quantity and quality. According to UN-Water (2014), the most severe water stress areas are in Africa and Asia where more than 60% of the world's populations live. As estimates, around 40% of world's population will suffer water stress during 2050.

1. Water demand

Water is indispensable for human life. It is required for various activities including drinking, health and sanitation, energy, food, and production of goods and services. Thus the higher population leads to the higher demand for water use (Bohmelt, et al., 2014; UN-Water, 2014). According to UN-Water (2014), the demand of water use has been tripled more than that in 1950, and it will continue to increase with the rapid growth of global population. The current global population (2013) of 7.2 billion is estimated to reach 9.3 billion in 2050. It means more water will be needed to supply to over 2 billion people in the next 40 years. As estimates, global water demand is predicted to rise by 55% in order to satisfy the increasing demand of manufacturing (400%), thermal electricity generation (140%) and domestic use (130%). Along with the worldwide increasing water demand, the availability of freshwater is projected to be increasingly strained during 2050 due to the depletion freshwater resources and population growth. Especially the problems will become more striking in the areas with severe water scarcity such as Africa, and South and Central Asia. Water stress is estimated to cover over 40% of global population during 2050.

2. Water quantity

As estimates of UNEP (2008), the total volume of water on our planet is around 1,400 million km^3, however, only 2.5% of which is fresh water. Of the overall world's fresh water, about 68.9% is stored in the form of ice and permanent snow, 30.8% is groundwater including soil moisture, swamp water and permafrost, and 0.3% is surface water.

The movement of freshwater on Earth is usually known as hydrological cycle, in which evaporation and precipitation deliver freshwater around the planet. From then, surface water as streams, rivers or lakes is renewed, groundwater is recharged, and the freshwater is restored in the form of snow and ice. The problem is that the total precipitation of the world mostly remains constant while the worldwide population is rapidly growing. This means the available amount of water per capita is decreasing. In addition, a large portion of water distributes in the sparsely populated regions while the high populated areas such as Asia and Africa get smaller water availability (UN-Water, 2012). In the meantime, under the effects of climate change, dry areas are expected to be drier while wet areas are supposed to be wetter, and the overall variability due to climate change will increase (UN-Water, 2014). Precipitation is supposed to significantly decline in the future in semi-arid and arid areas, which are homes of large part of world's population. The decrease in streamflow has been observed in many river basins around the world where major part of world's population live. Although the increasing streamflow occurs in some high latitudes, these regions are sparsely populated (Gössling, et al., 2012; UN-Water, 2012).

Similarly, according to UN-Water (2012), glaciers, the permanent water storage of the world, are also affected by climate change. Glaciers play a role as a water buffer that store water in the form of ice in the winter and contributes melt-water to the streams in the spring. With the increase of global temperature, the glaciers are shrinking worldwide, increasing the water supply in the short-term due to the addition of water into the stream flow. However, in the long-term, with the depletion of glaciers, the buffer water will decrease, leading to the shortage of water supply as a result. The shrinking rate of glaciers varies in different areas of the world, generally less than 1% of contribution to stream flow. Although in some areas, for example the Karakoram glaciers are gaining mass due to the increase of snow accumulation; some glaciers in Argentina, Chile and Peru are shrinking and even disappear. Areas suffer the most severe mass loss including Patagonia, Alaska, northwest USA, southwest

Canada, the European Alps, and the Arctic. In general, the gaining glacier mass cannot counterbalance the losing mass (UN-Water, 2012; Stocker and Qin, 2013).

Although groundwater only has been used and strongly exploited from twentieth century, it has become an important water supply worldwide, especially in the regions where surface water is not available. Approximately 26% of the overall water withdrawal and nearly 50% of drinking water in the world are made up by groundwater (UN-Water, 2012). In some countries, for example Denmark and Mexico, groundwater accounts up to 99% and 95%, respectively for the overall water supply of the country (UN-Water, 2014). The total volume of stored groundwater is estimated to be in the range from 15.3 to 60 million km^3, but only 8 to 10 km^3 of which is fresh water whereas the remaining is brackish and saline water. It is often considered to have higher quality compared to surface water due to the low microbial contamination. However, groundwater supply is currently rapidly diminishing in both quantity and quality. As estimates, about 20% of the aquifers worldwide are over exploited whereas the rate of groundwater abstraction continues to rise by 1% to 2% every year. The state of excessive groundwater abstraction has led to the falling of water tables, and land subsidence as a result. Mexico City is one of typical examples with the land subsidence of up to 9 m due to the water tables decline. Other cases have been reported including Bangkok, Beijing, Chennai, Manila, and Shanghai. Also, the groundwater recharge is estimated to decrease as a result of climate change. (UN-Water, 2012)

3. Water quality

Along with the quantity of water resources, water quality is the key parameter to determine the water availability. Water cannot be used for drinking, health and sanitation, and other activities if the water quality is not good enough to meet the standard for these water use purposes. In the other word, poor water quality reduces the amount of available water. Unfortunately, the decline of water quality due to resources overexploitation and wastewater discharge is currently an alarming issue (UN-Water, 2012).

The overuse of surface water leads to the increased concentration of natural pollutants. Rio Grandle River is an example, in which the decrease of stream flow has resulted in the increasing pathogen concentration of nearly 100 times in dry season. Similarly, many coastal and developing urban areas are facing with the increase of salinity level and naturally-occurring compounds in groundwater, respectively due to the over-abstraction. In Europe, approximately 40% of groundwater aquifers are reported to be subjected to saltwater intrusion (UN-Water, 2012).

In addition, wastewater discharge contributes a significant impact on water quality degradation. As estimates, 70% of the global water withdrawal is made up by agricultural irrigation, 20% is used for industrial activities, and 10% remaining is for domestic purposes. The huge amount of water used for irrigation along with fertilizer and pesticide applications can expose risks to both environment and human health. Rich nutrients discharge from irrigation is the major cause of eutrophication which is one of the considerable water contamination problems in the world. As estimate, the annual application in the world is around 2 million tonnes of pesticides which contain various toxic chemicals to aquatic ecosystems and human via food chain (UN-Water, 2012). Despite the smaller portions of water used for industrial and domestic purposes, their impacts to water resources are considerable as well. The fact is that several serious environmental contaminations have the origin in industrial discharges. Surface water resources, especially in Europe, Asia and South America, are reported to be polluted with treated or untreated discharges from various industries (Carneiro, et al., 2010). For example, Ganga River which supplies about 30% of the water consumption in India was extremely polluted due to leather industry and domestic wastewater discharge (Birol and Das, 2010). In Ho Chi Minh City, the highly polluted state of Thi Vai River due to the discharges of starch and amino acid production has been reported. The contamination of nitrate, heavy metals, organic chemicals, pesticides and pathogens in groundwater due to the leaking of domestic, agricultural and industrial wastewater is also a notable issue especially in populated areas (Hashim, et al., 2011; Lockhart, et al., 2013).

Wastewater reclamation and common treatment technologies

1. Wastewater reclamation

Water scarcity has become one of the most challenging issues of the world. The worldwide increase of water demand due to population growth along with the depletion of water resources in both quantity and quality are expected to result in a more severe scarcity (UN-Water, 2012; UN-Water, 2014). In the meantime, as estimates, over 80% of wastewater in the world is not treated before discharge (UN-Water, 2012). The untreated wastewater containing nutrients, organics and various toxic chemicals derived from agricultural, domestic and industrial applications has caused many adverse effects to water supply and human health around the world (Carneiro, et al., 2010; Das, 2010; Hashim, et al., 2011; UN-Water, 2012; Briol Lockhart, et al., 2013). Among of the proposed approaches to deal with the mentioned issues, wastewater reclamation and reuse has become a promising alternative due to its benefits to reduce water consumption and pollution (Hochstrata, et al., 2006; Fatta, et al., 2007; Azaïs, et al., 2014). Treated wastewater can be reused for various purposes including irrigation, domestic and industrial applications, and aquifer recharge (Metcalf and Eddy Inc., 2004; Aoki, et al., 2005). An overview of worldwide wastewater reuse shared by applications is presented in Table 1. Some examples of wastewater reclamation and reuse are summarized in Table 2.

Despite of benefits of wastewater reclamation and reuse, there are concerns about the quality and relating health issues of reused wastewater. Thus, demand of treated wastewater with high quality is increasing in order to satisfy the increasingly stringent standards for wastewater reuse and to reduce environmental contamination issues as well. As a result, advanced treatment units are invested to gain high-quality treated wastewater while new technologies are strongly investigated to enhance the efficiency of wastewater treatment (Metcalf and Eddy Inc., 2004; Aoki, et al., 2005; CDM Smith Inc., 2012)

Table 1 Global wastewater reuse shared by applications

Reused water applications	Shared percentage (%)
Agricultural irrigation	32%
Landscape irrigation	20%
Industrial applications	19.3%
Non-potable urban supply	8.3%
Environmental enhancements	8%
Recreational applications	6.4%
Indirect potable supply	2.3%
Groundwater recharge	2.1%
Other	1.5%

Source: CDM Smith, 2012

Table 2 Applications of treated wastewater

Reuse categories	Applications	Case study
Agricultural irrigation	Irrigation for food crops and non-food crops (i.e., flowers, pastures), commercial nurseries, and sod farm	Irrigation for citrus, olives, fodder and cotton crops in Tunisia Irrigation for artichoke, celery, broccoli, lettuce and cauliflower in Monterey, CA
Landscape irrigation	Landscape irrigation of parks, school yards, golf courses, cemeteries, greenbelts, residential	Landscape irrigation of sporting fileds, lawns and cemeteries in City of Waga Waga, Australia Landscape irrigation of parks, school yards, golf courses and residential lawns in City if St. Petersburg, Florida

Table 2 (cont.)

Reuse categories	Applications	Case study
Industrial uses	Cooling water, boiler feed, process water, heavy construction	Metal cooling and steel processing at the Bethlehem Steel Company in City of Baltimore, MD
Groundwater recharge	Groundwater recharge for potable water, saline intrusion and subsidence control	Groundwater recharge in Rio Hondo spreading grounds in Los Angeles, California Groundwater recharge at the Water Factory 21 in Orange County Water District, CA Groundwater recharge in Dan Regoin Project in Tel-Aviv, Israel
Recreational and environmental uses	Lakes and ponds for swimming, snowmaking, fishing, boating, marsh enhancement, stream-flow augmentation	Filling the moat in the landscape of Osaka Castle, Japan with treated wastewater Pilot study of snowmaking from treated wastewater in Aount Buller Alpine Resort, Melbourne, Australia
Non-potable urban uses	Fire protection, air conditioning, toilet flushing	In Shinjuku District, Tokyo, up to 8000 m^3/day of wastewater is treated in Ochiai Municipal Wastewater Treatment Plant and then used as toilet flushing water
Potable use	Blending with water supply, pipe to pipe water supply	Advanced wastewater treatment system to augment potable water supplies in City of Windhoek, Namibia

Source: Metcalf and Eddy Inc., 2004; Aoki, et al., 2005; CDM Smith, 2012

2. Wastewater constituents

Wastewater constituents are usually classified according to their physical, chemical and biological characteristics. The most considerable physical characteristic of wastewater is solids; others include turbidity, conductivity, color, temperature, odors and taste. Chemical constituents consist of inorganic, organic and trace constituents while biological constituents involve in pathogenic organisms. Wastewater constituents of concern are briefly introduced in Table 3.

Table 3 Commonly concerned wastewater constituents

Constituents	**Description**
Physical constituents	
Total solids (TS)	Residue remaining after a wastewater sample has been evaporated and dried at 105°C. The presence of solids can reduce the performance of wastewater treatment processes.
Total suspended solids (TSS)	The fraction of total solids remaining on a filter with a specific pore size, usually in the range from 0.45 - 2.0 µm. Suspended solids include silt and clay particles, plankton, algae, fine organic debris, and other particulates.
Total dissolved solids (TDS)	The fraction of total solids passing through the filter. Dissolved solids usually consist of calcium, chlorides, nitrate, phosphorus, iron, sulfur, and other ions.
Turbidity	A measure of the light transmission of water caused by the presence of colloidal and suspended matter.
Conductivity	A measure of the ability of water to conduct an electrical current, affected by the presence of inorganic dissolved solids such as chloride, nitrate, sodium, magnesium, calcium and other ions.
Color	Caused by organic material from decaying vegetation and certain inorganic matter. Concerned problems of color in water are usually about aesthetics rather than health issues.

Table 3 (cont.)

