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DEGRADATION OF ORGANIC COMPOUNDS USING NANOSIZED TITANIA

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จากการศึกษา ไททาเนีย 5 ชนิด ที่มีสมบัติที่แตกต่างกันทั้ง เฟส (M1 เป็นเฟส รูไทด์ ส่วน M2 T1 T1 และ N1 เป็นเฟส อะนาเทส) ขนาดเฉลี่ยของผลึก (M1: 90x45 M2: 11 T1: 26, T2: 6 และ N1: 37 และ140x110 นาโนเมตร) และ พื้นที่ผิวจำเพาะในช่วง 50-250 ตารางเมตรต่อกรัม โดยสมบัติทางกายภาพเหล่านี้ได้รับการวิเคราะห์ใหม่อีกครั้งหนึ่งด้วย เครื่องวัดอิเล็กตรอนแบบส่องผ่าน เครื่องเอกซเรย์ดิฟแฟรกชัน และเครื่องวัดพื้นที่ผิว หลังจากนั้นได้ศึกษาถึงการเสื่อมสลายของสารประกอบอินทรีย์ โดยนำเอาไททาเนียแต่ละชนิดไปกระจายตัวในสารละลายของสารประกอบอินทรีย์ ได้แก่ สารละลายเมทธิลีนบลู แบล็ค 5 และ ลิกนิน ที่มีความเข้มข้น 10 และ 20 มก.ต่อลิตร จากนั้นได้ทำการศึกษาถึงผลการการดูดซับของสารประกอบอินทรีย์เหล่านี้พบว่า ในการดูดซับสารละลายเมทธิลลีนบลู ไททาเนียชนิด M1 มีประสิทธิภาพในการดูดซับที่สูงที่สุดคือ 34.2% แต่ในการแตกสลายเมทธิลลีนบลูโดยทำการฉายแสงด้วยหลอดยูวีขนาด 30 วัตต์จำนวน 2 หลอด พบว่า ไททาเนียชนิด T1 กลับมีประสิทธิภาพในการแตกสลายที่ดีที่สุดคือ 88.1%

ในขณะที่ผลจากการดูดซับแบล็ค 5 ของไททาเนียทั้งหมด ไม่สามารถสังเกตเห็นได้ อย่างไรก็ตามหลังจากการฉายแสงยูวี ไททาเนียชนิด T1 ยังคงมีประสิทธิภาพในการแตกตัวสูงที่สุดคือ 92.5% ซึ่งในการดูดซับลิกนินก็ให้ผลที่ใกล้คล้ายคลึงกันคือ ไม่สามารถสังเกตเห็นผลของการเปลี่ยนแปลงเนื่องจากการดูดซับได้ ในทำนองเดียวกัน ในการแตกตัวลิกนิน ไททาเนียชนิด T1 ยังคงมีประสิทธิภาพในการแตกตัวสูงที่สุดคือ 96.8% ทั้งนี้ในงานวิจัยนี้ได้ทำการศึกษาถึงผลเนื่องจากแสงอาทิตย์ด้วย พบว่า ไททาเนียชนิด T2 ให้ประสิทธิรวมในการกำจัดสารประกอบอินทรีย์สูงขึ้น เนื่องจากค่าสเปกตรัมที่เหมาะสมในแสงอาทิตย์นั่นเอง

ในตอนท้ายของงานวิจัยนี้ ระบบชั้นบางของไททาเนียบนกระดาษกรองได้ถูกนำมาใช้ในการแก้ปัญหาของการสูญเสียไททาเนียในระบบการบำบัดน้ำเสีย แต่อย่างไรก็ตามระบบนี้มีประสิทธิภาพในการแตกตัวแบล็ก5 เพียงแค่ 6% เท่านั้น

ภาควิชา..........วิศวกรรมเคมี.................ลายมือชื่อนิสิต...
สาขาวิชา.........วิศวกรรมเคมี.................ลายมือชื่ออาจารย์ที่ปรึกษา..
ปีการศึกษา.......2547..............................ลายมือชื่ออาจารย์ที่ปรึกษาร่วม..

4670352021 : MAJOR CHEMICAL ENGINEERING
KEY WORD: PHOTOCATALYST / TITANIA / DECOMPOSITION / METHYLENE BLUE / REACTIVE DYE / LIGNIN / WASTE WATER

NAWIN VIRIYA-EMPIKUL : DEGRADATION OF ORGANIC COMPOUNDS USING NANOSIZED TITANIA. THESIS ADVISOR : ASSOC. PROF. TAWATCHAI CHARINPANITKUL, D.Eng., THESIS CO-ADVISOR : PROF. WIWUT TANTHAPANICHAKOON, Ph.D., 93 pp. ISBN 974-53-1252-5.

Five titania with different phases (rutile (M1), anatase (M2, T1, T2, and N1)), average crystallite sizes (M1: 9Øx45, M2: 11, T1: 26, T2: 6, and N1: 37 and 14Øx110 nm) and specific surface areas (50-250 m^2/g) were investigated in this work. To confirm their physical properties reported by manufacturers, TEM, XRD, and BET techniques were used and the obtained results agreed well with the reported values. To examine decomposition performance, each titania was dispersed in three different simulated wastewater contaminating: methylene blue (10, 20 ppm), black 5 (10, 20 ppm), and lignin (10, 20 ppm). Adsorption of each pollutant on the 5 titania was investigated in the absence of illumination. Based on experimental results on methylene blue removal, M1 was found to exhibit the best adsorption efficiency of 34.2%. However, T1 provided the best decomposition efficiency of 88.1% with irradiation by two 30-Watt UV lamps.

As for the wastewater with black 5, none of the titania exhibited any significant adsorption. Nevertheless, with irradiation by UV light, T1 again exhibited the best decomposition efficiency of 92.5%. Similarly, it was found that lignin could not be adsorbed by any of the 5 titania. As expected, T1 could again provide the best lignin removal performance with maximum efficiency of 96.8%. These results could be attributed to the fact that T1 is anatase titania with quite high specific surface area. Sunlight also used for activating the 5 titania. The total removal efficiency obtained by sunlight of T2-titania was higher because sunlight source had the suitable spectrum.

Finally, in order to avoid losing nanosize titania with the treated wastewater, application of titania thin layer depositing on glass microfibre filter (Whatman, GF/A) was employed. However, the efficiency of black 5 decomposition was drastically decreased to only 6%.

Department……Chemical Engineering...Student's signature.................................
Field of study….Chemical Engineering...Advisor's signature.................................
Academic year…2004............................Co-advisor's signature.............................

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NOMENCLATURE

C = Residual concentration at any time (ppm)

Co = Initial concentration (ppm)

$C_{b,NI}$ = the average residual concentration of the colorant in the blank samples in the absence of irradiation (ppm)

$C_{t,NI}$ = the average residual concentration of the colorant in the test samples in the absence of irradiation (ppm)

$C_{b,Ir}$ = the average residual concentration of the colorant in the blank samples in the irradiation experiment (ppm)

$C_{t,Ir}$ = the average residual concentration of the colorant in the test samples in the irradiation experiment (ppm)

C_i = the initial concentration of the colorant at the start of the experiment (ppm)

V_{meso} = Mesopore volume (cm^3/g)

S_{BET} = BET surface area (m^2/g)

t = Time (sec)

TOC = Total organic carbon ($mg\ L^{-1}$)

MW = Molecular weight (-)

XRD = X-Ray Diffraction

TEM = Transmission Electron Microscopy

CHAPTER I

INTRODUCTION

1.1 Background

Nanoparticulate TiO_2 becomes one of the most promising materials in the field of photocatalysis, since it could give rise to redox processes occurring at room temperature under solar or artificial UV light. A number of practical applications have been suggested including photoelectrochemical cells, antifog windows, and various cleaning devices (Martyanov *et al.*, 2004).

In the textile dyeing industry, the pollution by efflux wastewater containing residual colorants is a serious environmental problem. To treat such wastewater, physical methods (adsorption), biological methods (biodegradation), and chemical methods (chlorination, ozonation, and etc.) are available (Houas *et al.*, 2001). In the last category, heterogeneous photocatalysis is comparatively promising. Titanium dioxide is selected for wastewater treatment because it is non-toxic, inexpensive, and environmentally safe. In general, titanium dioxide powder exists in three crystalline structures (anatase, rutile, and brookite phase) which behave differently (Chamnan *et al.*, 2004). Even titania of the same phase could show different performances, depending on the specific surface area and crystallite size. The objective of this study is to investigate the decomposition of organic compounds using titanium dioxide powders of different crystallite sizes and shapes.

Finally, in the real treatment system, the understanding of pollutant removal is important. Correct selection of the titania photocatalyst and its reaction conditions would enhance the efficiency of a waste water treatment system.

1.2 Objectives of study

To investigate the decomposition of organic compounds by using titania of different crystallite size.

1.3 Scopes of Research

1. Characterization of the catalysts
    - 1.1 Specific surface area.
    - 1.2 Approximate size and shape.
    - 1.3 Particle size distribution.
2. Investigation of organic compound removed by TiO_2 in photocatalytic reaction with variation of the following parameters:
    - 2.1 Type of TiO_2: M1, M2, T1, T2, N1 (see table 1).
    - 2.2 Light source: none, UV lamp.
    - 2.3 Organic compound: Methylene Blue, Black 5, Lignin.
    - 2.4 Organic compound concentration: 10, 20 ppm.
    - 2.5 Irradiation time: 10, 30, 60, 90, and 120 min.

3. Applicability of photocatalytic decomposition in normal situation by irradiation with sunlight.

Table 1.1 Physical characteristicss of titania samples

Code	Crystal phase	Crystal shape	Average crystallite size (nm)	BET specific surface area (m^2/g)
M1^{+}	Rutile	cylinder	40x10Ø	170 (108*)
M2^{+}	Anatase	sphere	15	220 (104*)
T1$^{\Delta}$	Anatase	sphere	30	59 (52*)
T2$^{\Delta}$	Anatase	sphere	6	N/A (260*)
N1$^{\Diamond}$	Rutile, Anatase	N/A	N/A	N/A

$^{+}$Titania samples and their properties are provided by MODERN DYESTUFFS & PIGMENTS CO., LTD

$^{\Delta}$Titania samples and their properties are provided by Prof. Yasushige Mori, Doshisha University

$^{\Diamond}$ Titania samples and their properties are provided by NONAMI SCIENCE (Thailand) CO., LTD

* Estimated from the average crystal size and morphology

1.4 Expected Benefits

1. Knowledge of decomposition of industrially used dyes and organic compounds which are methylene blue, Black 5 and/or lignin by different sizes titania was investigated.

2. Data on the initial rate of decomposition.

CHAPTER II

FUNDAMENTAL KNOWLEDGE AND LITERATURE REVIEW

2.1 Organic compounds

An organic compound refers to any member of a large class of chemical compounds whose molecules contain carbon, with exception of carbides, carbonates and carbon oxides. The study of organic compounds is termed organic chemistry. Many of these compounds, such as proteins, fats, and carbohydrates (sugars), are also of prime importance in biochemistry.

Some of the classes of organic compounds include aliphatic compounds, chains of carbon which may be modified by functional groups; aromatic hydrocarbons, compounds containing one or more benzene rings; heterocyclic compounds which include non-carbon atoms as part of a ring structure; and polymers, long chains of repeating groups.

The dividing line between organic and inorganic is contended and historically arbitrary; generally speaking, however, organic compounds are defined as those compounds which have carbon-hydrogen bonds, and inorganic compounds, those without. Thus carbonic acid is inorganic, whereas formic acid, the first fatty acid, is organic, although it could as well be called "carbonous acid" and its anhydride, carbon monoxide, is inorganic.

The name "organic" is a historical name, dating back to 19th century, when it was believed that organic compounds could only be synthesised in living organisms through vis vitalis - the "life-force".

Most pure organic compounds are artificially produced--yet it is ironic that the term "organic" is also used to describe products produced without artificial chemicals.