Constituents	**Description**
Inorganic constituents	
Nonmetallic constituents	
Chlorides	Excessive concentration of chloride can cause adverse effects on aquatic life. Chloride concentration exceeding 250 mg/L can cause unpleasant taste. Domestic water supply should not contain more than 100 mg/L of chloride.
Fluorides	Excessive concentrations can cause dental fluorosis. Optimum concentrations for dental care are in the range from 0.7 to 1.2 mg/L.
Alkalinity	Caused by hydroxides, carbonates and bicarbonates of calcium, magnesium, sodium, potassium and ammonia. Alkalinity is an important parameter in chemical and biological treatment, and biological nutrient removal as well.
Nutrients (Nitrogen, Phosphorus)	Nitrogen and phosphorus are essential nutrients for growth of organisms. However, excessive concentrations of nitrogen and phosphorus result in eutrophication.
Metals	Some metals are trace elements for growth of organisms. However, the presence of excessive concentrations of metals originated from the wastewater discharges are a considerable issue due to their high acute toxicity as well as well as carcinogenicity and mutagenicity at even low concentrations. Some metals classified as priority discharged from commercial, industrial and agricultural activities include Arsenic (As), Barium (Ba), Cadmium (Cd), Chromium (Cr), Lead (Pb), Mercury (Hg), Selenium (Se) and Silver (Ag).

Table 3 (cont.)

Constituents	**Description**
Organic constituents	
Aggregate organic constituents	The fraction of organic constituents having similar characteristics that cannot be differentiated separately. Major constituents of organic compounds are carbon, hydrogen, oxygen and nitrogen in some cases. Aggregate organic constituents can be measured by various methods including biological oxygen demand (BOD), chemical oxygen demand (COD), and total organic carbon (TOC).
Oil and grease	Esters compounds formed by reaction between alcohols and fatty acids. Oils are liquid compounds while grease (or fats) is solid. The presence of oils and grease in wastewater can create unsightly thick films, interfere with biological activity and reduce performance of treatment processes. Oils and grease can be determined by extraction method using trichlorotrifluoroethane.
Surfactants	Surface-active agent usually composed of a nonpolar tail and a polar head. The presence of surfactants in wastewater can create stable foams in the surface during aeration process.
Individual organic compounds	The individual organic compounds of concern include priority pollutants and emerging organic compounds. They can be determined using gas chromatography (GC) and high-performance liquid chromatography (HPLC). Priority pollutants are determined by United State Environmental Protection Agency (US.EPA).

Table 3 (cont.)

Constituents	Description
Individual organic compounds	Some types of organic priority pollutants are volatile organic compounds (VOCs), trihalomethanes (THMs), chlorinated organic solvent, aldehydes, phenols, polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), pesticides and herbicides. Priority pollutants are in concern due to their high acute toxicity or suspected carcinogenicity, mutagenicity and teratogenicity. Emerging organic compounds are the non-regulated anthropogenic compounds widely detected in water bodies. Generally they consist of veterinary and human antibiotics, human prescription and non-prescription drugs, personal care products, sex and steroidal hormones, and industrial and household wastewater products, for example, pesticides, herbicides, wood preservative, food additives, and flame retardants. Emerging organic compounds are in concern due to their persistence, bioaccumulation, and widespread detection.
Pathogenic organisms	
Bacteria Protozoa Helminthes Viruses	There is a variety of organisms found in water and wastewater including bacteria, fungi, algae, protozoa, viruses, other plants and animals. Among of them, pathogenic organisms that are bacteria, protozoa, helminthes (worms), and viruses are the most concerned due to their disease infection to human. Common diseases caused by pathogenic organisms include diarrhea, food poisoning, and gastrointestinal infection. Some kinds of viruses can even cause respiratory disease, heart anomalies and meningitis.

Source: Sincero and Sincero, 2003; Metcalf and Eddy Inc., 2004; Davis, 2010; Withers, et al., 2011; CDM Smith, 2012; Khan, et al., 2013; Alidina, et al., 2014; Hou, et al., 2014; Valipour, et al., 2014; Corsi, et al., 2015

3. Wastewater treatment technologies

In order to remove the unexpected constituents in wastewater to meet requirements for various water use purposes and public health safety, several wastewater treatment technologies are applied to treat raw wastewater. In general, wastewater treatment technologies can be classified as conventional and advanced technologies. Conventional treatment technologies are divided into primary, secondary treatment that are widely applied in wastewater treatment plants with the aim of removing common found constituents in wastewater such as suspended solids, aggregate organic compounds, and pathogenic organisms. Some enhanced treatment units can be added for further removal and disinfection to meet the requirements of higher water quality for water use. In the meantime, advanced treatment technologies are those required for the removal of specific pollutants or persistent compounds that cannot be removed effectively by conventional treatment technologies. The removal efficiency of some conventional and advanced treatment technologies is presented in Table4.

Table 4 Pollutants removal efficiency of some wastewater treatment technologies

Constituents	Wastewater treatment technologies												
	Primary treatment	Flocculation Coagulation Sedimentation	Activated sludge (AS)	Filtration after AS	Chlorination	Ozone	MF	UF	NF	RO	Ammonia striping	Carbon adsorption	AOPs
Conventional constituents													
TSS	>50	>50	>50	>50						>50		>50	
TDS										>50			
Color	25	>50	25 – 50	25 – 50		>50				>50		>50	
BOD	25 – 50	>50	>50	25 – 50		25				>50		>50	
COD	25 – 50	>50	>50	25 – 50		>50				>50	25	25 – 50	
TOC	25 – 50	>50	>50	25 – 50		>50				>50		>50	
NH_3-N	25	25	>50	25 – 50						>50	>50	25 – 50	
NO_3-N				25 – 50						>50		25	
Phosphorus	25	>50	25 – 50	>50								>50	
Total Coliform		>50	>50		>50	>50						>50	

Table 4 (cont.)

Constituents	Wastewater treatment technologies												
	Primary treatment	Flocculation Coagulation Sedimentation	Activated sludge (AS)	Filtration after AS	Chlorination	Ozone	MF	UF	NF	RO	Ammonia stripping	Carbon adsorption	AOPs
Heavy metals													
Arsenic	25 – 50	25 – 50	25 – 50	>50								25	
Barium		25 – 50	25 – 50	25									
Cadmium	25 – 50	>50	>50	25 – 50								25	
Chromium	25 – 50	>50	>50	25 – 50								25 – 50	
Lead	>50	>50	>50	25								25 – 50	
Mercury	25	25	25	25 – 50								25	
Selenium	25	25	25	>50								25	
Silver	>50	>50	>50									25 – 50	

Table 4 (cont.)

Constituents	Wastewater treatment technologies												
	Primary treatment	Flocculation Coagulation Sedimentation	Activated sludge (AS)	Filtration after AS	Chlorination	Ozone	MF	UF	NF	RO	Ammonia stripping	Carbon adsorption	AOPs
Pharmaceuticals													
DZP					20 – 50	50 – 80	< 20	50 – 80	> 90	>95		50 – 80	50 – 80
CBZ		-			<20	50 – 80	< 20	50 – 80	> 90	>95		50 – 80	>80
DCF		10 – 50			>80	>95	< 20	50 – 80	> 90	>95		20 – 50	>80
IBP		>90			<20	50 – 80	< 20	50 – 80	> 90	>95		<20	>80
PCT					>80	>95	< 20	50 – 80	> 90	>95		50 – 80	>80

Table 4 (cont.)

	Wastewater treatment technologies												
Constituents	Primary treatment	Flocculation Coagulation Sedimentation	Activated sludge (AS)	Filtration after AS	Chlorination	Ozone	MF	UF	NF	RO	Ammonia stripping	Carbon adsorption	AOPs
Emerging organic compounds													
Antibiotics		10 – 50			>80	>95	< 20	50 – 80	>90	>95		20 – 80	50 – 80
Steroid (hormones)		>90			>80	>95	< 20	50 – 80	>90	>95		50 – 80	>80
Anabolic (hormones)					<20	>80			>90	>95			>80
Fragrance		50 – 90			20 – 80	50 – 90	< 20	50 – 80	>90	>95		50 – 80	50 – 80
NDMA		-			-	50 – 90			>90	25 – 50			>90

Source: CDM Smith, 2012; Metcalf and Eddy Inc., 2004.

3.1 Conventional treatment technologies

The conventional treatment technologies that are introduced in this Section include primary treatment, secondary treatment, and enhanced treatment.

3.1.1 Primary treatment

According to Metcalf and Eddy Inc. (2004; Davis, 2010; Edzwald, 2011), the purpose of primary treatment is to remove settable solids including a part of suspended solids and attached organic particulate matter in order to take the advantage for further treatment. The primary removal of suspended solids and organic matter helps to increase the dissolved oxygen concentration in wastewater, leading to the reduction of energy consumption for aeration and operational problems in biological treatment processes. The most common used technology in primary treatment is sedimentation. The principle of sedimentation is to settle particulate solids present in wastewater by gravity and remove settled solids (sludge) from the flow. The average removal efficiency of primary sedimentation is from 50 to 70% of suspended solids and from 25 to 40% of organic carbon in term of BOD. In order to enhance the settling process, additional chemicals and mixing can be applied, which are usually referred to flocculation and coagulation. The additional chemicals enhance the flocculation and coagulation of the particles in wastewater. As a result, the particles aggregate with each other, and increase their size and specific gravity so that they can settle down more efficiently. Alum ($Al_2(SO_4)_3.14H_2O$) or ferric chloride ($FeCl_3$) added in conjunction with anionic polymers are most common used additional chemicals. With the application of flocculation and coagulation, removal efficiency of sedimentation can increase up to 90% of suspended solids and 80% of organic carbon.

In case that there is the presence of floating materials and light particles that cannot be removed effectively by sedimentation, flotation can be used to remove these constituents. The principle of flotation is to apply gas bubbles into the stream and attach them to the light particles. The particles attached to bubbles have density less than water, thus can float to the surface water and be removed from the flow.

3.1.2 Secondary treatment

According to Metcalf and Eddy Inc. (2004), secondary treatment is the further step to remove remaining suspended solids and organic matter from primary effluent. In most cases, to deal with the wastewater containing high organic matter content, biological treatment is a good choice due to its advantages including high efficiency, non-toxicity, cost effectiveness and well-understood operation. The principle of biological treatment is the use of microorganisms to decay organic matter by using organic content in wastewater as a nutrient source for their growth. After biological oxidation process, the produced biomass is removed from the effluent in a sedimentation tank. Biological processes can be applied in form of suspended growth or attached growth, in which microorganisms are maintained in liquid suspension by mixing, or attached to an inert packing film such as rock, gravel, sand, or plastics, respectively. These processes can be operated under aerobic or anaerobic condition. In aerobic process, organic matter is oxidized in the presence of oxygen to form carbon dioxide and water as the final products. Meanwhile, anaerobic process is used for high organic loading concentration, in which organic matter is oxidized in the absence of oxygen to form carbon dioxide and methane gas, which are usually referred as biogas. The choice of different processes depends on many factors including treatment purpose, wastewater characteristics, constructed area and economic consideration.

According to Davis (2010), due to the increasing concern about the presence of nutrients in wastewater and their effects, typically eutrophication, biological treatment processes are improved to remove nitrogen and phosphorus along with organic carbon. Similar to organic carbon, nitrogen and phosphorus are essential nutrients for microorganisms' growth. Thus, it is possible for microorganisms to convert nitrogen and phosphorus via their metabolism. Biological nitrogen removal consists of two stages. The first step called nitrification is the oxidation of ammonia (NH_4-N) to nitrite (NO_2-N) and nitrate (NO_3-N) under the aerobic condition. The second step termed denitrification is the reduction of nitrate (NO_3-N) in the anoxic (low oxygen concentration) condition to nitrogen gas which is released into the atmosphere. In the meantime, phosphorus is removed from the flow using phosphorus accumulating organisms that are able to accumulate phosphorus in biomass. The design for phosphorus removal is an anaerobic tank followed by an aerobic tank. Many configurations are designed to combine the removal of organic carbon, nitrogen and phosphorus, for example modified sequencing batch reactor (SBR), modified 5-

stages Bardenpho reactor. These reactors generally consist of alternative stages of anaerobic, aerobic and anoxic condition in order to take the advantage for organic carbon, nitrogen and phosphorus removal process to occur.

Despite the advantages of biological treatment, one of the biggest limitations is that biological treatment are not highly effective to persistent organic compounds and even breakdown in the presence of toxic compounds to microorganisms (Jin, et al., 2013; Chen, et al., 2014). Therefore, biological treatment is widely applied to wastewater containing biodegradable organic compounds while advanced treatment is necessary for further removal of toxic or persistent compounds such as heavy metals, phenol, polycyclic aromatic hydrocarbons (PAHs), pesticides, pharmaceuticals, etc. (Prieto-Rodriguez, et al., 2012; Garcia-Seguraa, et al., 2015)

3.1.3 Enhanced treatment

According to Metcalf and Eddy Inc. (2004), to satisfy the stringent standard of wastewater discharge or reuse purpose, further treatment to remove suspended solids after secondary treatment is becoming more popular. One of the common technologies used in this enhanced treatment step is granular filtration, also called depth filtration. Depth filtration is the separation of suspended solids from the aqueous phase when wastewater passes through a filter bed. The filter bed is designed to consist of a deep filtration media and a support media at the bottom to prevent the filtration media from leaving the filter with the effluent. The filtration media is usually sand or coal while gravel is usually used as the support. When wastewater passes through the filtration medium, solids are retained within and on the surface of the filter bed by various mechanisms including straining, sedimentation, impaction, interception, adhesion, and flocculation. Among of these, straining is the dominant mechanism, in which, the solids with the size greater than the pore space of filtration medium are strained out the flow while the smaller size particles are trapped in the filtration medium by chance contact.

Disinfection is an important step of pathogen removal for public health safety before discharge. The principle of disinfection is the use of chemical or physical agents to inactivate pathogen in wastewater. Pathogen inactivation mechanisms of disinfection agents include cell wall damage, cell permeability alternation, protoplasm alternation, DNA or RNA alternation, and inhibition of enzyme activity. The most widespread disinfection agents are chlorine, ozone and ultraviolet (UV) radiation. In addition to disinfection, chlorine and ozone are also used to remove odor and biodegradable organic substances due to their strongly oxidizing activity. Ozone especially can be applied as an advanced treatment for oxidation of persistent organic compounds. (Metcalf and Eddy Inc., 2004; Edzwald, 2011)

3.2 Advanced treatment technologies

Some common advanced treatment technologies that are introduced in this Section consist of membrane filtration, gas stripping, carbon adsorption, and advanced oxidation processes (AOPs).

3.2.1 Membrane filtration

Membrane filtration is a technology to remove unexpected constituents (suspended solids or ions) from aqueous phase when wastewater passes through a thin membrane. Membrane is made of synthetic semipermeable material that is highly permeable to some constituents and less permeable to others. In general, membrane technology can be classified into microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO), and electrodialysis (ED). Microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) processes are driven by pressure while electrodialysis (ED) is driven by electrical voltage. These categories of membrane technologies are introduced briefly as follows, according to Metcalf and Eddy Inc. (2004; Davis, 2010).

1) Microfiltration (MF) and Ultrafiltration (UF)

MF and UF can be distinguished by the pore size of membrane. MF membranes have pore size of greater than 50 nm (macropores) while pore size of UF membranes is in the range from 2 to 50 nm (mesopores). MF and UF membranes are usually made of organic polymers. Among of those, polysulfone (PS) is one of the most widely used materials because of their high tolerance to pH and resistance to oxidants. In addition, polyethersulfone (PES) and polyvinylidene difluoride (PVDF) are also in common use. MF and UF are applied to separate suspended particles (colloidal matter, microorganisms, and viruses) from water. The dominant mechanism of MF and UF is straining, in which particles with the size greater than pore size of the membrane through which water can pass are retained. MF and UF are also used as pretreatment of NF, RO and ED.

2) Nanofiltration (NF) and Reverse Osmosis (RO)

Membranes of both NF and RO are usually made of cellulose and polyamide material, for example, cellulosic acetate (CA) and Polyamide (PA) with the pore size of less than 2 nm (micropores). They can be used to remove small molecules and even ions. However, their mechanisms of separation are slightly different. Similar to MF and UF, the driving removal mechanism of NF is straining. In addition, diffusion also plays a significant role, especially at the smaller pore size. Meanwhile, the removal mechanism of RO is reverse osmosis, in which an additional pressure is applied to the system to force water to pass through the membrane from the higher concentration side (wastewater influent) to lower concentration side (effluent). Only water and smaller molecules can pass through RO membranes while other molecules are retained.

3) Electrodialysis (ED)

Electrodialysis (ED) is a technique of using semipermeable selective ion exchange membranes to separate ions from water under the application of electrical voltage between two electrodes. When the applied electric current passes through the wastewater, cations in wastewater tend to move towards negative electrode (cathode) while anions move towards positive electrode (anode). Along with that, a set of cation and anion semipermeable membranes is placed alternatively. As a result, the cells of concentrated ions solution and diluted ions solution are formed alternatively in the spacing between membranes. Due to the separation by electromotive force, ED can remove even the smallest ions such as Na^+ and Cl^-. However, it cannot remove neutral substances such as silica, particulate matter, or pathogens. ED is widely applied in desalination with initial total dissolved solids less than 3,000 mg/L.

3.2.2 Gas stripping

According to Metcalf and Eddy Inc. (2004), gas stripping is a technique to transfer a gas from aqueous phase to gas phase following Henry's law equilibrium. In a typical stripping tower, wastewater is distributed downstream from the top of the tower in order to contact with an upstream gas (usually air) flow that does not contain the gas to be stripped. During the process of contact between air and aqueous phase, the concerned gas partitions from aqueous phase into the air flow according to Henry's law. Stripping towers are usually filled with packing material to restrain the flows and increase contact time to guarantee for the partition process to occur. However, not all compounds can be stripped out the aqueous phase. The stripping possibility of a compound depends on the ability to volatile from the solution which is indicated by Henry's law constant of each compound. Compounds with Henry's law constants greater than 500 atm such as benzene, toluene, and vinyl chloride are readily strippable while compounds with Henry's law constants less than 0.1 atm, for example acetone and methyl ethyl ketone are essentially not strippable. Some compounds such as ammonia with Henry's law constants of 0.75 atm and sulfur dioxide of 38 atm are slightly strippable. Therefore, gas stripping is usually applied to remove ammonia, odorous gases such as hydrogen sulfide, and volatile organic compounds (VOCs).

3.2.3 Carbon adsorption

As mentioned in Sincero and Sincero (2003; Metcalf and Eddy Inc., 2004; Edzwald, 2011), adsorption is a mass transfer process occurring at the interface of two phases (gas-solid or liquid-solid), in which a substance present in aqueous phase or gas phase is transferred to solid phase. The substance that is removed from the aqueous (or gas) phase and accumulated at the interface is called the adsorbate. The solid on which the adsorbate accumulates is called the adsorbent. The driving forces to hold the adsorbate on the surface of adsorbent consist of physical interaction (van der Waals forces, dipole-dipole interactions, and hydrogen bonding) and chemical bonding. Adsorbate molecules absorb on the surface of adsorbent until the equilibrium is reached. At equilibrium, the rate of the forward reaction (adsorption) and the reverse reaction (desorption) is equal, thus no more adsorbate molecules are absorbed.

In term of wastewater treatment, adsorption is applied to remove unexpected constituents in wastewater by transferring them to a suitable adsorbent. Surface properties of adsorbent including pore size, surface area, functional groups have a great effect on adsorption capacity. The adsorbents used in wastewater treatment include activated carbon, activated alumina, zeolites, clays, and other synthetic polymeric adsorbents. Among of these, activated carbon is the most widely used due to its porous structure with high surface area (about from 800 to 1500 m^2/g), ready availability and cost effectiveness.

Activated carbon is synthesized from organic materials. Common raw materials include coal, lignite, wood, coconut shells, almond shells, walnut hulls, and other types of biomass. In general, there are two methods to synthesize activated carbon, defined as physical and chemical activation. In physical activation, raw material is converted to a char by carbonization in an inert atmosphere at temperatures less than 700°C. After that, steam or carbon dioxide (CO_2) is introduced at temperatures of 800 to 900°C steam to develop internal porous structure in the char. On the other hand, in chemical activation, carbonization stage and activation stage is combined, in which chemicals such as acids (HNO_3, H_3PO_4), base (NaOH, KOH), and salts ($NaNO_3$, KNO_3) are mixed with the raw material, then the mixture is heated at high temperature in the absence of oxygen. Chemical activation provides the advantages of using lower temperature and modifying surface characteristics with the introduction of functional groups in order to increase the adsorption efficiency of specific pollutants (Ahmad and Hameed, 2010;Edzwald, 2011; Bhatnagar, et al., 2013).

Activated carbon can be used in form of granular activated carbon (GAC) with the particle size greater than 0.1 mm, and powdered activated carbon (PAC) with the particle size ranging from 5 to 50 μm. Adsorption using activated carbon is one of the most practical available method to remove persistent organic compounds as well as residue of inorganic compounds such as nitrogen, sulfides, and heavy metals (Metcalf and Eddy Inc., 2004; Davis, 2010)

3.2.4 Advanced oxidation processes (AOPs)

Advanced oxidation processes (AOPs) are the application of hydroxyl radicals ($HO^•$) to oxidize organic compounds to form carbon dioxide and water as final products (Mascolo et al., 2007; De la Cruz, et al., 2013). Hydroxyl radicals are a very strong and non-selective oxidizing species with the oxidation potential value of 2.80 V (Fontecha-Camara, et al., 2011). Thus, hydroxyl radicals are able to oxidize a wide range of compounds without restriction to their specific classes or group, for example halogenated hydrocarbons, aromatic compounds, volatile organic compounds (VOCs), pentachlorophenol (PCP), pesticides, and inorganic pollutants such as cyanides, sulfides and nitrites (Soon and Hameed, 2011; CDM Smith Inc., 2012). A comparison of oxidation potential of various oxidants is shown in Table 5. AOPs are preferred in the presence of organic compounds that are persistent to biological degradation and chemical oxidation of other oxidants such as oxygen, ozone and chlorine (Metcalf and Eddy Inc., 2004). The advantages of AOPs compared to physical treatment or other oxidation processes include the degradation of pollutants rather than the transfer from one phase to another phase, the mineralization of pollutants without secondary products generation, and no need of materials regeneration or disposal (Metcalf and Eddy Inc., 2004; Soon and Hameed, 2011). In addition, AOPs can be operated under normal condition (room temperature and atmospheric pressure) (Hawari, et al., 2015). AOPs can be classified into different categories according to the process of generation of hydroxyl radicals as presented in Table 6.

Table 5 Oxidation potential of various oxidizing species

Oxidizing species	Oxidation potential (V)
Fluorine	3.06
Hydroxyl radicals	2.80
Oxygen (atomic)	2.42
Ozone	2.08
Hydrogen peroxide	1.78
Hypochlorite	1.49
Chlorine	1.36
Oxygen (molecular)	1.23

Source: Metcalf and Eddy Inc., 2004.

Table 6 Examples of Advanced Oxidation Processes

Categories	Examples
Electrical and mechanical processes	Corona discharge
	Electrohydraulic discharge
	Electron beam irradiation
	Ultrasonic
	Non-thermal plasma
	Radiolysis
Ozone-based processes	Ozonation : O_3
	Photo-ozonation: O_3 + UV, O_3 + UV + H_2O_2
	Ozonation + catalysis: O_3 + H_2O_2, O_3 + Fe^{2+}/Fe^{3+}, O_3 + TiO_2
	Ozonation + electron beam irradiation
	Ozonation + ultrasonic
Hydrogen peroxide-based processes	H_2O_2 + UV
	Fenton reaction: $H_2O_2 + Fe^{2+}/Fe^{3+}$
	Photo-Fenton reaction: $H_2O_2 + Fe^{2+}/Fe^{3+}$ + UV
	Heterogeneous Fenton reaction: $H_2O_2 + Fe^{2+}$-solid/Fe^{3+}-solid
Photocatalysis	Semiconductor + UV: TiO_2 + UV
	ZnO + UV
	CdS + UV
	GaP + UV
	ZnS + UV

Source: Metcalf and Eddy Inc., 2004; Pera-Titus, et al., 2004; Chong, et al., 2010.

Titanium dioxide (TiO_2) catalyst

As illustrated above, Advanced Oxidation Processes (AOPs) is a promising technology because of their prominent advantages compared to physical and other chemical oxidation processes. Among of the AOPs, photocatalysis is considered to be under better control of hydroxyl radical generation and toxic secondary pollutants formation compared to other processes, for example, the application of ozone and hydrogen peroxide (Al-Baastaki, 2004). Photocatalysis is a process of using a semiconductor catalyst which is activated by photonic energy to generate hydroxyl radicals (Assadi, et al., 2013). There is a variety of photocatalysts that has been investigated including titanium dioxide (TiO_2), zinc oxide (ZnO), zinc sulfur (ZnS), ferric oxide (Fe_2O_3), cadmium sulfur (CdS), gallium phosphide (GaP) (Chong, et al., 2010). Among of these, titanium dioxide is the most common used photocatalyst due to its high photo-activity, photo-corrosive resistance, thermal resistance, nontoxicity, cost effective, and possible application under natural (solar) UV light having the wavelength range from 300 to 390 nm (Zhang, et al., 2012; De la Cruz, et al., 2013).