2.1.1 Classification of dyestuffs

Dyestuffs are classified into fourteen groups which are presented in Table 2.1. There are four physical or chemical force (bonds) linking fibers and dye molecules. These are: hydrogen bond, Van der Waal's forces, ionic forces, and covalent bonds. Wongchaisuwan (1982) reviewed that dyestuffs appear colored because of chromophores, group(s) of atoms, in dye molecules causing wavelength specific light absorption and reflection. Chromophore is an unsaturated functional group in organic compound which can cause the absorption in the ultraviolet-visible range due to $n \rightarrow \pi^*$ and/or $\pi \rightarrow \pi^*$ transitions. Each chromophore has its adsorption maxima affected by solvent and structural detail of the molecule containing the chromophore such as the conjugation in molecule (Skoog and Leary, 1992). There are seven groups of chromophores in dyestuff as follows :

- nitroso group : -NO or =N-OH
- nitro group : -NO2 or =NO.OH
- azo group : -N=N-

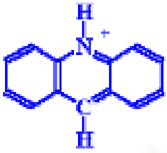
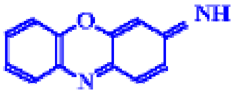
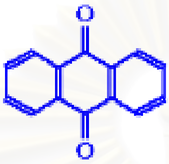
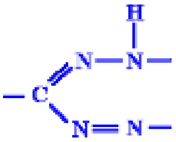
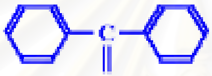
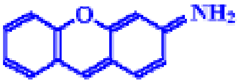
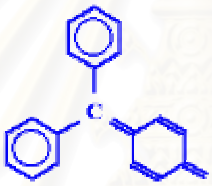
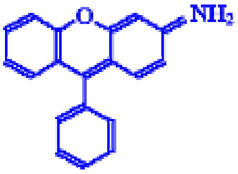
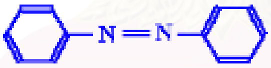
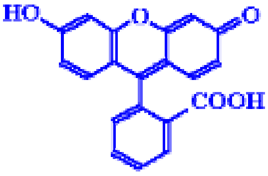
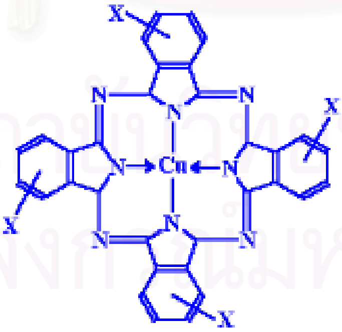
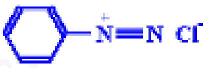
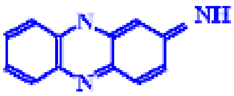
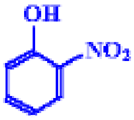
- ethylene group : >C=C<
- carbonyl group : >C=O
- carbonyl-nitrogen group : >C=NH or >CH=NH
- sulfer group : >C=S or –C-S-S-

Reactive dye are colored compounds which contain one or two groups capable of forming covalent bonds between a carbon or phosphorus atom to the dye ion or molecule and an oxygen, nitrogen or sulfur atom of a hydroxyl, an amino or a mercapto group, respectively, of the substrate. Such covalent bond are formed with the hydroxyl groups of cellulose fibers, with the amino, hydroxyl and mercapto groups of protein fibers and with the amino groups of polyamides. Approximately 80% of all reactive dyes are based on the azo chromogen. Azo dyes are compounds containing azo groups (-N=N-) which are linked to sp^2-hybridized carbon atoms. The azo groups are mainly bound to benzene or naphthalene rings, but in some cases they are also attached to aromatic heterocycles or enolizable aliphatic group. No azo compound has been found to occur in nature (Zollinger, 1987).

2.1.2 Lignin

Lignin, a binding macromolecule for cellulosic fibers, is an important constituent of wood. It has a very complicated structure (Fig 2.1) and the variations in the processes for its separation from wood influence its molecular weight. The polyphenolic nature of lignin is well established. Lignin is obtained from the delignification process used in paper manufacturing. Disposal of lignin is a serious environmental problem.

Table 2.1 Structural Classification

Class	***General formula***	***Class***	***General formula***
Acridine		Quinone-imine (Thiazin)	
Anthraquinone		Tetrazolium	
Diarylmethane		Xanthene (Fluorene – Pyronin)	
Triarylmethane		Xanthene (Fluorene – Rhodamine)	
Azo		Xanthene (Fluorone)	
Phthalocyanine		Diazonium	
Quinone-imine (Azin)		Nitro	

Source: http://stainsfile.info/StainsFile/dyes/class/clscomp.htm

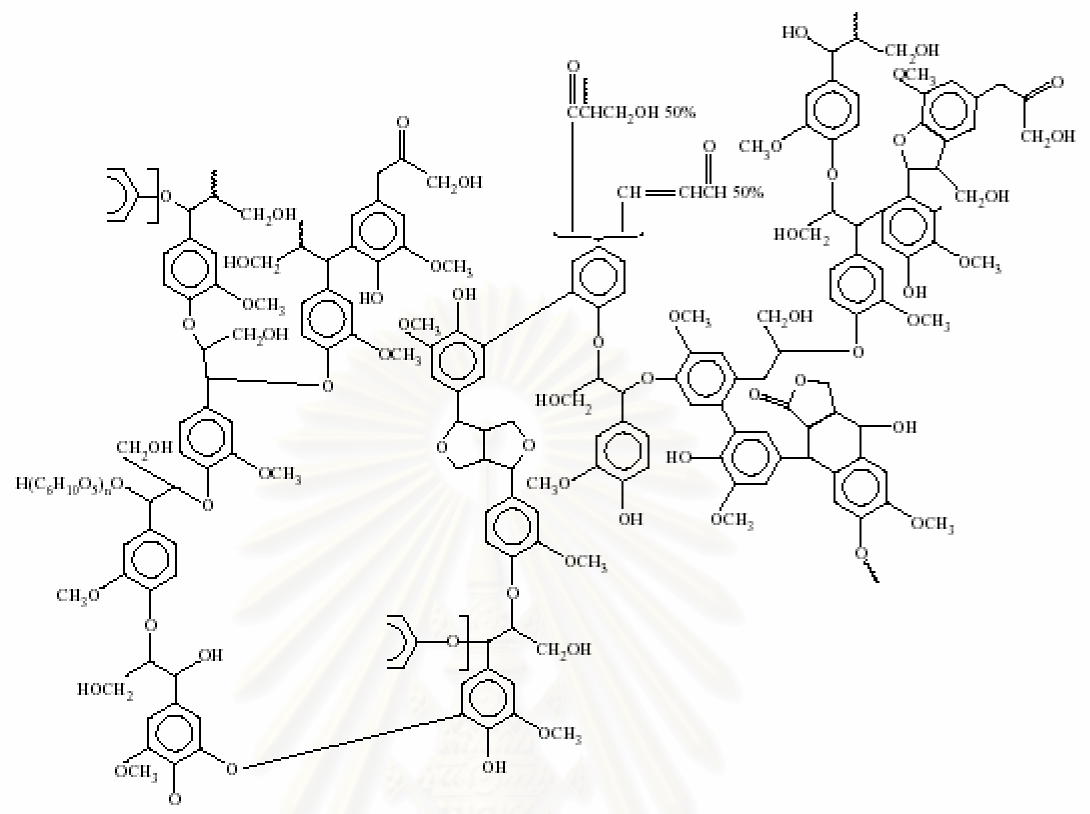


Figure 2.1. Representative structure of lignin (KHARADE and KALE, 1997)

2.2 Titanium dioxide photocatalyst

Starting in the late 1960s, Fujishima et al. have been involved in an unfolding story whose main character is the fascinating material titanium dioxide (TiO_2). This story began with photoelectrochemical solar energy conversion and then shifted into the area of environmental photocatalysis, including self-cleaning surfaces, and most recently into the area of photoinduced hydrophilicity, which involves not only self-cleaning surfaces, but also antifogging ones. One of the most interesting aspects of TiO_2 is that the types of photochemistry responsible for photocatalysis and hydrophilicity are completely different, even though both can occur simultaneously on the same surface.

Titania is commercially very important as a white pigment because of its maximum light scattering with virtually no absorption and because it is non toxic, chemically inert, and a dielectric ceramic material for its higher dielectric constant (Cheng et al., 1995). Recently, it has been suggested that monodisperse oxide powders are preferable to ceramic raw materials (Ogihara et al., 1991). Titania is know to have several natural polymorphs: Rutile is thermodynamically stable which tends to be more stable at high temperatures and thus is sometimes found in igneous rocks, but anatase is metastable at high temperatures (both belonging to the tetragonal crystal system), and bookite is found only under hydrothermal conditions or usually found only in minerals and has a structure belonging to the orthorhombic crystal system (Keesmann, 1966). Anatase type titania has been used as a catalyst for photodecomposition and solar energy conversion, because of its high photoactivity (Lason and Falconer, 1994; Kamat and Dimitrijevic, 1990; Herrmann et al., 1997; Fox and Dulay, 1993; Fujishima et al., 1999). On the other hand, rutile-type titania has been use for white pigment materials, because of its good scattering effect, which protects materials from ultraviolet light. Anatase titania has been reported to be unstable at high temperature and its transformation temperatures to be scattered in a wide range (Zzandena et al., 1958; Yoganarasimhan and Rao, 1962). Polymorphic transformation of ceramic materials generally depends on the grain size, impurities, composition, nature of the dopant, amount of dopant, and processing (Hirano et al., 2002).

2.2.1 Properties of titanium dioxide

Titanium (atomic number 22; ionization potentials: first 6.83 eV, second 13.67 eV, third 27.47 eV, fourth 43.24 eV) is the first member of Group IVB of the periodic chart. It has four valence electrons, and Ti (IV) is most stable valence state. The lower valence state Ti (II) and Ti (III) exist, but these are readily oxidized to the tetravalent state by air, water, and other oxidizing agent. The ionization potentials indicate that the Ti^{4++} ion would not be expected to exist and, indeed, Ti (IV) compounds are generally covalent. Titanium is able to expend its outer group of electrons and can form a large number of addition compounds by coordination other substances having donor atom, e.g., oxygen or sulfur. The most important commercial forms are titanium (IV) oxide and titanium metal.

Titanium (IV) oxide occurs naturally in three crystalline form: anatase, which tends to be more stable at low temperature, brookite, which is usually found only in materials, and rutile, which tends to be more stable at higher temperatures and thus is sometimes found in igneous rock. These crystals are substantially pure titanium (IV) oxide but usually amounts of impurities, e.g., iron, chromium, which darken them. A summary of three varieties is given in Table 2.2.

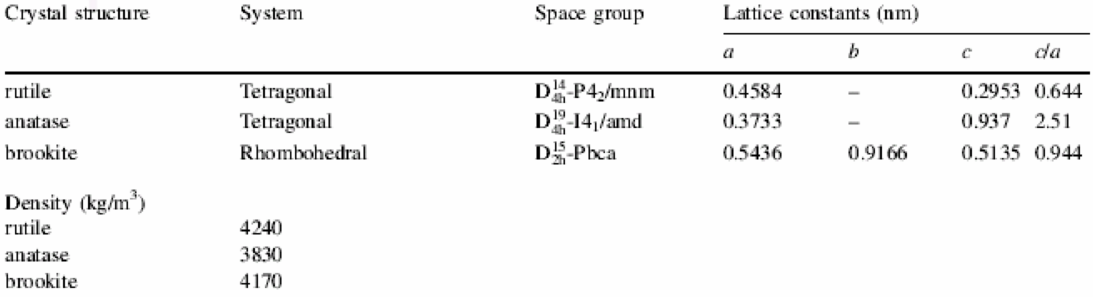
Although anatase and rutile are both tetragonal, they are not isomorphous (fig. 2.2). Anatase occurs usually in near-regular octahedral, and rutile forms slender prismatic crystal, which are frequently twinned. Rutile is the thermally stable form and is one of the two most important ores of titamium.

The three alltropic forms of titanium (IV) oxide have been prepared artificial but only rutile, the thermally stable form, has been obtained in the form of transparent large single crystal. The transformation form anatase to rutile is accompanied by the evolution of ca. 12.6 kJ/mol (3.01 kcal/mol), but the rate of transformation is greatly affected by temperature and by the presence of other substance which may either catalyze of inhibit the reaction. The lowest temperature at which conversion of anatase to rutile takes place at a measurable rate is ca. 700 °C, but this is not a transition temperature. The change is not reversible; ΔG for the change from anatase to rutile is always negative.