1. Structure and properties

According to Zhang, et al., 2009; Luis, et al., 2011; Pelaez, et al., 2012, titanium dioxide (TiO_2) is a semiconductor, in which each titanium (Ti^{4+}) atom is coordinated to six oxygen (O^{2-}) atoms to form TiO_6 octahedron. Titanium dioxide has three polymorphs which are anatase, rutile and brookite. Both anatase and rutile have a tetragonal structure, in which the octahedron share vertices at planes and share edges at planes, respectively. Meanwhile, brookite has an orthorhombic structure as a result of the octahedron sharing of both edges and vertices. Among of three polymorphs of titanium dioxide, rutile is the most stable form. Anatase and brookite is subjected to transform to rutile under the thermal treatment at temperatures exceeding $\sim 600^{\circ}$C. In general, brookite is relatively unstable and difficult to synthesize in pure form compared to anatase and rutile. Therefore, most of investigations into titanium dioxide are focused on anatase and rutile.

Anatase and rutile has the band gap of 3.2 eV and 3.0 eV, respectively (Zhang, et al., 2009; Bellardita, et al., 2011). Due to the relatively large band gap, titanium dioxide is opaque to UV light and transparent to visible light. Thus, it has been used as a material for UV filtering, UV protection cosmetics and other products (Zhang, et al., 2009). On the other hand, the UV light absorption of titanium dioxide leads to the hole and electron formation. The generated holes react with reducing species present in the medium to produce hydroxyl radicals, which is known as a strong oxidant for pollutant removal. More details on photocatalytic mechanism of titanium dioxide are mentioned in Section 3.2. In addition to the reaction between holes and reducing agents, a small amount of generated holes may be trapped at lattice oxygen sites and react with titanium dioxide itself. This process weakens the lattice titanium and oxygen bonding, leading to the formation of hydroxyl groups in the presence of water molecules. As a result, the titanium dioxide surface becomes superhydrophilic (Nakata and Fujishima, 2012; Nakata, et al., 2012). Due to its photocatalytic reactivity, transparent to visible light, and super-hydrophilic surface properties, titanium dioxide has been applied in various applications including dye synthesized solar cells, antifogging mirror and glass, water splitting, self-cleaning, and water purification (Nakata, et al., 2012; Liang, et al., 2013; Murugan, et al., 2013; Freitas, et al., 2014).

2. Mechanism and applications in wastewater treatment

In term of wastewater treatment application, titanium dioxide has proven to be able to remove a variety of organic compounds. The specific wastewater treatment applications along with synthesis methods and activity performances of titanium dioxide are presented in Table 7. The photocatalytic mechanism of titanium dioxide to mineralize organic pollutants is proposed by other authors (Houas, et al., 2001; Rizzo, et al., 2007; Pelaez, et al., 2012) as follows:

Absorption of efficient photons

$TiO_2 + h\nu \rightarrow e_{cb} + h^{+}_{vb}$

Formation of hydroxyl radical by photo-holes

$H_2O + h^{+}_{vb} \rightarrow H^{+} + {}^{\bullet}OH$

The formation of radical species by electron

$O_2 + e_{cb} \rightarrow O_2^{\bullet -}$

$O_2^{\bullet -} + H^{+} \rightarrow {}^{\bullet}OOH$

${}^{\bullet}OOH + {}^{\bullet}OOH \rightarrow H_2O_2 + O_2$

Oxidation of organic (R) by hydroxyl radical, holes, and other radical species

$R + {}^{\bullet}OH \rightarrow R'^{\bullet} + H_2O \rightarrow \rightarrow \rightarrow CO_2 + H_2O$

$R + h^{+} \rightarrow R^{\bullet +} \rightarrow \rightarrow \rightarrow CO_2 + H_2O$

$R + O_2^{\bullet -} \rightarrow \rightarrow \rightarrow CO_2 + H_2O$

$R + {}^{\bullet}OOH \rightarrow \rightarrow \rightarrow CO_2 + H_2O$

When titanium dioxide catalyst is excited by a light source that has the energy equal to or greater than the band gap of the catalyst, an electron (e_{cb}) moves from the valence band to the conduction band, leading to the formation of a hole (h^+_{vb}) in the valence band. Along with the excitation process, the photo-excited electrons and holes can be de-excited by various pathways including the recombination of electrons and holes on the catalyst surface or in the bulk volume, and the transfer of electrons and holes to the absorbed redox species (Zhang, et al., 2009). The removal of organic pollutants is based on the second pathway, in which the generated holes in the valence band can be transferred to the surface of titanium dioxide particles. In the presence of water molecules as a reducing species, these holes react with water and form hydroxyl radicals ($^{\bullet}OH$). In the meantime, a set of reactions between the generated electrons and oxygen result in the formation of other radical species such as $O_2^{\bullet\,-}$ and $^{\bullet}OOH$. The organic molecules present in the aqueous solution can be oxidized directly by the generated holes or indirectly by the produced radicals to form simpler products, or even carbon dioxide and water as the final products of mineralization.

3. Synthesis methods of titanium dioxide

Titanium dioxide can be synthesized and applied in form of spheres (zero-dimension), fibers and tubes (one-dimension), nanosheets (two-dimension), and interconnected architecture (three-dimension), depending on the purposes of use. Among of these, nanosized particles (zero-dimension) is the most applied in wastewater treatment due to the high efficiency (Nakata and Fujishima, 2012). There are several methods that have been developed to synthesize nanosized TiO_2 particles such as sol–gel method, flame or aerosol process, electrodeposition, precipitation, thermal decomposition reactions, hydrothermal method, and microwave assisted method (Zhang, et al., 2009; Le, et al, 2012). In this section, the most common methods of nanosized TiO_2 synthesis including sol–gel, aerosol, and precipitation method are briefly introduced, according to Zhang, et al. (2009; Moiseev, et al., 2011; Prasad, et al.,2011; Joks, et al., 2012; Assadi, et al., 2013).

3.1 Sol-gel method

Sol-gel method is a wet chemical process to synthesize nanomaterials from a liquid phase. The precursors used in sol-gel method can be inorganic or metal-organic compounds. The most common applied precursors are metal alkoxides [$Ti(OR)_n$], in which R can be an alkyl, inorganic salt, or organic salt. In order to synthesize nanomaterials, solvents and catalysts are mixed with precursors to stimulate hydrolysis and condensation reactions as follows:

Hydrolysis: $TiOR + HOH \leftrightarrow TiOH + ROH$

Condensation: $TiOR + TiOH \leftrightarrow TiOTi + ROH$

$TiOH + TiOH \leftrightarrow TiOTi + HOH$

$TiOH_2 + TiOR \leftrightarrow Ti(OH)Ti + ROH$

The solvents are normally the alcohol parents of the precursors. The hydrolysis occurs under the addition of water. However, an acid or base is preferred in the presence of electronegative metals and metalloids. After hydrolysis and condensation processes, the formed gel is dried and then followed by thermal treatment in order to form the crystalline structure. The crystalline phase (anatase or rutile) of synthesized titanium dioxide can be controlled by temperature. Depending on the drying process, the formed gel can be classified into aerogels which are produced under the supercritical drying and xerogels which are formed in the absence of supercritical fluid. Although both of gel types achieve the porous structure, aerogels have lower density, higher porosity and surface area compared to xerogels.

3.2 Flame aerosol method

Aerosol process is a widely used method to synthesize titanium dioxide in commercial scale due to the use of inexpensive precursors and the ease of metal oxides formation. One of the most common precursors in aerosol method is titanium tetrachloride ($TiCl_4$). At first, the precursors are evaporated into aerosol by an evaporator using dry argon gas. Produced aerosols are then are mixed with oxygen, and other inert gases and fuels such as hydrogen and methane. The mixture is injected into a burner for the reaction to occur. The general reaction occurs as follows:

$$TiCl_4(g) + O_2(g) + CH_4(g) \leftrightarrow TiO_2(s) + HCl(g) + CO_2(g) + H_2O(g)$$

After flame treatment, the particles are formed and collected on a glass fiber placed in a filter holder that is fixed about 50 cm above the flame.

3.3 Precipitation method

Precipitation is one of the oldest methods to synthesize nanoparticles. In precipitation process, the precursors are dissolved in a solvent, usually water with the addition of a base such as sodium hydroxide or ammonium hydroxide to promote the precipitation. The precipitation reactions involve the simultaneous occurrence of nucleation, growth, coarsening, and/or agglomeration processes. The nucleation process is a key step of the precipitation process in that a large number of small particles will be formed. After the precipitation, the formed precipitates are filtered, dried and then treated at high temperature to develop crystalline structure.

Table 7 Applications of TiO_2 in wastewater treatment

Catalysts	Precursors	Synthesis method	Pollutants	TiO_2 dosage	Removal efficiency	Ref
Degussa P-25 powders /UV	-	-	Pharmaceutical propanolol (50 mg/L)	0.4 g/L	94% of PRO removal, 240 min 30% of mineralization, 240 min	De la Crus et al., 2013
TiO_2 powders/UV	$Ti(OC_2H_5)_4$	Hydrolysis + thermal treatment	MB (0.025 mM)	0.5 g/L	98% of MB removal, 30 min	Luis et al., 2011
TiO_2 nanoparticles /UV	TTIP	Vapor condensation	MB (50 mg/L)	1 g/L	~95% of MB removal, 120 min	Le et al., 2012
TiO_2 nanoparticles /UV	$Ti(OBu)_4$	Solvethermal	Phenol (10mg/L); RhB (10 mg/L)	1.5 g/L	85% of phenol removal, 30 min 80% of RhB removal, 30 min	Gao et al., 2014
TiO_2 nanoparticles /UV	TTIP	Thermal decomposition	MB (150 mg/L)	0.16 g/L	80% of MB removal, 120 min	Chin et al., 2012

Table 7 (cont.)

Catalysts	Precursors	Synthesis method	Pollutants	TiO_2 dosage	Removal efficiency	Ref
TiO_2 powders/UV	$TiCl_4$	Hydrolysis + thermal treatment	MB (10 mg/L)	0.5 g/L	~100% of MB removal, 30 min	Arbuj et al., 2010
TiO_2 nanoparticles /UV	TTIP	Sol-gel	Phenol (50 mg/L)	1 g/L	~100% of phenol removal, 4h ~83% of TOC removal, 4h	Silva and Faria, 2009
Degussa P-25 powders /UV	-	-	Phenol (50 mg/L)	0.5 g/L	~100% of phenol removal, 5h	Zainudin et al., 2010
TiO_2 powders/UV	TTIP	Sol-gel	Phenol (50 mg/L)	1 g/L	~85% of phenol removal, 25h	Khraisheh et al., 2012
Degussa P-25 powders /UV	-	-	4-chlorophenol (10^{-4} M)	0.25 g/L	~80% of 4-chlorophenol removal, 120 min	Naeem and Ouyang, 2013
TiO_2 powders /solar	-	Sol-gel	Malathion pesticide (12 mg/L)	1 g/L	100% of malathion removal, 180 min	Ramos-Delgado et al., 2013

4. Drawbacks of titanium dioxide and alternative technologies

As presented in Section 3.2, photocatalytic pathways of titanium dioxide include the reactions of electrons and holes with redox agents to generate the active radicals, and the recombination of electrons and holes. The generation of active radicals is the key mechanism to mineralize organic pollutants present in the solution while the recombination of electrons and holes acts as a competitive pathway to reduce the number of electrons and holes that can participate in the active radical generation process. Thus, in order to enhance the photocatalytic activity of titanium dioxide, recombination rate should be limited, which can be achieved by using nanosized titanium dioxide particles. According to Chong, et al. (2010), the nanosized titanium dioxide particles have a large specific surface area which can enhance the electrons-holes separation, photon adsorption, and photocatalytic activity as a result. However, one of the biggest drawbacks of nanosized titanium dioxide is the particles separation. After treatment, titanium dioxide particles need to be separated from the fluid with the aim of reuse as well as prevention of catalyst loss into the environment as a contaminant. The applicable separation processes consist of sedimentation with coagulation, cross-flow filtration, and membrane filtration show difficulties. Nevertheless, due to the nanosized of separated particles, the separation efficiency of these processes is not quite high. In addition, problems relating to the use of membrane filtration for separation such as pore size and blockage, regeneration and fouling are another barrier to large scale application of nanosized titanium dioxide.

Recently, many investigations are focused on the immobilization of titanium dioxide on a micron adsorbent in order to improve the efficiency of particle separation (Kanakaraju, et al., 2015). In addition to enhance the separation process by increasing the overall particle (titanium dioxide and adsorbent) size, the use of adsorbents as immobilizers also promote the efficiency of pollutant removal by the combination of adsorption by adsorbents and photo-oxidation by titanium dioxide (Liu, et al., 2014). Some examples of adsorbents used as immobilizers (Table 8) are activated carbons, zeolite, silica and clays (Chong, et al., 2010; Liu, et al., 2014).

Table 8 Some examples of TiO_2 immobilized on an adsorbent

Pollutants	Catalysts	Adsorbent precursors	Synthesis method	Removal efficiency	Ref.
Methylene Blue (MB)	TiO_2/AC powders	Coconut shells	Vapor condensation	100% of MB removal, 60 min	Le et al., 2012
Humic acid (HA)	TiO_2/commercial AC	-	Self-assembly	98% of HA removal, 250 min	Liu et al., 2014
Amoxicillin	TiO_2/natural zeolite	-	Sol-gel	100% of amoxicillin removal, 240 min	Kanakaraju et al., 2015
Methyl orange (MO)	TiO_2/commercial AC	Coal	Sol-gel	88% of MO removal, 3 min microwave	Zhang et al., 2012
Acid Red (AR) 88	TiO_2/AC	-	Sol-gel	>90% of AR removal, 180 min	Gao et al., 2011
RhB dye	TiO_2/AC	Pine sawdust	Reflux	~100% of RhB removal, 120 min	Asilturk and Sener, 2012

Table 9Applications of adsorbents from biomass in wastewater treatment

Pollutants	Adsorbents	Precursors	Synthesis method	Adsorption capacity/ Removal efficiency	Ref.
Methylene Blue	Activated carbons	Coconut shell	-	80% of MB removal, 120 min	Le et al., 2012
-	Mesoporous silica	Sedge weed	Leaching and refluxing treatment followed by combustion	-	Ghorbani et al., 2013
Phenol	Activated carbons	Pokeweed plants	Chemical activation	172 mg/g	Chen et al., 2012
Fluoride	Sawdust	Sawdust	Formaldehyde treatment	50% of fluoride removal, 60 min	Yadav et al., 2013
Fluoride	Wheat straw	Wheat straw	Formaldehyde treatment	50% of fluoride removal, 60 min	Yadav et al., 2013
Hexavalent Chromium	Carbonaceous adsorbents	Sunflower heads Sunflower stems	Sulfuric acid treatment and carbonization at 150°C	75.7% of Cr^{6+} removal, 2h (heads) 85.4% of Cr^{6+} removal, 2h (stems)	Jain et al., 2010

Table 9 (cont.)

Pollutants	Adsorbents	Precursors	Synthesis method	Adsorption capacity/ Removal efficiency	Ref.
Methylene Blue	Activated carbons	Bamboo chips	Steam activation	250 mg/g	Zhang et al., 2014
2,4,6-trichlorophenols	Activated carbons	Coconut husk	KOH activation	716 mg/g	Hameed et al., 2008
Pb^{2+}	Zeolite	Rice husk ash	-	85% of Pb^{2+} removal, 24 h	Ali et al., 2011

Potential adsorbent derived from vetiver grass

1. Adsorbents from agriculture wastes and their application in wastewater treatment

Along with the common adsorbents used in wastewater treatment typically activated carbon, low-cost adsorbents derived from agricultural wastes are gaining several interests (Jain, et al., 2010; Chen, et al., 2012; Ghorbani, et al., 2013; Yadav, et al., 2013). Adsorbents synthesis from agricultural wastes takes advantage not only in term of cost effectiveness due to inexpensive and readily available precursors but also in term of agricultural waste disposal in a more useful way (Le, et al., 2012; Zhang, et al., 2014). Various types of agricultural wastes including coconut shells, wheat straw, rice husk, bamboo chips, sedge weed, pokeweed plants, and sugarcane bagasse have been used to produce adsorbents which are then applied to wastewater treatment. Some examples of adsorbents derived from agricultural wastes and their applications in wastewater treatment are presented in Table 9. In addition, absorbents derived from agricultural wastes have been applied as a precursor to synthesize hybrid TiO_2 catalyst as shown in Table 8. These hybrid catalyst has provided the promising efficiency of organic pollutant removal. In the next Section 4.2, a kind of agricultural waste that has potential to be used as precursor for adsorbent synthesis is introduced.

2 Vetiver grass

Vetiver grass is a tropical plant which has tall stems, thin and quite rigid leaves, and long and massive roots system. Vetiver grass is a fast growing plant through tiller and usually appears in a dense clump with the height up to 2 meters (Ye, et al., 2014). The origin of vetiver grass is India. However, it can be found in at least 70 countries around the world throughout tropical subtropical regions including Haiti, Indonesia, India, Brazil, China, La Réunion, Vietnam, El Salvador, Madagascar, Nepal, and Thailand (Paillat, 2012; Filippi, et al., 2013). **Vetiveria zizanioides L. Nash and Vetiveria nemoralis A. Camus** are the commonly found species of vetiver grass in Thailand (Methacanon, et al., 2003). Due to the massive and complex root system that can be up to 3 meters (Makris, et al., 2007), vetiver grass is planted as an alternative of erosion control in many countries (Danh, et al, 2010; Oshunsanya, 2013). In addition, **Vetiveria zizanioides L. Nash species** is widely cultivated in order to extract oil from its roots. The fragrant and volatile oil extracted from

Vetiveria zizanioides L. Nash has a wide range of commercial applications such as perfumery, cosmetics, soap, other fragrant materials production (Methacanon, et al., 2003; Lal, et al., 2013). Vetiver oil also applied in pharmaceutical industry due to the antifungal, antibacterial, anticancer, anti-inflammatory and antioxidant activities (Singh, et al., 2014 and Yaseen, et al., 2014). As estimate, the annual global production of vetiver oil is approximately 300–350 tonnes while the consumption and demand of vetiver oil is supposed to continue increasing (Lal, et al., 2013).

In term of environmental treatment, vetiver grass has been introduced as an inexpensive phytoremediation alternative. Many studies have reported the ability of vetiver grass to accumulate persistent organic pollutants (POPs) (Ye, et al., 2014), polycyclic aromatic hydrocarbons (PAHs) (Makris, et al., 2007), phenol (Ho, et al., 2013), and a variety of heavy metals, including manganese (Mn), iron (Fe), zinc (Zn), copper (Cu), arsenic (As), chromium (Cr), lead (Pb), cadmium (Cd) from contaminated soil and water (Singh, et al., 2014; Zhang, et al., 2014).

In general, vetiver grass is applicable in environmental treatment and highly demanded for industrial applications. However, it has to be noted that only the roots of vetiver grass are in demand while there is no point of use of the leaves. Only considering one application of vetiver grass that is oil extraction, the oil yield is estimated around 1%wt. of the raw vetiver roots while the annual production of vetiver oil is about 300–350 tonnes (Lal, et al., 2013). This means approximately 300 thousand tonnes of vetiver roots is globally demanded for oil extraction every year. Although the leaves of vetiver grass are sometimes used for thatching, mulch, cattle feeding, handicrafts and composting (Lal, et al., 2013; Yaseen, et al., 2014), a huge amount of vetiver leaves are still free at the point of use and are discarded as agriculture wastes or burned in the field (Methacanon, et al., 2003). Thus, regarding vetiver leaves as a biomass source rather than a waste, vetiver leaves are a potential precursor to synthesize adsorbents to be applied in wastewater treatment.

3 Adsorption mechanism

According to Metcalf and Eddy Inc. (2004), adsorption is a mass transfer process in which a substance present in aqueous phase or gas phase (adsorbate) is transferred to solid phase (adsorbent). The forces to keep the adsorbate attached on the adsorbent can be Coulombic-unlike charges, point charge and a dipole, dipole-

dipole interactions, point charge neutral species, Van der Waals forces, covalent bonding with reaction, and hydrogen bonding. Adsorption can occur on the surface and in the pores of the adsorbent, following four more or less steps:

3.1 Bulk

Bulk solution transport involves the advection and dispersion of adsorbate molecules to the boundary layer of the liquid surrounding the adsorbent.

3.2 Film

Film diffusion transport involves the diffusion of adsorbate molecules to the entrance of the adsorbent pores.

3.3 Pore

Pore transport involves the molecular diffusion of adsorbate molecules through the pores.

3.4 Adsorption

Adsorption involves the attachment of adsorbate molecules to adsorbent at adsorption sites.

Adsorbate molecules absorb on the surface of adsorbent until the rate of the forward reaction (adsorption) and the reverse reaction (desorption) is equal (equilibrium). At equilibrium, no more adsorbate molecules are absorbed. In order to determine the amount of adsorbate adsorbed on an adsorbent, a certain amount of adsorbate is exposed to varying amounts of adsorbent until the adsorption equilibrium is reached. After that, the remaining concentration of adsorbate is measured. The amount of adsorbate adsorbed on the adsorbent is calculated as follows:

$$q_e = \frac{(C_o-C_e)V}{m}$$

In which, q_e is the mass of adsorbate adsorbed on adsorbent at equilibrium (mg/g) C_0 is the initial concentration of adsorbate (mg/L) Ce is the concentration of adsorbate in solution at equilibrium (mg/L) V is the volume of liquid in the reactor (L) and m is the mass of adsorbent (g)

CHAPTER III

RESEARCH METHODOLOGY

The experiment includes following parts:

1. Synthesis of adsorbent involves the use of vetiver leaves as a precursor.
2. Synthesis of TiO_2-vetiver catalyst involves the immobilization of TiO_2 on vetiver adsorbent.
3. Characterization of synthesized materials involves the physical and chemical properties of the vetiver adsorbent and the TiO_2-vetiver catalyst using various analytical methods.
4. Methylene blue (MB) removal test involves the use of MB as a contaminant to test the adsorption capacity and photocatalytic activity of the synthesized vetiver adsorbent and the TiO_2-vetiver catalyst, respectively.

Materials

1. Vetiver grass

As presented in Section 4.3, vetiver grass is a tropical plant that is commonly found in Thailand. It has a long stem that can be up to 2 meters in height. Vetiver grass is monthly collected in the field in Phitsanulok province, Thailand. Only the leaves of vetiver grass are used for the synthesis of adsorbent while the roots are removed. The chemical composition of fresh vetiver grass is presented in Table 10.

2. Methylene blue (MB)

Commercial methylene blue (MB) powder is used as a contaminant to be removed in the experiment. MB is a dye compound of which the molecular formula and molecular weight is $C_{16}H_{18}ClN_3S$ and 319.85 g/mol, respectively. The stock MB solution of 100 ppm was prepared by dissolving 0.1 g of MB powder in DI water and diluting to 1000 mL. Standard MB solutions with different concentrations are prepared by diluting stock MB solution with DI water.

Table 10 Chemical composition of fresh vetiver grass

Chemical composition	Percentage (%wt.)
Potassium (K)	50
Silica (Si)	24.4
Calcium (Ca)	11.5
Phosphorus (P)	6.4
Sulfur (S)	4.6
Iron (Fe)	1.6
Aluminum (Al)	1.5

Synthesis of vetiver adsorbent and TiO_2-vetiver catalyst

The procedure to synthesize the vetiver adsorbent, which is briefly summarized in Figure 1, involves the following steps:

1. Vetiver grass was collected from the field in Phitsanulok Province, Thailand.
2. Only the leaves of vetiver grass were used to synthesize adsorbent. After other parts of the grass were removed, vetiver leaves were rinsed with tap water and then cut into small pieces.
3. Pieces of vetiver leaves were dried in an air oven at 105°C for 12 h in order to remove moisture content.
4. The dried vetiver leaves were ground and sieved in order to obtain the fraction of the dried vetiver leaves with a particle size ranging from 0.1 to 0.6 mm
5. The dried vetiver leaves with the particle size of 0.1 to 0.6 mm were calcined in a muffle furnace in ambient condition at 600°C for 3 h in order to remove carbon content.
6. After calcination, the calcined vetiver leaves which were called vetiver adsorbent (VG) were naturally cooled and then stored for use.

The procedure to synthesize the TiO_2-vetiver catalyst by sol-gel method (Rajamanickam and Shanthi, 2014), which is briefly summarized in Figure 1, involves the following steps:

1. 0.540 g of calcined vetiver adsorbent was added to the mixture of 12.5 mL of titanium isopropoxide (TTIP), 80 mL of 2-propanol and 3 mL of deionized (DI) water under magnetic stirring for 4 h.
2. The resulting suspension was filtered, washed with DI water and dried in an air oven at 105°C for 12 h in order to remove moisture content.
3. The dried sample was calcined in a muffle furnace in ambient condition at 450°C for 5 h in order to form crystalline structure of TiO_2.
4. After calcination, the obtained TiO_2-vetiver catalyst were naturally cooled and then stored for use.
5. Pure TiO_2 was prepared by a similar procedure without the addition of calcined vetiver adsorbent.