Brookite has been produced by heating amorphous titanium (IV) oxide, prepared from an alkyl titanates of sodium titanate with sodium or potassium hydroxide in an autoclave at 200 to 600 °C for several day. The important commercial forms of titanium (IV) oxide are anatase and rutile, and these can readily by distinguished by X-ray diffraction spectrometry.

Since both anatase and rutile are tetragonal, they are both anisotropic, and their physical properties, e.g. refractive index, very according to the direction relative to the crystal axes. In most applications of these substances, the distinction between crystallographic direction is lost because of the random orientation of large numbers of small particles, and it is mean value of the property that is significant.

Table 2.2 Crystallographic properties of rutile, anatase, and brookite. (Ulrike, 2003)



Crystal structure	System	Space group	Lattice constants (nm)			
			a	*b*	*c*	*c/a*
rutile	Tetragonal	D_{4h}^{14}-$P4_2/mnm$	0.4584	–	0.2953	0.644
anatase	Tetragonal	D_{4h}^{19}-$I4_1/amd$	0.3733	–	0.937	2.51
brookite	Rhombohedral	D_{2h}^{15}-$Pbca$	0.5436	0.9166	0.5135	0.944
Density (kg/m^3)						
rutile	4240					
anatase	3830					
brookite	4170					

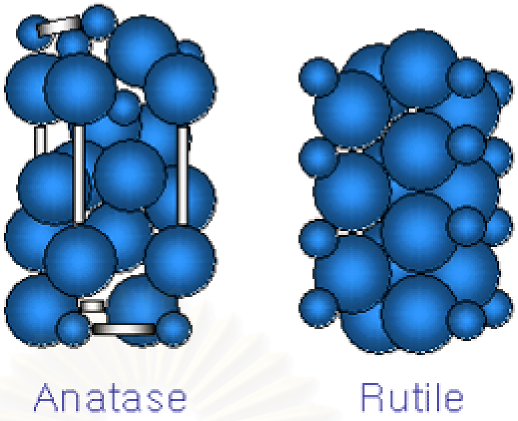


Figure 2.2. Crystal structure of TiO_2. (Fujishima et al., 1999)

2.2.2 Principles of photocatalytic reaction (Hoffmann et al., 1995)

Semiconductor photocatalysis with a primary focus on Ti02 as a durable photocatalyst has been applied to a variety of problems of environmental interest in addition to water and air purification. It has been shown to be useful for the destruction of microganisms such as bacteria (Ireland et al., 1993) and viruses (Sjogren et al., 1994), for the inactivation of cancer cells, (Cai et al., 1992) for odor control (Suzuki, 1993), for the photosplitting of water to produce hydrogen gas, (Karakitsou and Verykios, 1993; Gratzel, 1981; Borgarello et al., 1981; Duonghong et al., 1981; Kalyanasundaram et al., 1981; Borgarello et al., 1981) for the fixation of nitrogen, (Khan et al., 1992; Schiavello, 1993; Khan and Rao, 1991; Wold, 1993) and for the clean up of oil spills (Gerischer and Heller, 1992; Jackson et al., 1991; Heller, 1991).

Semiconductors (e.g., TiO_2, ZnO, Fe_2O_3, CdS, and ZnS) can act as sensitizers for light-reduced redox processes due to their electronic structure, which is characterized by a filled valence band and an empty conduction band (Nair et al., 1993). When a photon with an energy of hv matches or exceeds the bandgap energy, E_g, of the semiconductor, an electron, e_{cb}^-, is promoted from the valence band, VB, into the conduction band, CB, leaving a hole, h_{vb}^+ behind (see Fig. 2.3). Excitedstate conduction-band electrons and valence-band holes can recombine and dissipate the input energy as heat, get trapped in metastable surface states, or react with electron donors and electron acceptors adsorbed on the semiconductor surface or within the surrounding electrical double layer of the charged particles.

In the absence of suitable electron and hole scavengers, the stored energy is dissipated within a few nanoseconds by recombination (Boer, 1990). If a suitable scavenger or surface defect state is available to trap the electron or hole, recombination is prevented and subsequent redox reactions may occur. The valence-band holes are powerful oxidants (+1.0 to +3.5 V vs NHE depending on the semiconductor and pH), while the conduction-band electrons are good reductants (+0.5 to -1.5 V vs NHE) (Memming, 1988). Most organic photodegradation reactions utilize the oxidizing power of the holes either directly or indirectly; however, to prevent a buildup of charge one must also provide a reducible species to react with the electrons. In contrast, on bulk semiconductor electrodes only one species, either the hole or electron, is available for reaction due to band bending (Rothenberger et al., 1985). However, in very small semiconductor particle suspensions both species are present on the surface. Therefore, careful consideration of both the oxidative and the reductive paths is required.

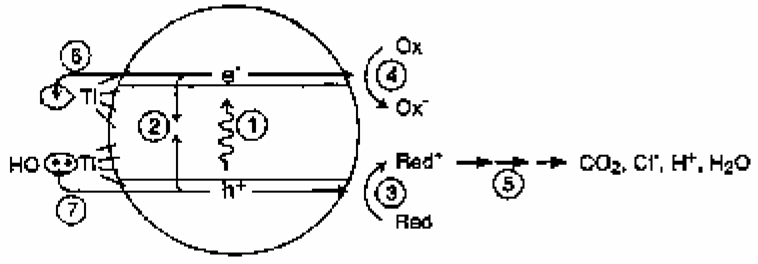


Figure 2.3. Primary steps in the photoelectrochemical mechanism: (1) formation of charge carriers by a photon; (2) charge carrier recombination to liberate heat; (3) initiation of an oxidative pathway by a valence-band hole; (4) initiation of a reductive pathway by a conduction-band electron; (5) further thermal (e.g., hydrolysis or reaction with active oxygen species) and photocatalytic reactions to yield mineralization products; (6) trapping of a conduction-band electron in a dangling surficial bond to yield Ti(III); (7) trapping of a valence-band hole at a surficial titanol group.

2.2.3 Mechanism of pollutant treatment by titanium dioxide

Chloroform

Kormann et al. have proposed the following mechanism for chloroform oxidation after generation of the electron-hole pair due to excitation at wavelengths less than 380 nm:

$$>TiOH^{\bullet+} + >HCCl_3 \rightarrow >TiOH_2^{+} + >^{\bullet}CCl_3 \tag{2.1}$$

$$>Ti^{III}OH^{-} + >TiOH_2^{+}:O_2 \rightarrow >Ti^{IV}OH + >TiOH_2^{+}\text{--}{}^{\bullet}O_2^{-} \tag{2.2}$$

$$>^{\bullet}CC1_3 + O_2 \rightarrow {}^{\bullet}O_2CCl_3 + > \tag{2.3}$$

$$2^{\bullet}O_2CCl_3 \rightarrow 2^{\bullet}O_2CCl_3 + O_2 \tag{2.4}$$

$${}^{\bullet}OCCl_3 + HO_2^{\bullet} \rightarrow C1_3COH + O_2 \tag{2.5}$$

$$Cl_3COH \rightarrow Cl_2CO + H^+ + C1^- \qquad (2.6)$$

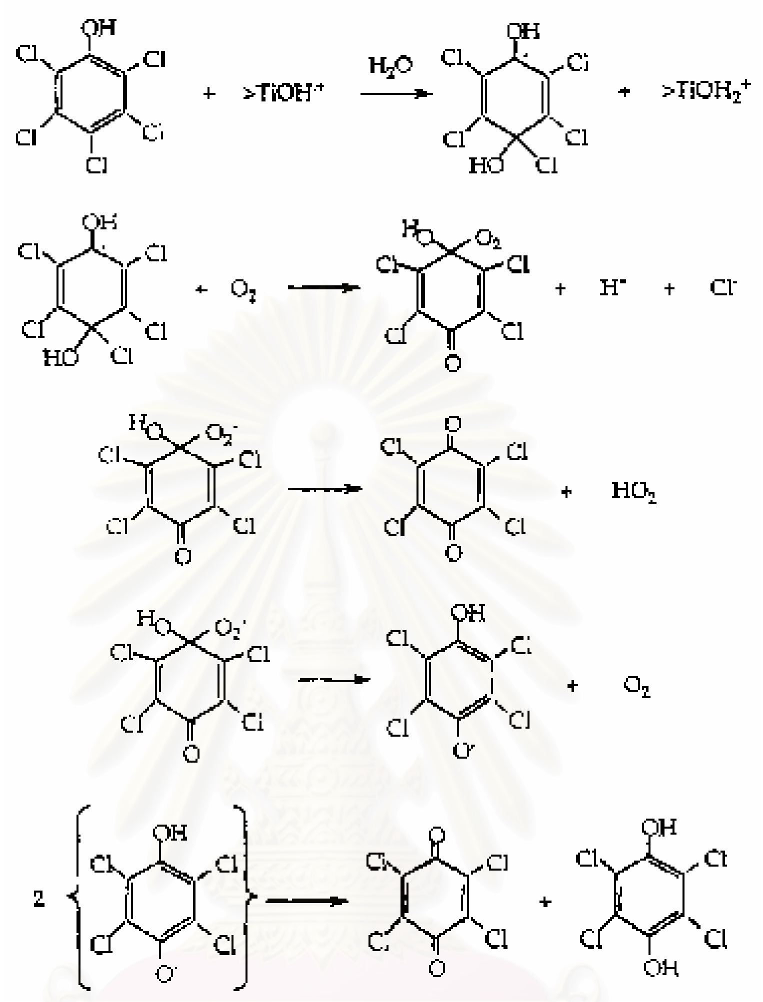
$$C1_2CO + H_2O \rightarrow CO_2 + 2H^+ + 2C1^- \qquad (2.7)$$

Pentachlorophenol

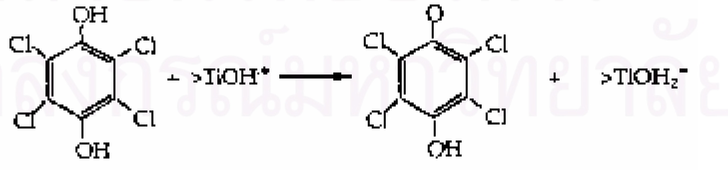
Pentachlorophenol (C_6Cl_5OH, PCP) has been used widely as a pesticide and a wood preservative. The photooxidation of PCP in the presence of TiO_2 proceeds via the following stoichiometry:

$$2HOC_6C1_5 + 7O_2 \rightarrow 4HCO_2H + 8CO_2 + 10HCl \qquad (2.8)$$

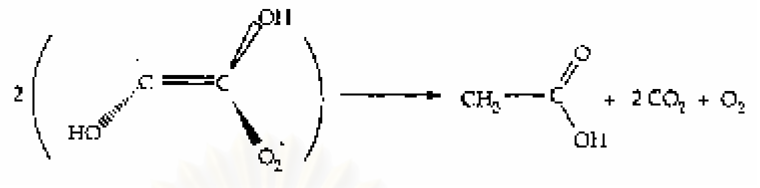
In homogeneous solution, photolysis of PCP has been shown to produce toxic byproducts such as tetrachlorodioxins; however, in the presence of illuminated TiO_2 suspensions, the intermediate dioxins are effectively destroyed. Mills et al. reported that complete dechlorination of 47 pM PCP was achieved after 3 h of illumination at high intensity with apparent quantum efficiencies for ranging from 1 to 3%. p-Chloranil, tetrachlorohydroquinone, H_2O_2, and o-chloranil were formed as the principal intermediates. Formate and acetate were formed as products during the latter stages of photooxidation. The mechanism for photooxidation of PCP appears to proceed primarily via hydroxyl radical attack on the para position of the PCP ring to form a semiquinone radical which in turn disproportionates to yield p-chloranil and tetrachlorohydroquinone. The initial steps in the photocatalytic degradation of PCP as proposed by Mills et al. are as follows:



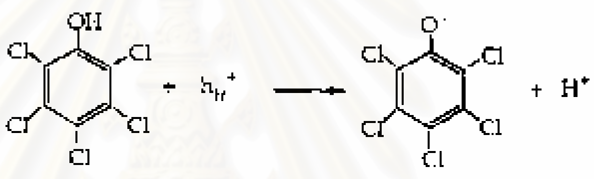
Under high-intensity illumination, the PCP-$^{\bullet}$OH reaction intermediates are attacked further by $^{\bullet}$OH to yield HCO_2^-, $CH_3CO_2^-$, CO_2, H^+, and $\mathrm{C1}^-$ with initiation as follows:



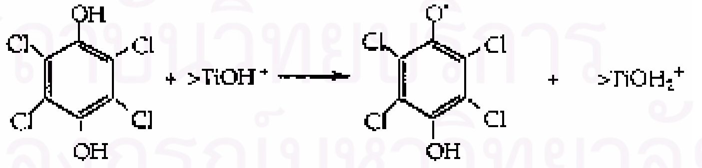
Ring fragmentation appears to be a slow process and probably occurs between carbon atoms of the ring which have no chlorine atoms, since chloroacetic acid is not found among the detectable products. The formation of acetate appears to involve a reduction of carbon centers and probably proceeds via disproportionation reactions of free-radical intermediates as proposed below for a likely ring-fragmentation biradical:



The direct electron-transfer reaction between a surface-trapped hole and a surface-bound PCP molecule is expected to yield a phenoxy1 radical as follows:



The resulting pentachlorophenoxyl radical is most probably a strong oxidant which will be reduced by electrons from the conduction band or by peroxide radicals to regenerate PCP, thus yielding a closed-loop reaction with no net degradation (vide infra). Experimental results suggest that $^{\bullet}$OH radicals react at least 10 times faster with tetrachlorohydroquinone than with p-chloranil:



2.3 Processing for eliminating the pollutants by titanium dioxide

Nowadays several researches try to use the titanium dioxide to solve the problems of environment, waste water and air pollution. There are many methods to treat or clean air and water as follow:

Disperse titanium dioxide in water: many reported used this method to treat the impurity in water, methylene blue, reactive dyes, and lignin, because this method was acknowledged that easy to find the kinetic or rate of titanium dioxide.

Xu et al. (1999) showed that the influence of particle size of TiO_2 on the photocatalytic degradation of methylene blue in a suspended aqueous solution has been studied. The results suggested that the adsorption rate and adsorbability of methylene blue on suspended TiO_2 particles increased as the particle sizes of TiO_2 decreased. Photocatalytic activity of TiO_2 also increased as the particle size of TiO_2 became smaller, especially when the particle size is less than 30 nm.

Randorn et al. (2004) and Houas et al. (2001) investigated the degradation of methylene blue by TiO_2-Degussa P25. They studied many conditions such as pH, light sources and initial concentration of solution in several irradiation times.

Lachheb et al. (2002) illustrated that the five different dyes (Methylene Blue, Orange G, Alizarin S, Methyl Red, and Congo Red) were successfully not only decolorized, but also totally degraded and mineralized. The organic part was totally converted into CO_2 as testified by the elimination of both COD and TOC.

Tanaka et al. (1999) investigated that lignin was adsorbed to TiO_2 quickly, and the subsequent illumination resulted in the desorption and degradation simultaneously. In the degradation process lignin was depolymerized successively and aromatic ring was opened, which produced oxygenated compounded such as carboxylate and aldehyde. The prolonged illumination led to the complete mineralization.

Supported on substrate, and used as thin film: a lot of researches to solve the problem of the loss of titanium dioxide in the processes by many applications such as synthesis composite material which high efficiency and easy to recovery, and used as thin film.

Bhattacharyya et al. (2004) reported that TiO_2 was impregnated on three different kinds of adsorbents, mesoporous (MCM-41), microporous (b-zeolite) and pillared structure (montmorillonite) where different loadings (10–80%) of TiO2 were obtained using sol–gel method. The catalysts were characterized by several analytical techniques including XRD, SEM–EDX, XPS, and BETanalyzer. Subsequent to the dark adsorption studies, photocatalytic efficiency of the supported catalysts was evaluated using an azo-dye, orange II in water as model compound under different operating conditions. All supported catalysts exhibit good photodegradation efficiency of orange II, and their overall removal efficiency was always better than that of bare TiO_2 produced by the sol–gel method and commercial catalyst, Degussa-P25.

Ao and Lee (2004) showed that the TiO_2/AC filter for practical application, it was installed in an air cleaner available in the commercial market and tested inside an environmental chamber. Nitrogen oxide (NO) and toluene were selected as target pollutant. Results showed that a higher removal efficiency of NO was achieved using shorter wavelength ultraviolet lamp than longer wavelength ultraviolet lamp. A higher NO removal was achieved using TiO_2/AC filter compared to TiO_2 filter only. The intermediate, NO_2, generated from the photodegradation of NO was also successfully suppressed from exiting the system using TiO_2/AC filter.

Nonami et al. (2004) investigated that a TiO_2 photocatalyst was soaked in PBS (pseudo-body solution) containing an excess of phosphate ions. After soaking for 1 h, an apatite phase was formed on the TiO_2 surfaces. This composite is able to absorb and decompose bacteria and various other materials.

Zhang et al. (2003) illustrated that a new type of tubular photocatalytic reactor was developed to realize practical application of TiO2 photocatalyst for water purification. The principal part of the reactor consists of the ceramic cylindrical tube whose inner surface is coated with Pt-loaded TiO2 film and the 30 W ultraviolet light lamp which is set longitudinally in the center of the tube. The water to be treated is circulated through the reactor via a buffer reservor for aeration. The performance of the reactor was evaluated through the experiment of decomposing aqueous phenol, tetrachloroethylene (TCE) and bisphenol A. It was shown that all the tested organic compounds are decomposed in moderately shorter time by the reactor. It would be expected that the reactor could be commercialized for its high efficiency in purifying polluted water and for its simple set up ensuring maintenance free.

CHAPTER III

EXPERIMENTAL

3.1 Synthetic wastewater

Each synthetic wastewater used in this work contains methylene blue, Black 5, and lignin, respectively. They were prepared by dissolving powder of methylene blue (MW=320), Black 5 (MW=993) and lignosulfonic acid sodium salt (MW=8000) into distilled water. Methylene blue, Black 5 and lignosulfonic acid were supplied from Allied Chemical Corporation, Asia Dyestuff Industries LTD and Aldrich, respectively They were used without any purification. All solution were made from deminerialized water (conductivity = 2 microcement). Fig. 3.1 showed the structure of Black 5, methylene blue, and monomer of lignin.

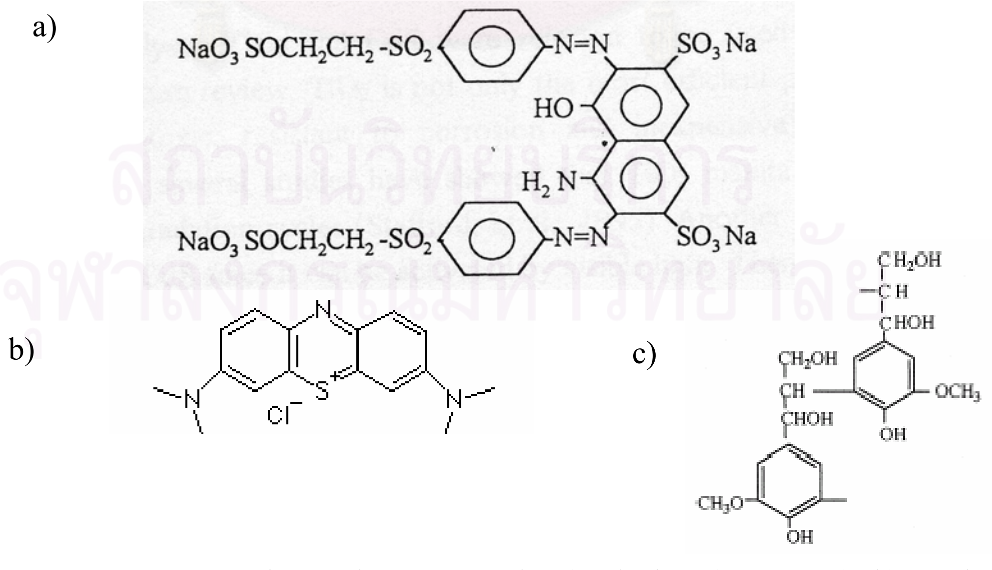


Figure 3.1. Structures of organic compounds: a) Black 5 (MW=993), b) Methylene Blue (MW=320) and c) main monomer unit of coniferous wood lignin.

3.2 Photocatalysts

The five kinds of photocatalyst, TiO_2, used in this work, were supported by three companies, Modern Dyestuffs & Pigments Co.Ltd., Prof. Yasushige Mori, Doshisha University, and Nonami Science (Thailand) Co.Ltd. The data of properties which received from supporter was shown in Table 1.1. Their properties were different phase, shape, size, and specific surface area.

3.3 Photocatalytic reactor

The main apparatus using in this research was shaker which its in side was composed of 2 UV-C lamps and state for inserting the quartz tubes as the photoreactors. The power of each UV lamp is 30 Watt and maximum intensity of its spectrum is 253.7 nm. Fig. 3.2 showed outside and inside of the shaker.

Figure 3.2. Outside (left) and inside (right) of shaker

3.4 Experimental procedure

The experimental procedure of this work was separated into two parts as follow:

a) Characterization of catalysts

The data of properties; size, shape, phase, and specific surface area, of each titania from companies were measured from different analyzer so these properties were adjusted to the same analyzer. The data of properties of each titania were confirmed by TEM (JEOL, JEM-1230), XRD (Philips, PW3710), and BET (BELSORP, 28SA) for finding size and shape, phase, and specific surface area, respectively. Further more, DLS technique was used to investigate the size distribution of titania when dispersed in liquid.

b) Investigation of organic compound removal

Each type of titania (Table 1.1) was dispersed in the aqueous solutions of each organic compound (methylene blue, Black 5, and lignin solution) which their initial concentration were about 10 ppm and 20 ppm, and the test samples were irradiated with UV-C light for 10, 30, 60, 90, and 120 min. while they are shaken to ensure good dispersion and saturated adsorption of the titania in each sample. This experimental unit consists of 6 quartz-tube photoreactors (each with 50 ml effective volume), 4 of which contain 2 mg each of the nanosize titania of interest dispersed in 20 ml of aqueous solution the remaining two blank reactors contain only the organic solution without any titania. The position of each test tube was shown in fig.3.3. Residual concentration of organic compound in the blank and test samples were averaged to reduce experimental error. Especially fluorescent light and sunlight were also used as the light source. In this research, each titania were exposed to fluorescent for 60 min and sunlight for 60 min too. These titania were also suspended in the aqueous solution of each organic compound while shaking but without UV-C light irradiation for investigation of adsorption time.

Prior to each residual concentration analysis, TiO_2 powder suspended in the aqueous sample will be separated by centrifuging (3800 rpm, 15 min). Then residual concentration of Black 5, methylene blue or lignin in the supernatant liquid will be analysed by a UV-Vis spectrophotometer (Jan Way, 6405 UV/Vis) at wavelength 595 nm, 660 nm or 280 nm, respectively.

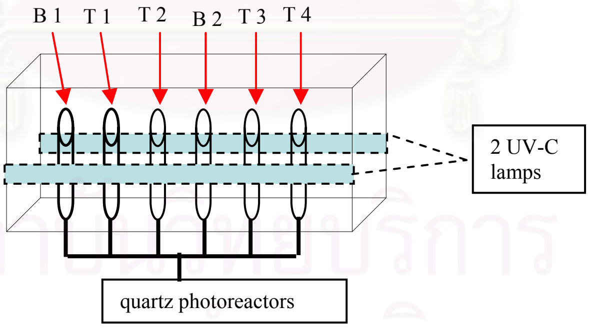


Figure3.3. Arrangement of reactors and lamps in the shaker (T1, T2, T3, and T4 are test tubes having organic solution and titania, B1 and B2 are test tubes having only organic solution)

3.5 Analytical instruments

The instruments used to characterize titania properties are TEM (JEOL, JEM-1230), XRD (Philips, PW3710), BET (BEL Japan Inc. , BELSORP 28SA), and DLS (ZETASIZER 300HSA) for finding size and shape, phase, specific surface area, size distribution in liquid respectively, while the instrument for measuring concentration or finding photocatalytic reaction is the UV-Vis spectrophotometer (Jenway, 6405 UV/Vis).