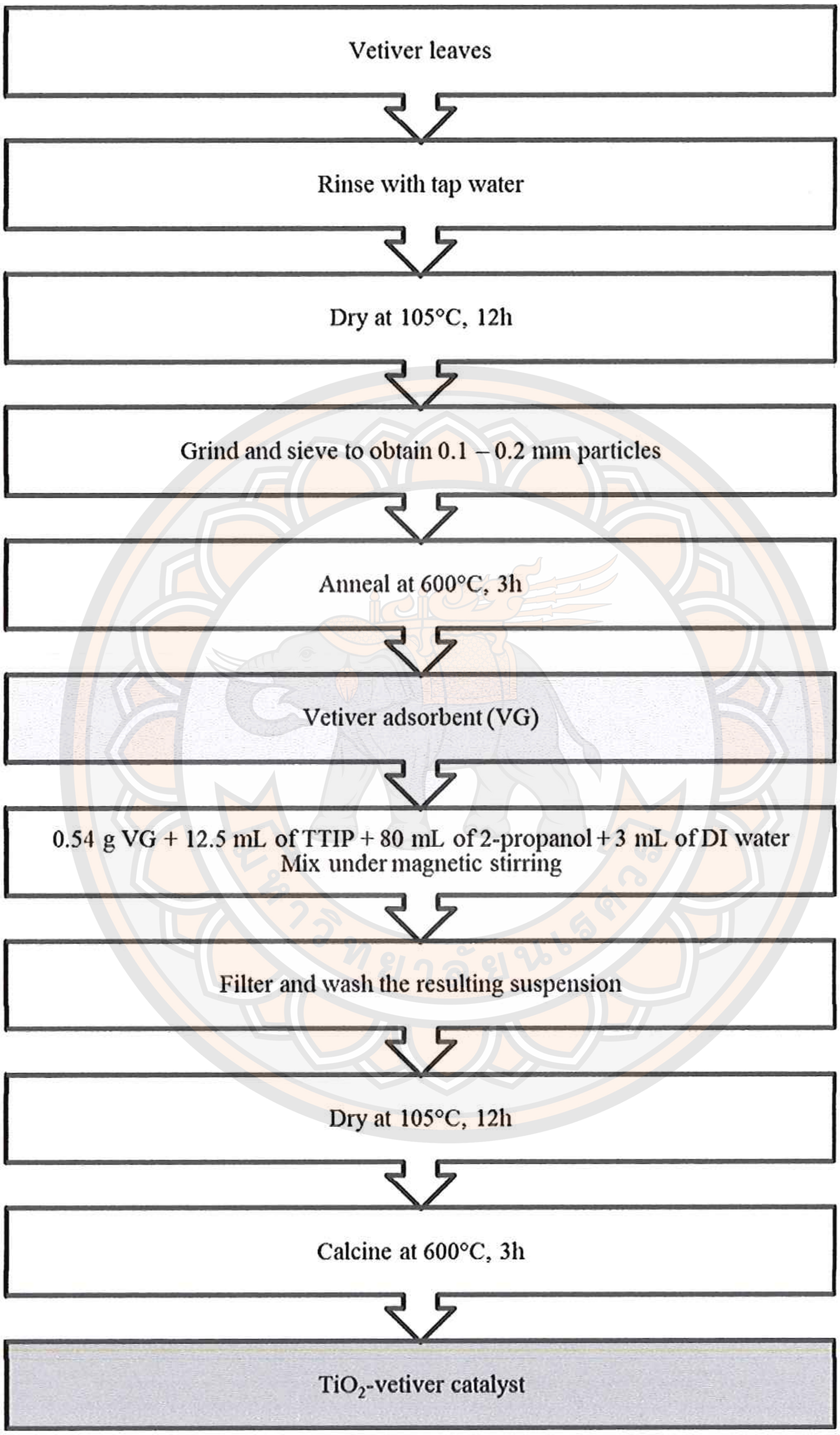

Figure 1 Procedure to synthesize vetiver adsorbent and TiO_2-vetiver catalyst

Characterization

The techniques that were used for characterization of the synthesized vetiver adsorbent and TiO_2-vetiver catalyst are presented in Table 11.

Table 11 Characterization of synthesized materials

Characterization techniques	**Application**
X-Ray Fluorescence (XRF)	Elemental composition
X-ray Diffraction (XRD)	Crystalline structure
Brunauer–Emmett–Teller (BET)	Specific surface area and pore size distribution
Transmission Electron Microscopy (TEM)	Surface morphology, crystallinity
UV-Vis Diffuse Reflection Spectroscopy (DRS)	Band gap energy
Photoluminescene (PL)	Photo-excitation and relaxation characteristics

Methylene blue (MB) removal batch test

Batch experiment was conducted using MB as a contaminant to be removed to evaluate the MB removal efficiency of the synthesized vetiver adsorbent and TiO_2-vetiver catalyst. The MB removal efficiency of synthesized vetiver adsorbent was evaluated by MB adsorption test. In the meantime, MB removal efficiency of TiO_2-vetiver catalyst achieved by adsorption-photocatalysis bi-mechanism was evaluated by photodegradation experiment. The photodegradation experiment was conducted in a black box that comprised two 20W UV-A lamps (370 nm) and a magnetic stirrer. The experiment involves the investigation into the effect of TiO_2-vetiver catalyst, the effect of UV-A irradiation, and the effect of pure TiO_2 on the MB removal efficiency over the reaction time.

1. Adsorption of vetiver adsorbent

The procedure to evaluate the adsorption ability and reusable possibility of vetiver adsorbent involves following steps:

1.1 A MB solution with the concentration of 10^{-5} M was prepared by DI water.

1.2 50 mL of prepared MB solution was placed in a 200 mL beaker with the addition of an appropriate amount of vetiver adsorbent (0.4 g/L to 4 g/L).

1.3 The mixture was mixed by a magnetic stirrer in ambient condition for 10 min.

1.4 After that, vetiver adsorbent was filtered using filter paper with the pore size of 0.45 μm.

1.5 The concentration of MB filtrate was measured using UV-Vis spectroscopy. Meanwhile, vetiver adsorbent was washed with DI water in ultrasonic bath for 30 min and then reused to evaluate the reusable possibility of the adsorbent.

1.6 The same procedure was applied to a kind of commercial granular activated carbon (AC).

2. Adsorption-Photocatalysis of TiO_2-vetiver catalyst

The procedure to evaluate the photocatalytic activity of TiO_2-vetiver catalyst to remove MB involves following steps:

2.1 A MB solution with the concentration of 10^{-5} M was prepared by DI water.

2.2 50 mL of prepared MB solution was placed in a 200 mL beaker with the addition of 0.2 g/L of TiO_2-vetiver catalyst.

2.3 The mixture was mixed by a magnetic stirrer in dark for 12 hours, followed by UV-A irradiation for 4 hours.

2.4 At each specific time interval (1 hour), MB sample was collected, in which TiO_2-vetiver catalyst was filtered using filter paper with the pore size of 0.45 μm.

2.5 The concentration of MB filtrate is measured using UV-Vis spectroscopy.

2.6 To identify the MB removal efficiency of photocatalysis, the TiO_2-vetiver catalyst was replaced with the synthesized pure TiO_2.

2.7 To identify the MB removal efficiency of UV-A irradiation, neither TiO_2-vetiver catalyst nor pure TiO_2 was added into the MB solution.

Analytical method

The MB removal efficiency was evaluated using UV-Vis spectroscopy data. The concentrations of MB were determined by UV-Vis spectroscopy method (Potgieter and Strydom, 1999; Ramasamy and Anandalakshmi, 2008). In this work, the absorption wavelength of MB was investigated to determine the maximum absorbance. The correlation of MB concentration and absorbance at the peak wavelength was obtained by plotting a calibration curve. The concentrations of MB samples derived from MB removal experiment were interpolated from the calibration curve. The percentage of MB removal was calculated from the difference of MB concentrations as follows:

$$\text{MB removal efficiency (\%)} = \frac{C_0 - C_t}{C_0} \times 100\%$$

In which, C_0 is the initial MB concentration (mg/L) and C_t is the MB concentration at time t (mg/L)

CHAPTER IV

RESULTS AND DISCUSSION

Vetiver adsorbent

1. Characterization

Chemical composition and crystalline structure of the synthesized vetiver adsorbent determined by XRF and XRD techniques are shown in Table 12 and Figure 2, respectively. The XRF results show that the main chemical composition of vetiver adsorbent is potassium (K) with 45%. Other compositions are 27% of silicon (Si), 11% of phosphorus (P) and small amount of other elements including calcium (Ca), magnesium (Mg), sulphur (S) and chlorine (Cl). In addition, according to XRD data, the crystalline structure of vetiver adsorbent could be potassium sulfate (K_2SO_4), silicon dioxide (SiO_2), and calcium phosphate (CaP) according to JCPDS no. 00-005-0613, 01-082-0512 and 00-016-0728, respectively. These data confirm that the main composition of vetiver adsorbent is potassium (K). The same observation was reported in other investigation (Methacanon, et al., 2003).

Table 12 Chemical composition of vetiver adsorbent

Tested Items	Tested Results	Unit
K	44.9	% w/w
Si	27.2	% w/w
P	10.7	% w/w
Ca	7.8	% w/w
S	3.7	% w/w
Mg	2.3	% w/w
Cl	2.1	% w/w
Fe	0.8	% w/w
Mn	0.5	% w/w

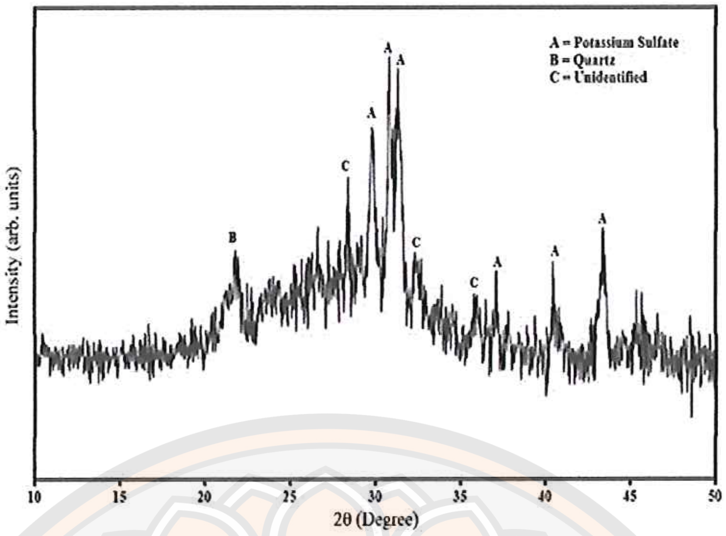

Figure 2 XRD pattern of vetiver adsorbent

Figure 3 shows the SEM images of surface morphology of the vetiver adsorbent before calcination (dried vetiver) and after calcination (calcined vetiver adsorbent). The images present that calcined vetiver adsorbent is in form of porous and fine particles. Before calcination process, the vetiver leaves are solid particle with 0.1-0.2 mm of size. However, after calcination at 600°C, the particles change to be fine particles with a size less than 1 micron. It can be said that calcination process can be used to synthesis fine particles with high porosity and surface area.

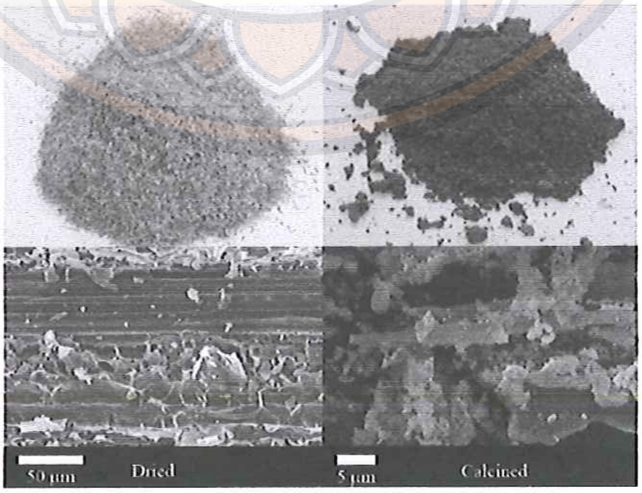

Figure 3 SEM image of vetiver adsorbent

1.1 Methylene blue (MB) removal test

Figure 4 shows the MB removal efficiency of various amounts of vetiver adsorbent. The results illustrate that the MB removal efficiency increased dramatically from 66% to 98% with the increase of vetiver adsorbent loading from 0.2 g/L to 4 g/L. It can be seen that 95% of MB solution was removed by an optimum vetiver adsorbent concentration of 3 g/L after 10 min. In addition, MB removal efficiency of vetiver adsorbent and commercial activated carbon (AC) in three cycles of reuse is presented in Figure 5. It can be seen that the vetiver adsorbent provided the higher MB removal efficiency, particularly 97%, than commercial activated carbons which can remove only 46% of MB. When reusing the vetiver adsorbent for three times, there was only a minor change in the range of 97% to 95% in term of MB removal efficiency while the efficiency of commercial activated carbons significantly dropped from 46% to 29%. These results suggest that the vetiver adsorbent was reusable.