Transmission Electron Microscopy (TEM)

TEM analysis was studied using JEOL-1230 as shown in fig. 3.4. The titanium dioxide powder was suspended in alcohol before ultrasonic treatment with the sufficient time (15 min) for ensuring its uniform dispersion. A drop of clearly solution was then dripped onto a copper-grid (fig. 3.5). The specimen was loaded into sample chamber and waiting for the vaccum condition and steady state inside the chamber for 30 min.

Figure 3.4. Transmission Electron Microscopy (TEM)

Figure 3.5. Copper grid for Transmission Electron Microscopy

X-Ray Diffraction (XRD)

The XRD (Philips, PW3710) was used to analyze phase of the investigated titanium dioxide. Figure 3.6 shows the XRD analysis system used in this work. The titania sample was spread on the glass slide and then set in the equipment which provide x-ray beam for the analysis.

Figure 3.6 X-Ray Diffraction (XRD)

BET surface area analyzer

The BET surface area (Fig. 3.7) S_{BET}, mesopore volume V_{meso}, micropore volume V_{micro}, and pore size distribution, of each samples were determined from N_2 adsorption-desorption isotherms measured at 77 K using the adsorption apparatus (BELSORP 28SA, BEL Japan Inc., Japan). Pore size distribution and V_{meso} were evaluated by applying the Dollimore-Heal method to the desorption isotherm, whereas the t-plot method was used to estimate V_{micro}.

Figure 3.7. BET surface area analyzer

Dynamic Light Scattering (DLS)

For particle size distribution analysis, Dynamic Light Scattering (DLS) using ZETASIZER 300HSA as shown in figure 4.3.3.1 was applied. It should be noted that DLS is based on the measurement of the dispersion of light scattering by particles motion in a static solvent such as toluene, water, acetone or ethanol, the measured particle size should correspond to hydrodynamic diameter but not to the real diameters of the particles with complex structures. However, DLS results were expected to give at least the qualitative trend in particle sizes distribution. For preparation of the sample, DLS specimens were also prepared by suspending in water before ultrasonic treatment with the sufficient time (15 min) for ensuring its uniform dispersion. Afterwards, the specimen was diluted by water again until they became transparent and ultrasonicated again for 10 min before loading to the sample cell for analysis.

Figure 3.8. Dynamic Light Scattering (DLS)

UV-Vis spectrophotometer

A UV/VIS spectrophotometer (Jenway, 6405 UV/Vis) was used to measure the photoabsorptivity at 660, 595 or 282 nm to estimate the concentration of methylene blue, Black 5 and lignin, respectively. Figure 3.8 showed the UV/VIS spectrophotometer.

Figure 3.9. UV/VIS spectrophotometer

3.6 Preventing loss of titanium dioxide by immobilization as cake layer

The apparatus for preventing loss of titanium dioxide by immobilization as cake layer was constructed because this work and other research works were found the same problem losing titania photocatalyst in the wastewater treatment system. This apparatus composed of a UV lamp as a light source and a acrylic reactor. Figure 3.9 showed the apparatus for preventing loss of titanium dioxide by immobilization as cake layer.

This experiment was separated into 2 parts. First, the titania cake was generated by dispersing titania powder into deminerized water before forming it as the cake layer on micro filter. Second, the titania cake layer was set up into the apparatus in fig. 3.10 and then the Black 5 solution (20 ppm, 1 L) was circulated for 1 night for eliminating water in the titania cake and in the micro filter. After that the UV lamp was turned on and the treatment water sampling was average measured in 20 min for each time.

Figure 3.10. The apparatus for preventing loss of titanium dioxide by immobilization as cake layer

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Characterization of commercial titanium dioxide

To recheck and confirm the data of properties of 5 titanium dioxide from the companies, we measured these titania on same based measurement. The 3 analyzers, TEM, XRD, and BET, was applied for characterizing; shape, size, phase, and specific surface area. Size distribution in liquid was also investigated by DLS.

4.1.1 Shape and size by TEM

From the TEM images, figures 4.1-4.5, the size and shape of each titanium dioxide was investigated. The approximate size of each titania was obtained and shown in the Table 4.1. In the Table 4.1, the comparing of size and shape between data from the companies and this work was revealed. We found that value of shape and size of each titania measured in this work was slightly different from the data of companies.

Table 4.1 Data of size and shape measured in this work and from the companies

Code	Data in this work		Data from companies	
	Shape	**Size (nm)**	**Shape**	**Size (nm)**
M1	cylinder	45x9Ø	cylinder	40x10Ø
M2	sphere	11	sphere	15
T1	sphere	26	sphere	30
T2	sphere	6	sphere	6
N1	sphere, cylinder	37, 110x14 Ø	NA	NA

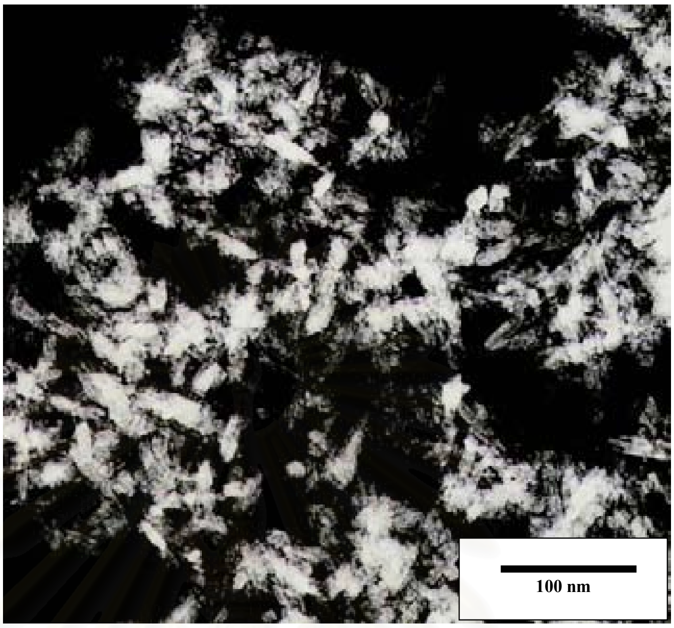


Figure 4.1. M1-titania TEM image

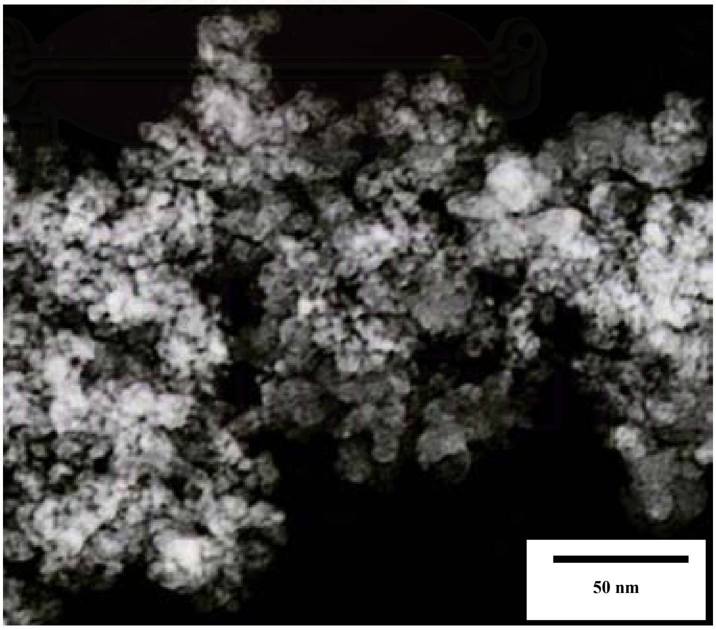


Figure 4.2. M2-titania TEM image

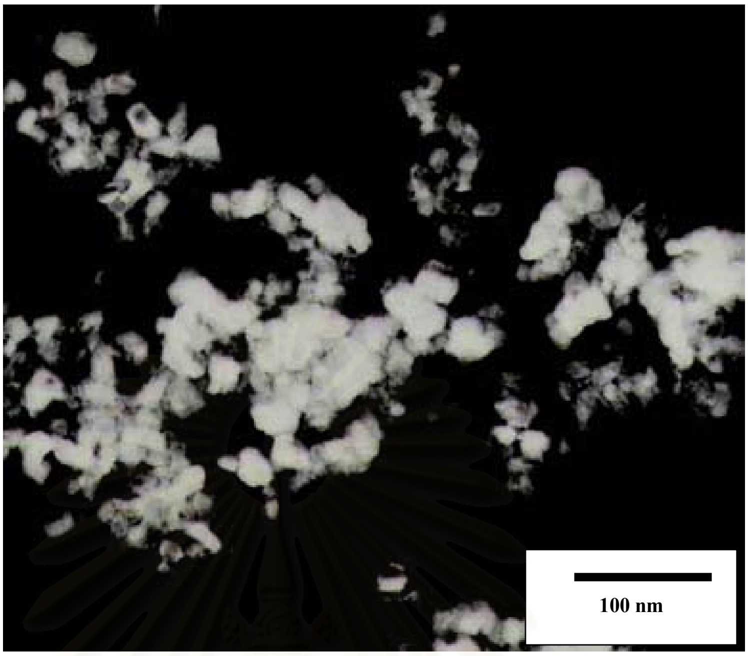


Figure 4.3. T1-titania TEM image

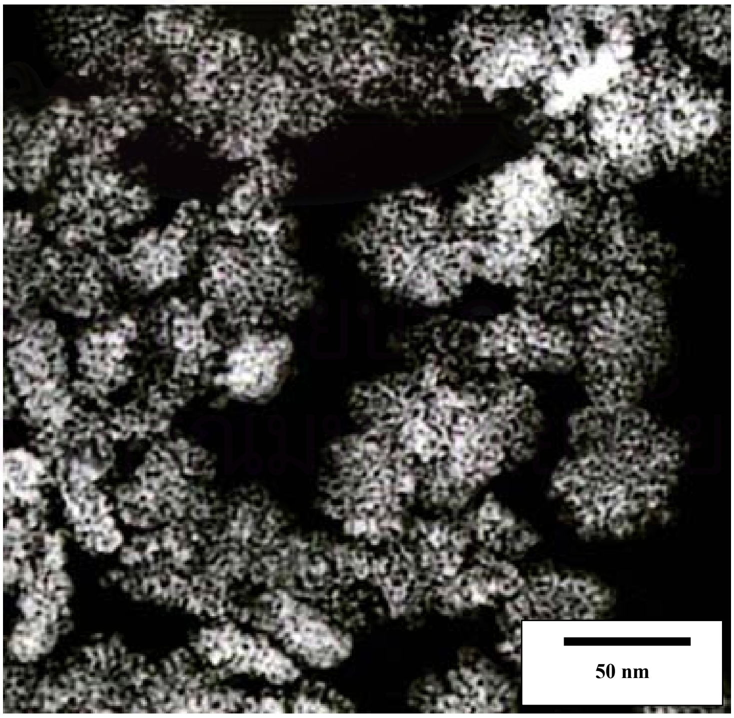


Figure 4.4. T2-titania TEM image

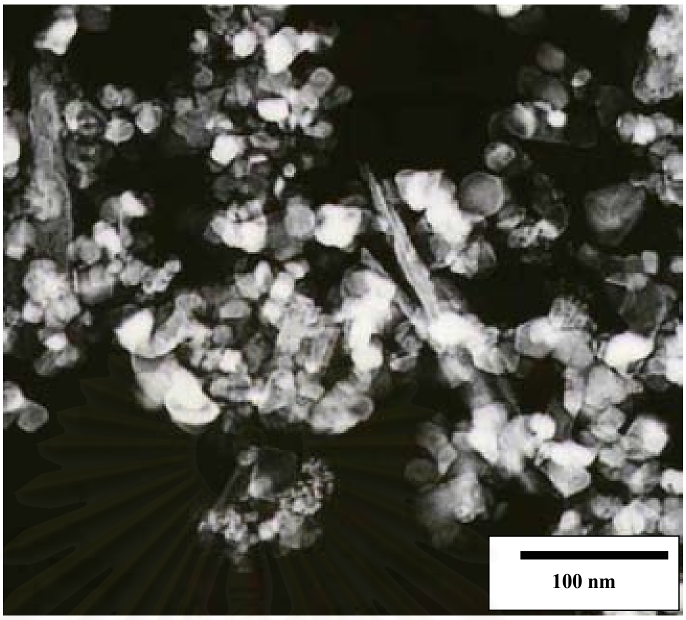


Figure 4.5. N1-titania TEM image

4.1.2 Phase analysis by XRD

From XRD technique, phase of titanium dioxide could be analyzed as shown in figures 4.6-4.10. The phase of each titanium dioxide revealed in this work was similar to the companies. Phase of each titanium dioxide was shown as follow: M1 = rutile phase, M2 = anatase phase, T1 = anatase phase, T2 = anatase phase, and N1 = anatase and rutile phase. In the XRD result of N1-titania, calcium oxide was found because N1-titania (from NONAMI SCIENCE (Thailand) CO., LTD) was apatite coated titania composed of calcium oxide as a main coat compound.