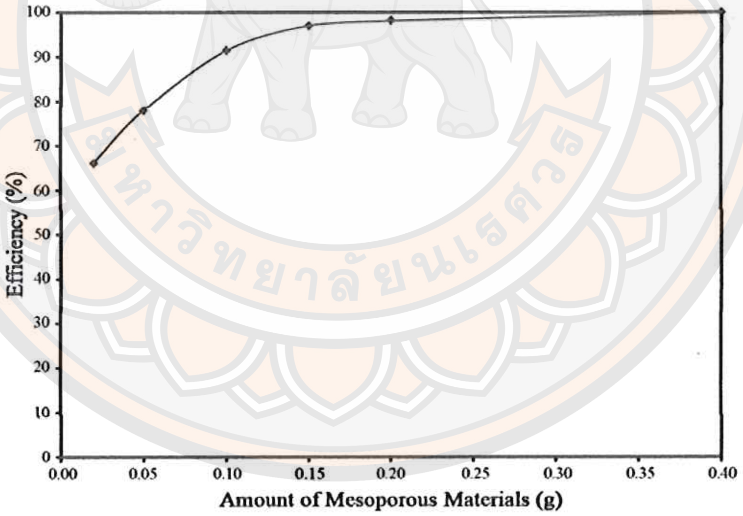

Figure 4 MB removal efficiency of various vetiver adsorbent amounts

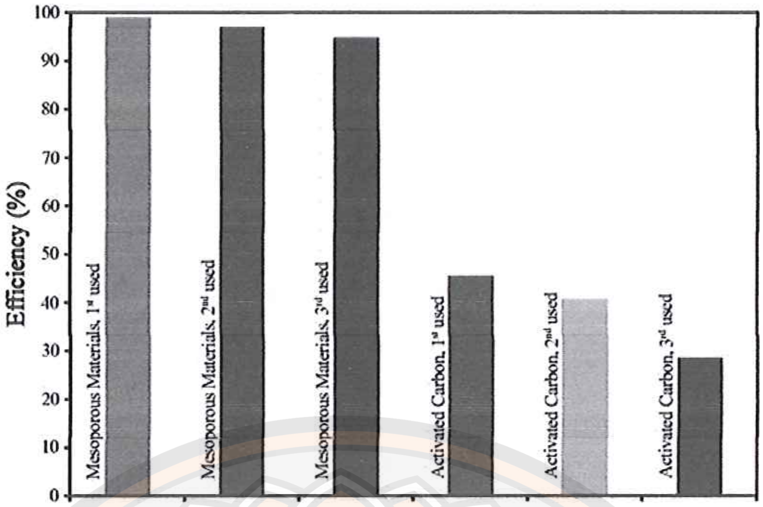

Figure 5 MB removal efficiency of vetiver adsorbent and commercial activated carbon (AC) in three reuse cycles

TiO_2-vetiver catalyst

1. Characterization

Figure 6 shows the XRD patterns of the synthesized TiO_2-vetiver catalyst and pure TiO_2. The sharp peaks at 2θ of 25.2°, 37.6°, 48.0°, 54.9°, 62.6°, 70.3°, and 75.0° present the anatase phase of TiO_2. The peaks observed in XRD pattern of TiO_2-vetiver catalyst confirmed the presence of crystalline phase of TiO_2 in the structure. In addition, the lower peak intensity of TiO_2-vetiver catalyst compared to pure TiO_2 revealed the presence of vetiver adsorbent. The addition of vetiver adsorbent decreased the crystallinity of the catalyst because vetiver adsorbent consists of silicon (Si) element as reported above, which is known as a grain growth inhibitor (Lin, et al., 2013).

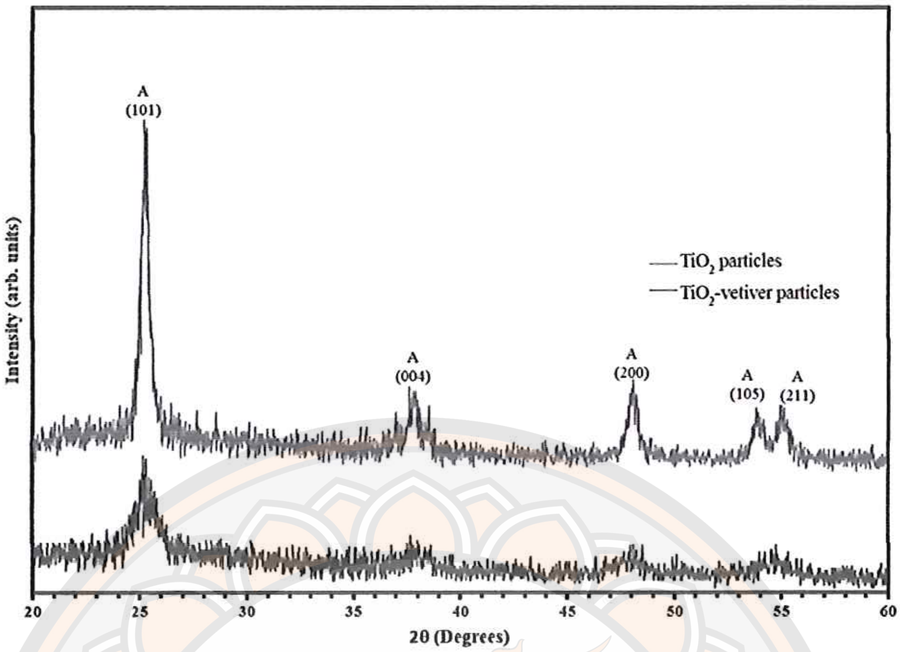

Figure 6 XRD patterns of pure TiO_2, and TiO_2-vetiver catalyst

The band gap of the synthesized particles was calculated from DRS data using Kubelka-Munk equation and presented in Figure 7. The TiO_2-vetiver catalyst and pure TiO_2 was found to have the band gap of 3.66 eV and 3.58 eV, respectively. The band gap of pure TiO_2 was a little higher than common value (3.2 eV). However, the band gap of anatase TiO_2 in the range of 3.20–3.56 eV is not uncommon (Nakaruk, et al., 2010). The high band gap of the TiO_2-vetiver catalyst is due to the silicon contamination. One of the main composition of vetiver adsorbent is silicon (27%w/w) (Le, et al., 2015). Therefore, during the calcination process, silicon can diffuse into TiO_2 lattice causing lattice expansion. The effect of silicon contamination to the band gap increase was reported in other studies (Nakaruk, et al., 2010, 2012).

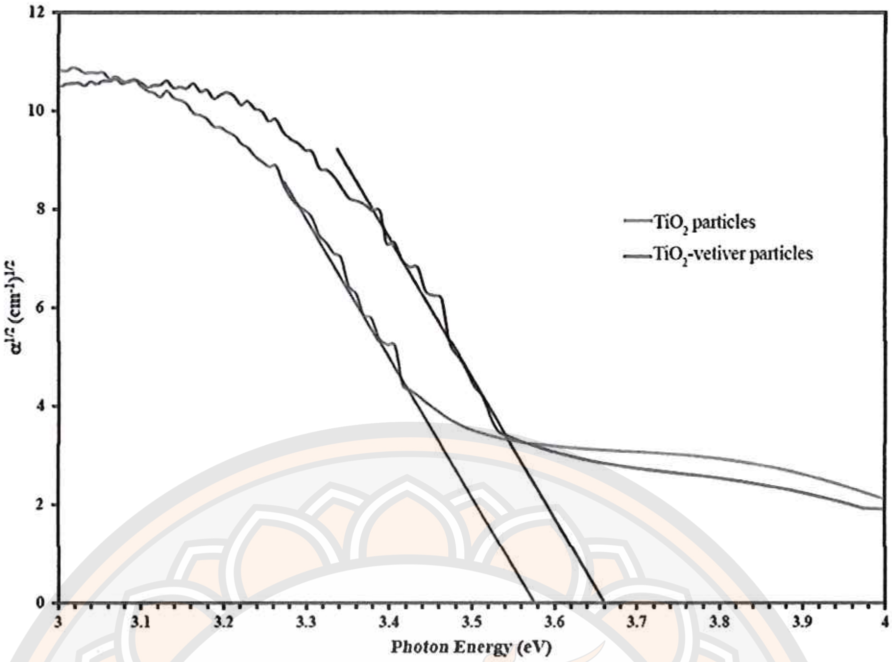

Figure 7 Optical band gaps calculated from DRS data of pure TiO_2, and TiO_2-vetiver catalyst

Figure 8 shows photoluminescence (PL) spectra of synthesized TiO_2-vetiver catalyst and pure TiO_2. The PL emission occurs with the recombination of the photogenerated electrons and holes (Yu, et al., 2003). It can be seen that PL intensity of TiO_2-vetiver catalyst was less than that of pure TiO_2. This decrease of PL intensity suggested that the addition of vetiver adsorbent enhance the transfer and separation of photogenerated electrons and holes (Zhang, et al., 2011; Tian, et al., 2015). The suppression of charge carrier recombination leads to the increase of probability for electrons and holes to react with target molecules (such as water and oxygen), generate hydroxyl radicals, and raise the photocatalytic activity (Rajamanickam and Shanthi, 2014; Tian, et al., 2015).

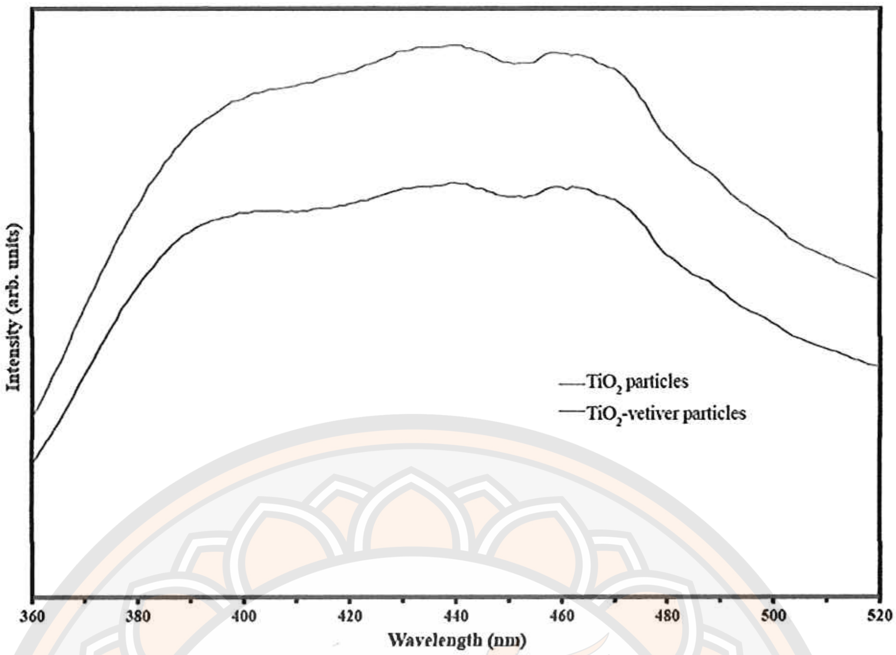

Figure 8 Photoluminescence (PL) spectra of pure TiO_2 and TiO_2-vetiver catalyst.

Figure 9 shows the TEM images of synthesized TiO_2-vetiver catalyst and pure TiO_2. The pure TiO_2 contained the spherical shape with particle size of approximately 20 nm (Figure 9a), while the size of TiO_2-vetiver catalyst was various depending on the vetiver substrate (Figure 9b). In addition, the TiO_2-vetiver catalyst showed the core-shell structure, in which the vetiver acted as a core and was coated by TiO_2 shell.

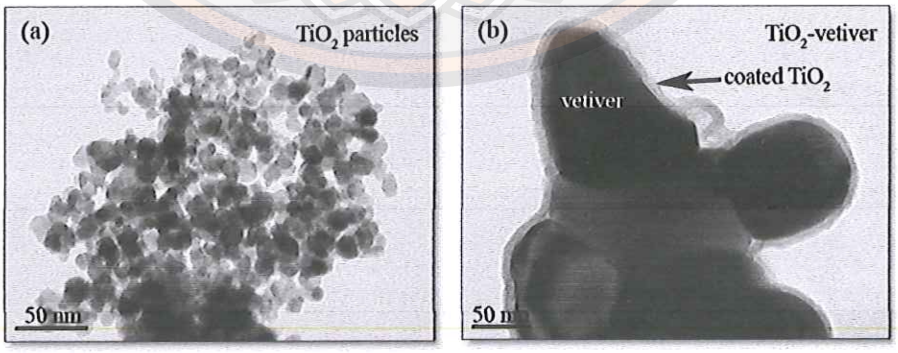

Figure 9 TEM images of pure TiO_2 and TiO_2-vetiver catalyst.