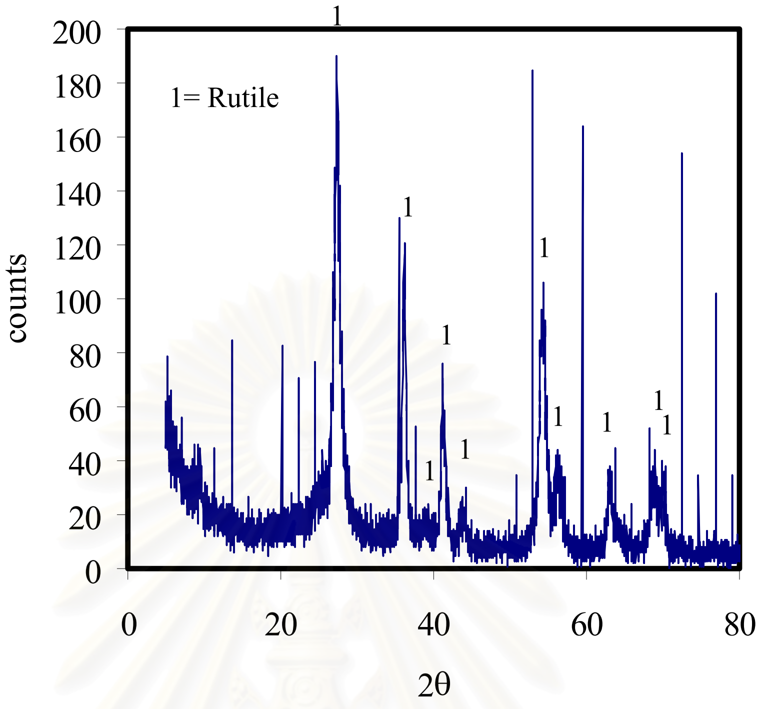


Figure 4.6. XRD result of M1-titania

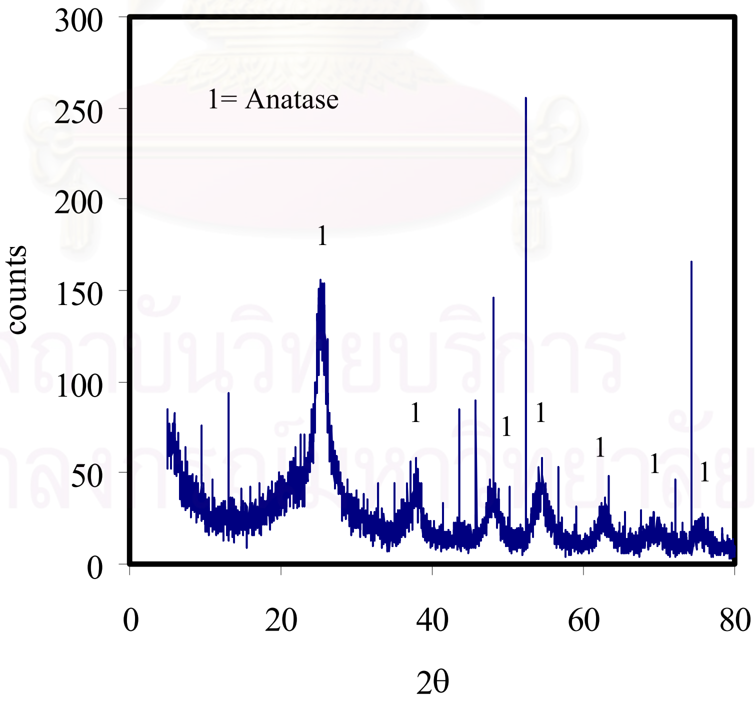


Figure 4.7. XRD result of M2-titania

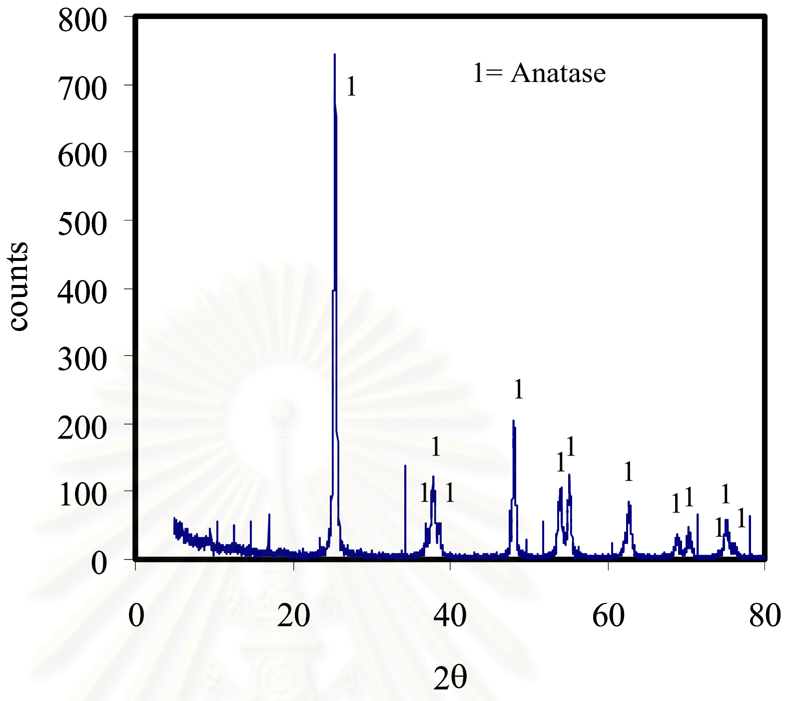


Figure 4.8. XRD result of T1-titania

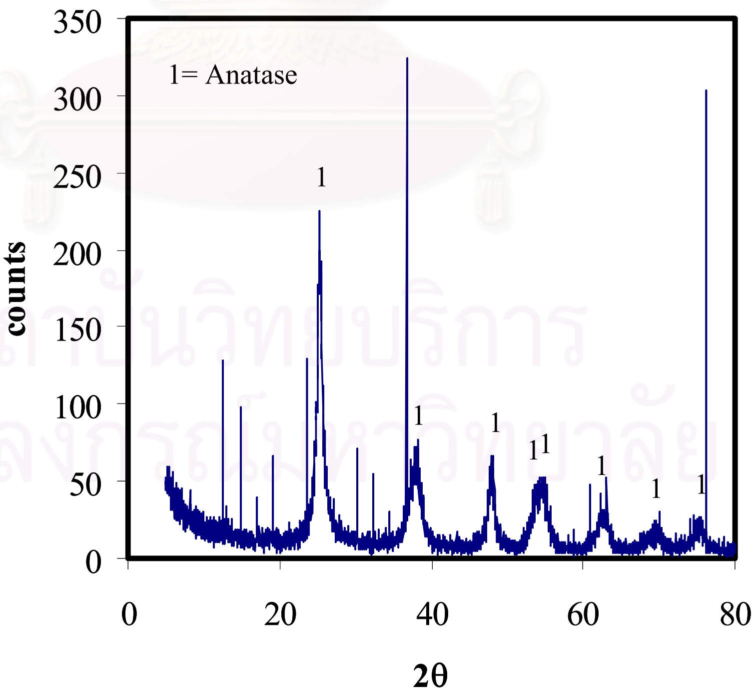


Figure 4.9. XRD result of T2-titania

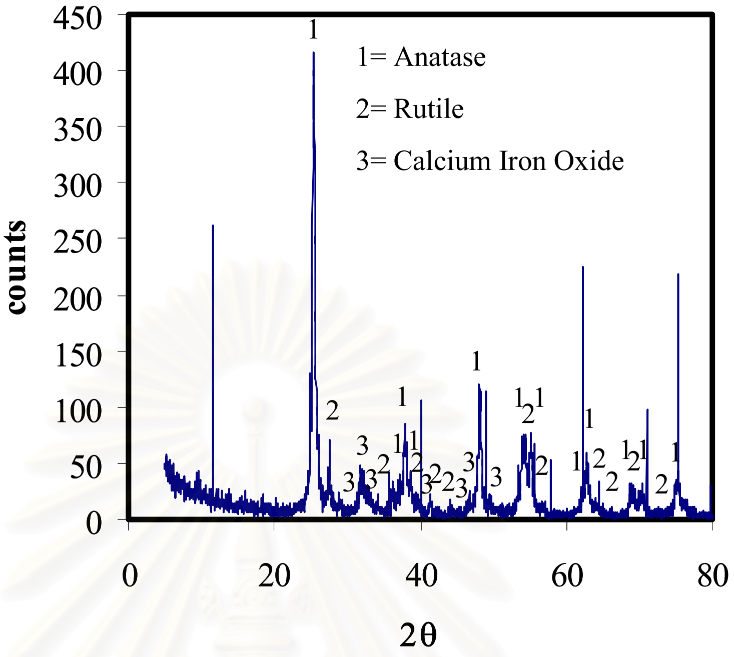


Figure 4.10. XRD result of N1-titania

4.1.3 BET surface area

The BET surface area of 5 titania was shown in Table 4.2. This property was similar as the data from the companies, in Table 1.1. The T2-titania was very hard to be measured by BET technique. In the limitation for this technique, the sample must be a dry powder but T2-titania was the slurry so it must spend long time to remove the humidity in the sample.

Table 4.2 BET surface area and $V_{mesopore}$ of the titania in this work

Code	BET surface area (m^2/g)	$V_{mesopore}$ (mm^3/g)
M1	77.79	474.77
M2	251.19	840.28
T1	56.04	270.76
T2	NA	NA
N1	64.27	255.59

4.1.4 Size distribution by DLS

The size distribution in liquid of each titania was measured by DLS technique, zetasizer. The results were shown in figures 4.11-4.15. Graphs in figures 4.11-4.15 revealed the relation between size and volume and/or number of particles of each titania. The average size of each titania was summarized in Table 4.3. In this analyzing technique, 5 titania in this work were dispersed in water, except the N1-titania must drop the surfactant as the dispersant because it precipitated or agglomerated when dispersed in water. We can conclude that the titania cluster which have size lass than about 871 nm could well dispersed into water.

Table 4.3 Average size of 5 titania by DLS technique

Code	Average size (nm)	Medium
M1	312.1	water
M2	534.8	water
T1	871.2	water
T2	122.8	water
N1	167.0	water and dispersant

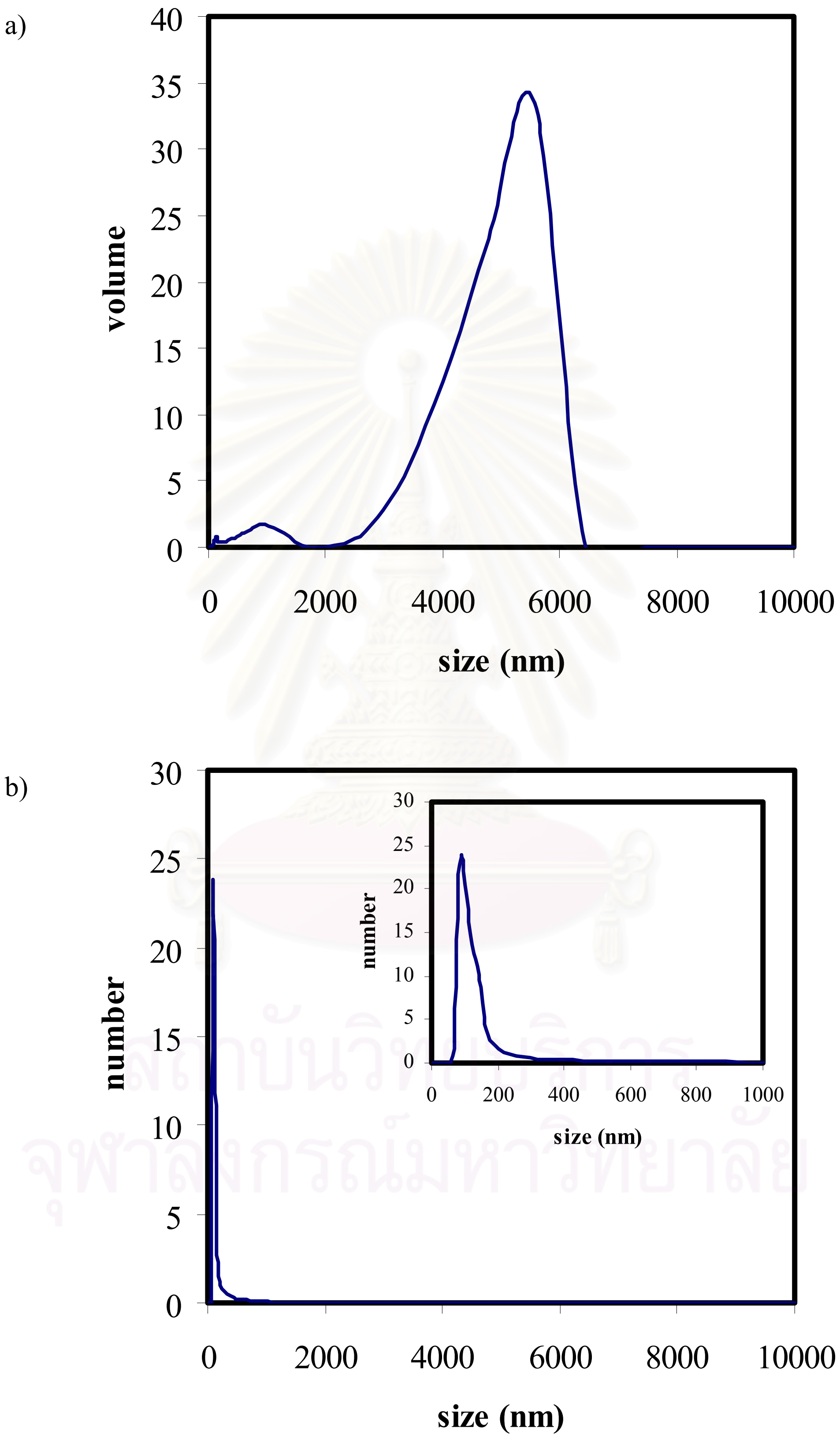
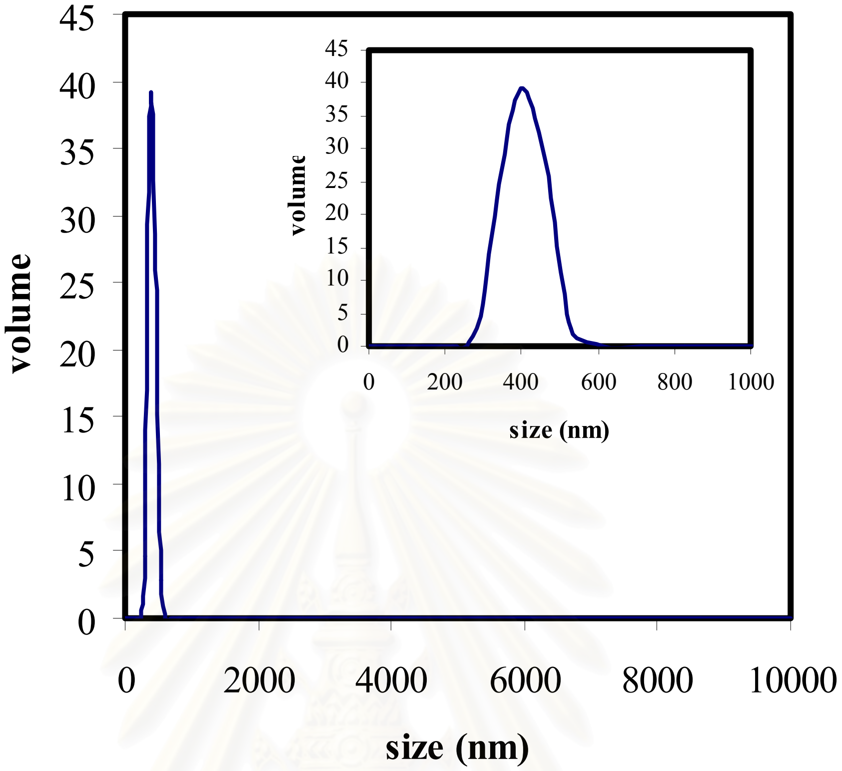


Figure 4.11. Size distribution of M1-titania in term volume (a) and number (b)

a)



b)

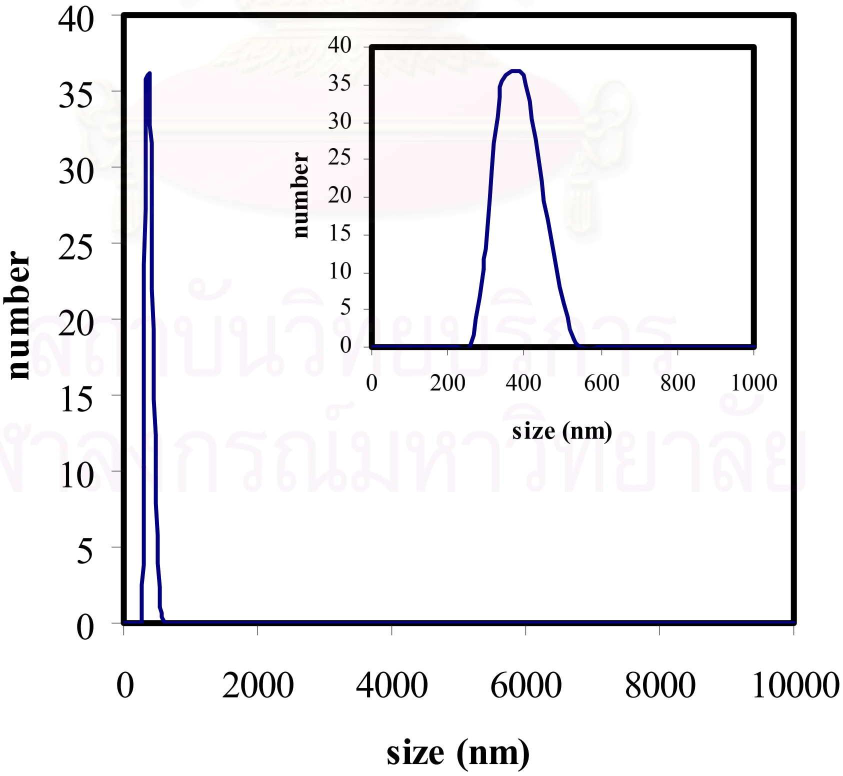


Figure 4.12. Size distribution of M2-titania in term volume (a) and number (b)

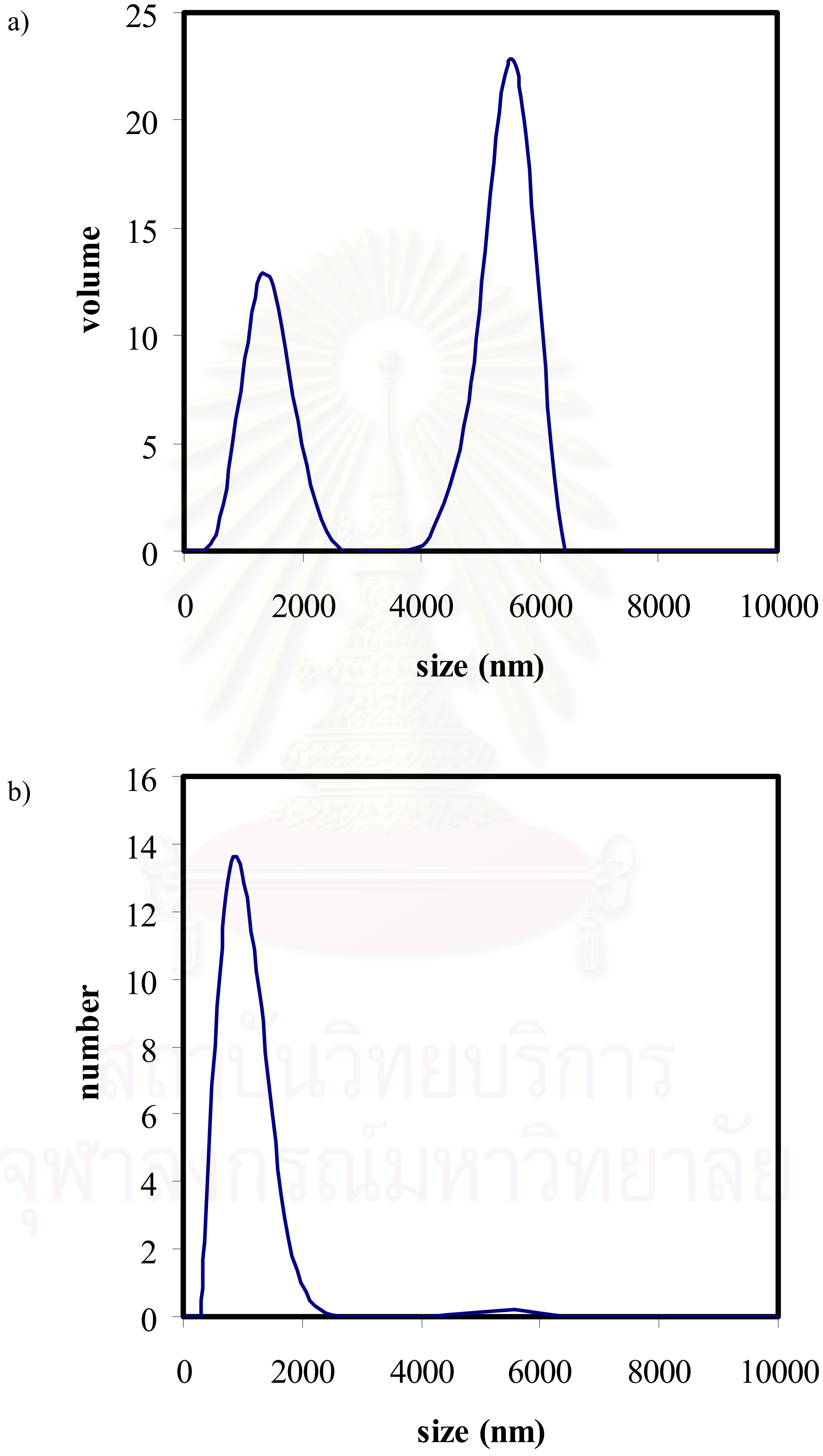


Figure 4.13. Size distribution of T1-titania in term volume (a) and number (b)