The specific surface area and total pore volume of TiO_2-vetiver catalyst was analyzed using BET, and the results are present in Table 13. The specific surface area and pore volume of the TiO_2-vetiver catalyst were higher than that of the pure TiO_2. This is because there was little agglomeration affecting to the TiO_2-vetiver catalyst. In the calcination process, the TiO_2 particle was agglomerated easily, leading to the decreasing specific surface area and pore volume. However, in the presence of vetiver adsorbent, the vetiver adsorbent acted as a carrier for TiO_2 attachment and avoid the agglomeration of TiO_2.

Table 13 Surface properties of TiO_2-vetiver catalyst and pure TiO_2

Samples	Specific surface area (m^2/g)	Total pore volume (cm^3/g)
Pure TiO_2	40.06	0.1252
TiO_2-vetiver	86.66	0.3065

1. Methylene blue (MB) removal test

Figure 10 illustrates the methylene blue (MB) removal of TiO_2-vetiver catalyst and the pure TiO_2. It has to be noted that during 12 hours of adsorption in dark, the TiO_2-vetiver catalyst showed the better ability of MB adsorption in accordance with its high specific surface area and total pore volume. Under the UV-A irradiation, MB was removed rapidly during 4 hours by both TiO_2-vetiver catalyst and pure TiO_2. The changes of UV-Vis spectra and wavelength peaks of MB at different intervals (see in Figure 11) insist on the generation of by-products during UV-A irradiation. Furthermore, the noticeable point is that in the first hour of UV-A irradiation, the MB concentration was reduced sharply when the TiO_2-vetiver catalyst was used. This observation can be explained by the photocatalytic mechanism of TiO_2-vetiver catalyst. As above discussion, the pure TiO_2 structure presented the individually spherical-like particle. After complete adsorption in dark, the TiO_2 surface was fully covered by MB. This reduced the transmission of UV-A light to the TiO_2 and the generation of oxidizing radical from photocatalysis. On the other hand, in case of TiO_2-vetiver catalyst, the TiO_2 was attached together with MB on the vetiver surface. Therefore, the TiO_2 can generate the oxidizing radical and oxidized the MB effectively. The mechanism of MB degradation by TiO_2-vetiver catalyst and pure TiO_2 is illustrated in Figure 12.

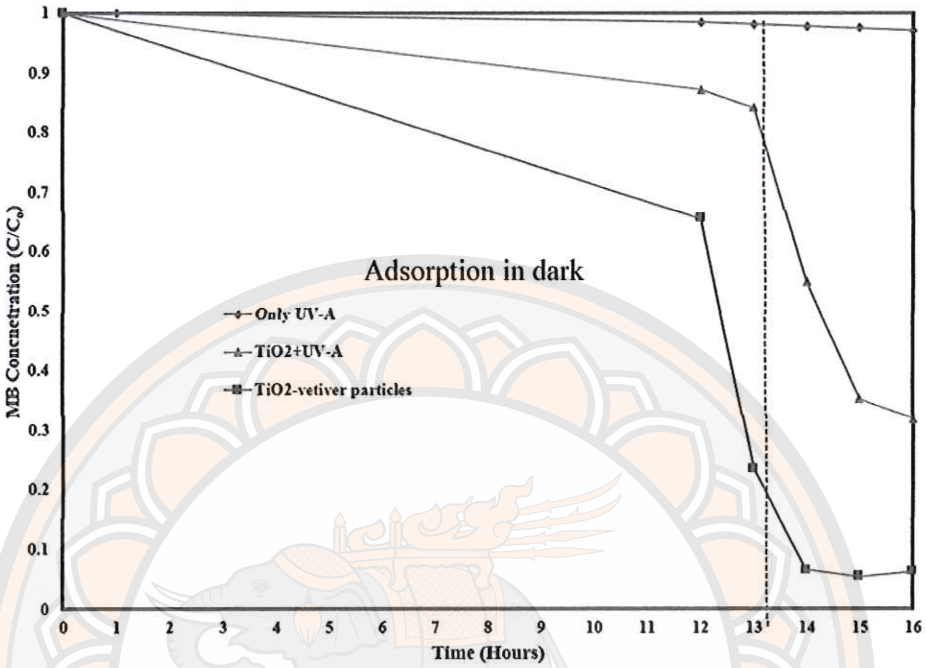

Figure 10 Photocatalytic activity of pure TiO_2 and TiO_2-vetiver catalyst

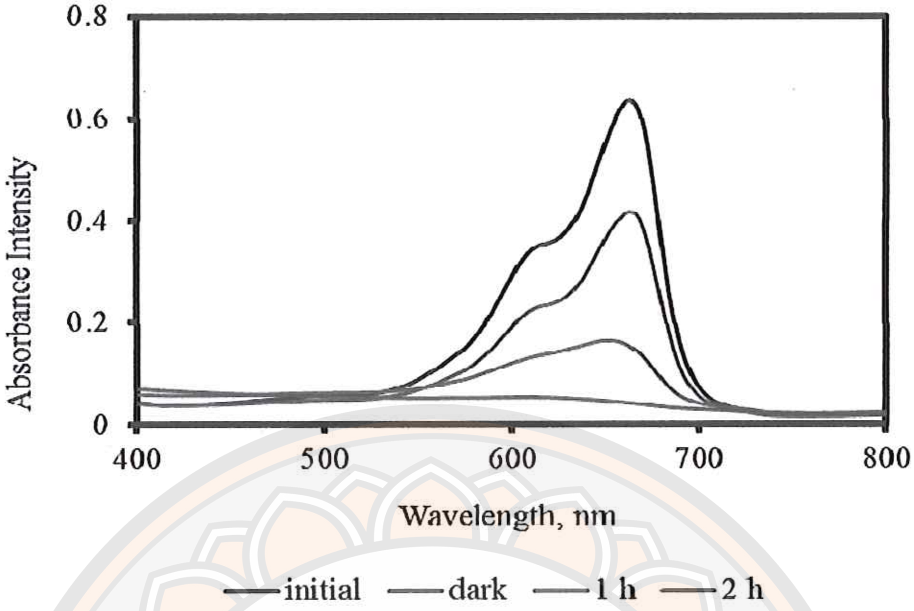

Figure 11 UV–vis spectra of MB in the presence TiO_2-vetiver catalyst: initial MB solution, 12 hour of dark adsorption, 1 hour of UV-A irradiation, and 2 hour of UV-A irradiation

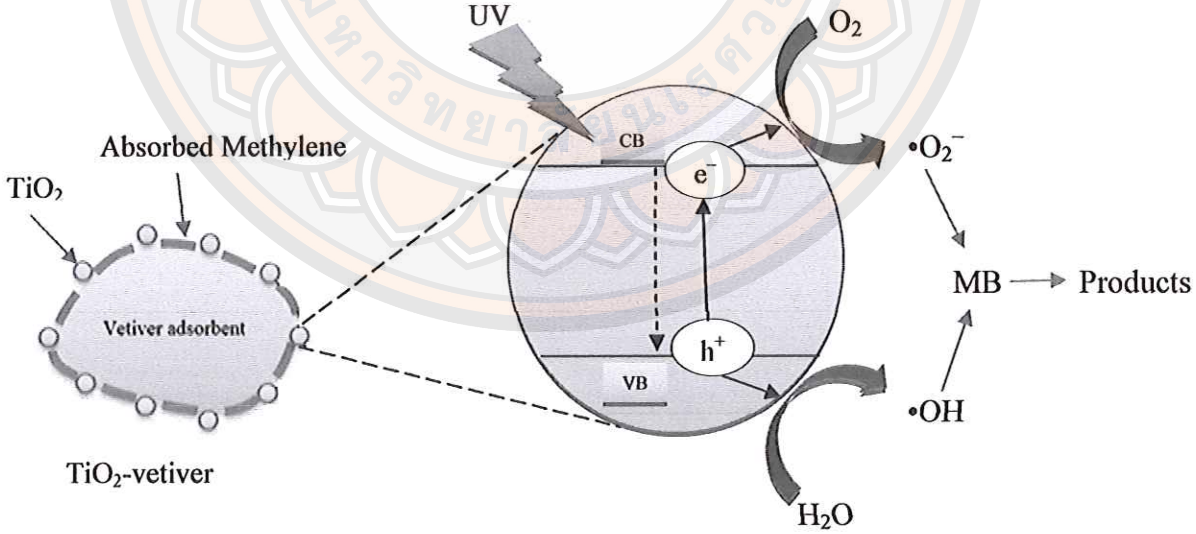

Figure 12 Mechanism of Methylene Blue (MB) degradation by TiO_2-vetiver catalyst

CHAPTER V

CONCLUSION AND RECOMMENDATION

Conclusion

In this work, vetiver adsorbent was successfully synthesized by calcining the leaves of vetiver grass at 600°C. The physico-chemical characteristics of the vetiver adsorbent was investigated using X-Ray Fluorescence (XRF) and X-ray Diffraction (XRD) while the adsorption ability was tested using Methylene blue (MB) adsorption test. The XRF data indicates that main chemical compositions of vetiver adsorbent were potassium (K), phosphorus (P), and silicon (Si). In addition, vetiver adsorbent was found to be able to adsorb MB with the efficiency of 95% at a loading of 3 g/L. Moreover, the vetiver adsorbent was also proven to be reusable.

Furthermore, vetiver adsorbent was used to synthesize TiO_2-vetiver catalyst by sol-gel method. The physico-chemical characteristics of the synthesized catalyst was examined using X-ray Diffraction (XRD), Brunauer–Emmett–Teller (BET) method, Transmission Electron Microscopy (TEM), UV-Vis Diffuse Reflection Spectroscopy (DRS), and Photoluminescence (PL) spectra. Besides, methylene blue (MB) photo-degradation test was conducted to examine photocatalytic activity of the catalyst. The characterization results reveal that TiO_2-vetiver catalyst contained the anatase crystalline structure of TiO_2. Moreover, TiO_2-vetiver catalyst is found to have higher specific surface area and pore volume, and lower electron-hole recombination than pure TiO_2. In addition, MB degradation test indicates that TiO_2-vetiver catalyst showed higher adsorption and photocatalytic activity compared to pure TiO_2. In particular, TiO_2-vetiver catalyst provided the MB removal efficiency of 35% by adsorption, and 59% by photocatalysis. Meanwhile, MB removal efficiency of pure TiO_2 is 13% and 55% by adsorption and photocatalysis, respectively. These results suggest the hybrid mechanism of adsorption and photocatalysis of TiO_2-vetiver catalyst enhanced the MB removal efficiency rather than the single mechanism of pure TiO_2 photocatalysis and pure vetiver adsorption.

Recommendation

In this work, the TiO_2-vetiver catalyst has been proved to be potentially applicable for wastewater treatment, typically MB removal. The MB removal efficiency of TiO_2-vetiver catalyst is relatively comparable to other hybrid TiO_2 materials, as shown in Table 14. The hybrid mechanism of adsorption and photocatalysis is the key to enhance the MB removal efficiency. Therefore, in order to achieve more understanding of the adsorption and photocatalysis mechanism of the TiO_2-vetiver catalyst, more investigations are need to be conducted. Further studies can be included:

1. Physical-chemical characteristics of vetiver adsorbent and TiO_2-vetiver catalyst.
2. The change of TiO_2-vetiver catalyst activity in various synthesis condition, for example, at different ratios of TiO_2 and vetiver adsorbent, temperature, calcination time, etc.
3. The change of TiO_2-vetiver catalyst activity in various reaction condition, for example, pollutant kinds, initial pH, initial pollutant concentration, etc.

Table 14 Comparison between studies of hybrid TiO_2 catalyst

Methylene Blue (MB)	Catalyst	Catalyst loading	MB Removal efficiency	Ref.
10 mg/L	TiO_2-zeolite-4A	0.5 g/L	100% for 100 min	Nagarjuna, et al., 2015
10^{-4} M	TiO_2-ZnFe-LDH	1 g/L	80% for 120 min (pH 6)	Seftel, et al., 2015
10^{-4} M	TiO_2-ZnFe-LDH	1 g/L	60% for 120 min (pH 10)	Seftel, et al., 2015
25 mg/L	RGO-TiO_2-Zeolite-4A	1 g/L	100% for 80 min	Nagarjuna, et al., 2015
25 mg/L	TiO_2/Zeolite-4A	1 g/L	40% for 120 min	Nagarjuna, et al., 2015
30 mg/L	TiO_2/charcoal	0.25 g/L	100% for 90 min	Wu, et al., 2015
10^{-5} M	TiO_2-vetiver	0.2 g/L	94% for 120 min	This, work

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