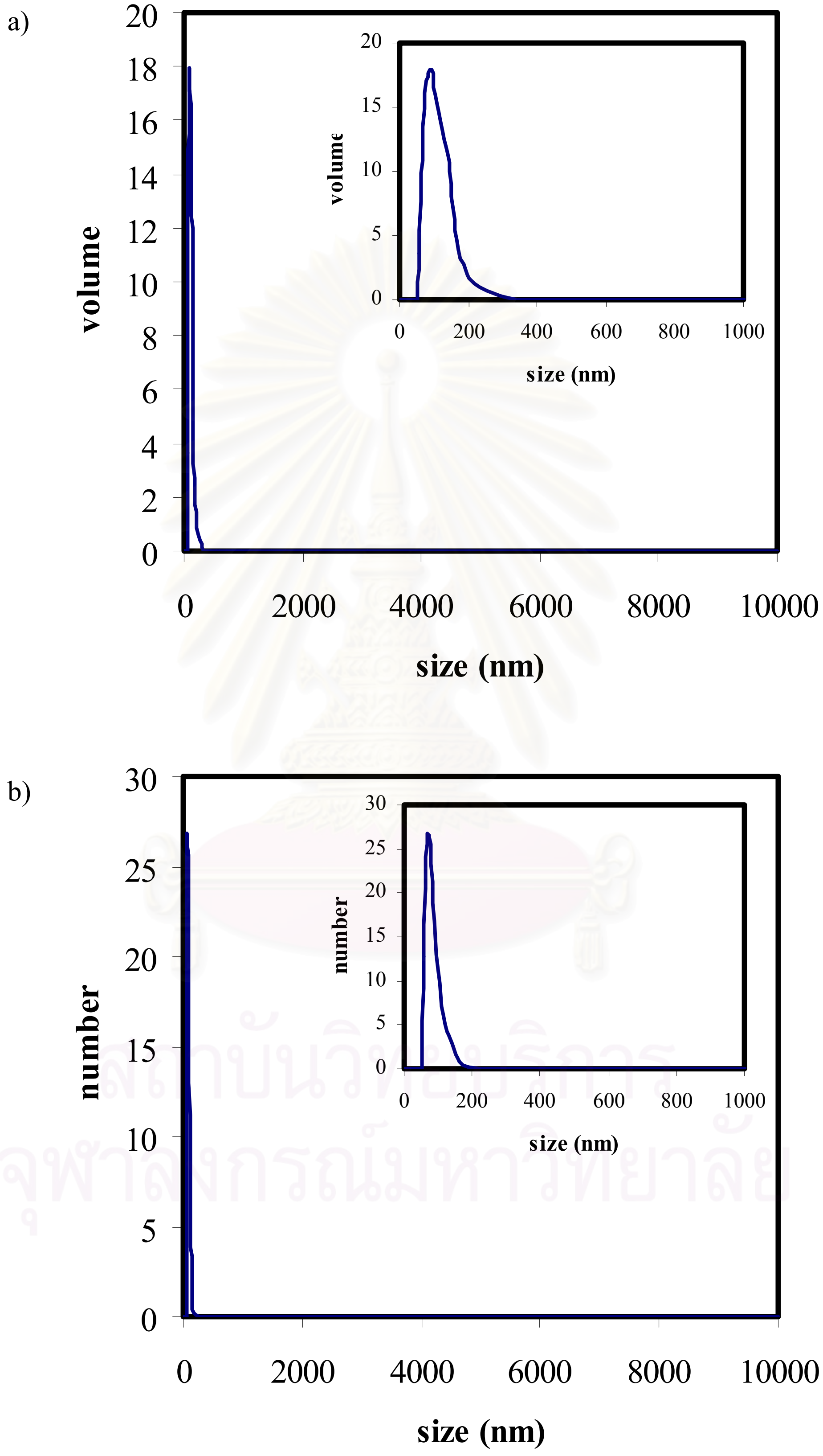
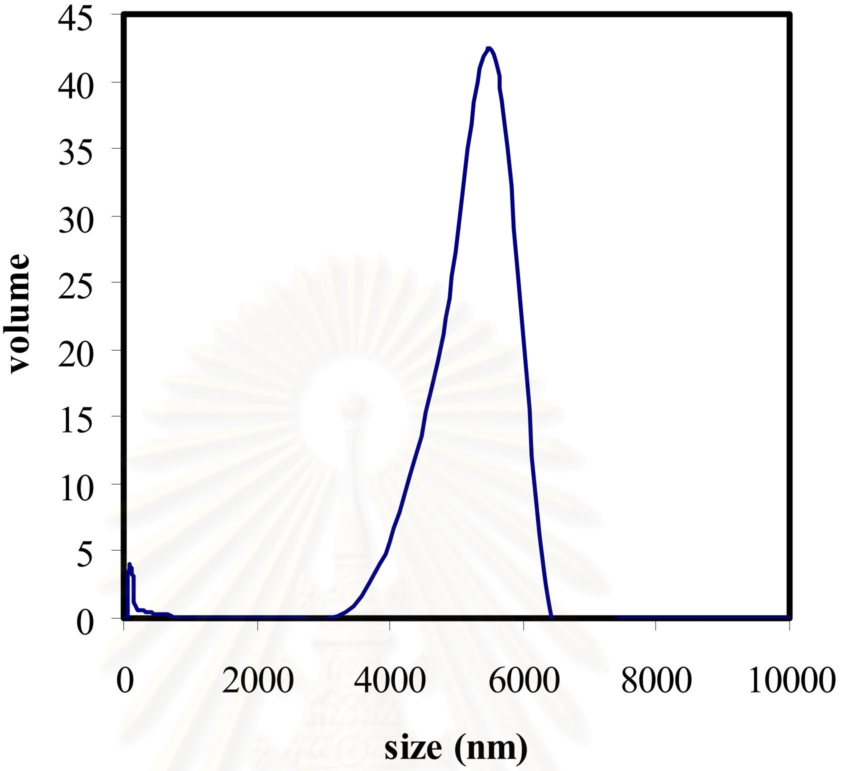


Figure 4.14. Size distribution of T2-titania in term volume (a) and number (b)

a)



b)

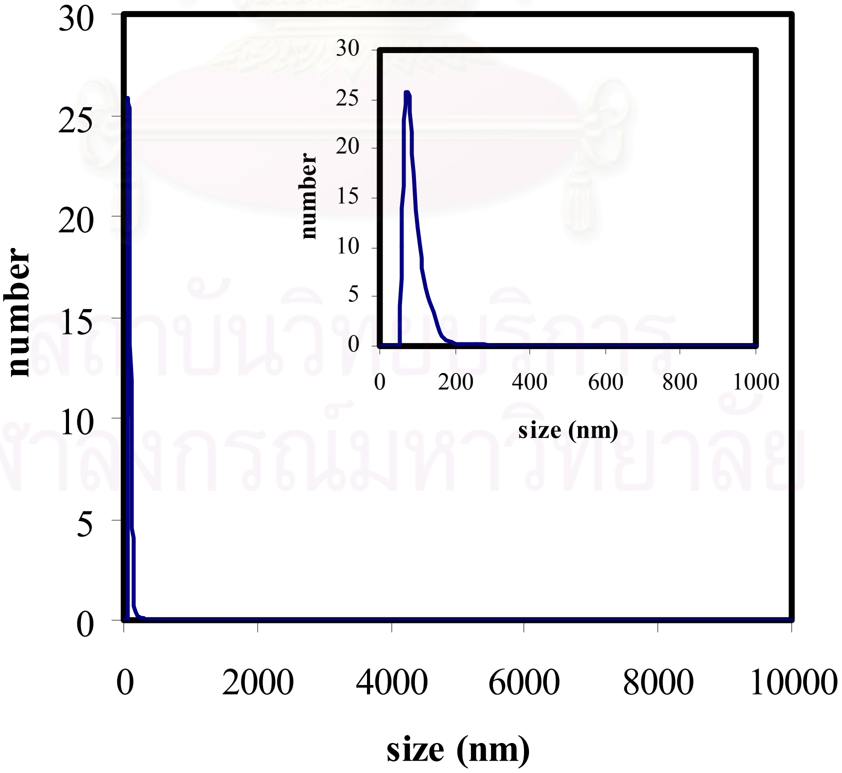


Figure 4.15. Size distribution of N1-titania in term volume (a) and number (b)

4.2 Finding the best catalyst for removal of organic compounds by titanium dioxide in this thesis

In this work, the best titanium dioxide was selected by many considerations such as removal efficiencies, decomposition rate, and/or separation of titanium dioxide from solution.

4.2.1 Removal of methylene blue

Fig. 4.16 shows the results of total Methylene Blue removal using various types of TiO_2. The disappearance of methylene blue from solutions was due to both physical adsorption and photo-oxidation of the organic dye (Xu et al., 1999, Randorn et al., 2004, Houas et al., 2001, Lachheb et al., 2002). Effect of photo-oxidation was singled out and shown in Fig. 4.17. The different initial concentration of methylene blue indicated in the figure 4.17 resulted from the varied adsorption capacity of each TiO_2 used. It was found that M1 adsorbed the highest amount of methylene blue while the opposite result was observed for T1. Ten ppm of methylene blue was degraded within 60 minutes of irradiation time using M2 and T1 types of titanium dioxide powders. The rest of them shows slower degradation rate. Without TiO_2 insignificant removal rate of methylene blue was observed.

In pre-choosing titania from methylene blue removal, we can conclude that M2 and T1 are higher ability than another.

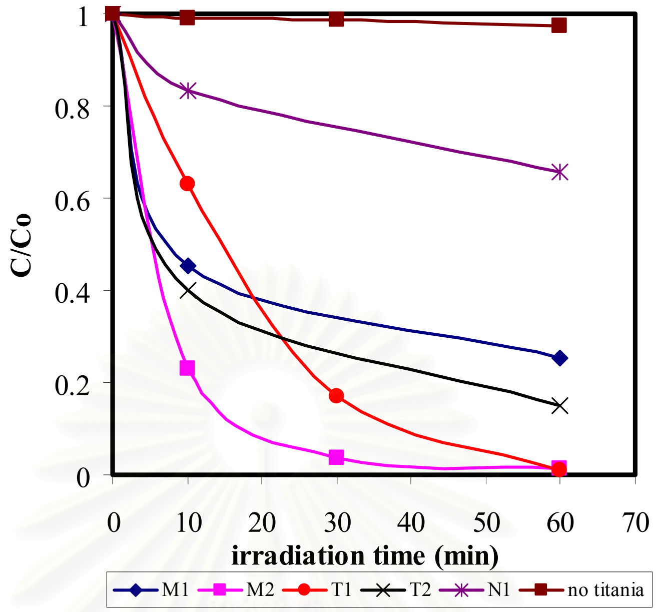


Figure 4.16. Total removal of Methylene Blue with irradiation time using various types of titanium dioxide powders. C and C_0 are defined as Methylene Blue concentrations at specified and initial irradiation time, respectively.

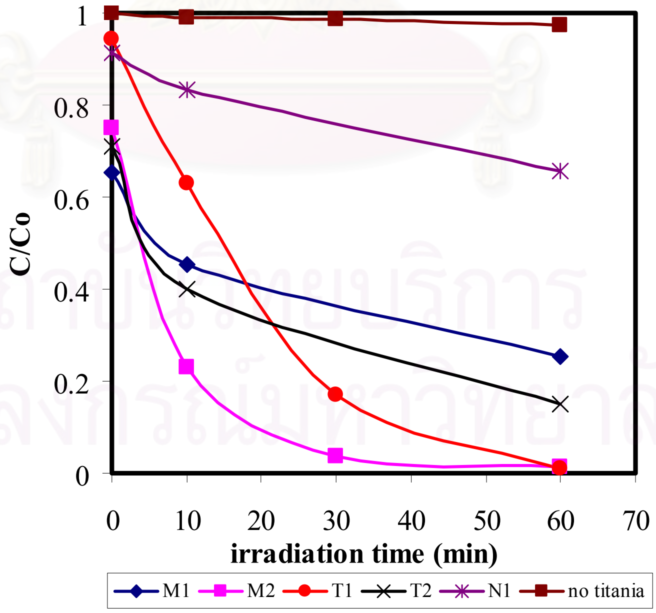


Figure 4.17. Photocatalytic removal of Methylene Blue with irradiation time using various types of titanium dioxide powders. C and C_0 are defined as Methylene Blue concentrations at specified and initial irradiation time, respectively.

4.2.2 Removal of Black 5

Since a Black 5 molecule is of much larger size than methylene blue, adsorption of Black 5 on any of the TiO_2 powders was not observed while many researches using P25-titania (Degussa, anatase and rutile phase, crystallite size = 25.5 nm, BET surface area = 52 m^2/g) reported that large organic dyes (MW > 500) was adsorbed onto P25-titania surface (Beata et al., 2003, Lechheb et al., 2002, and Qamar et al., 2005). Photocatalytic removal of Black 5 by TiO_2 is shown in Fig. 4.18. With T1 type, complete removal of color of Black 5 was evidenced within thirty minutes of UV irradiation so we can summarize that T1 was the best titania from the five titania. However, at 60 minutes, M2 –titania removed the color of Black 5 completely.

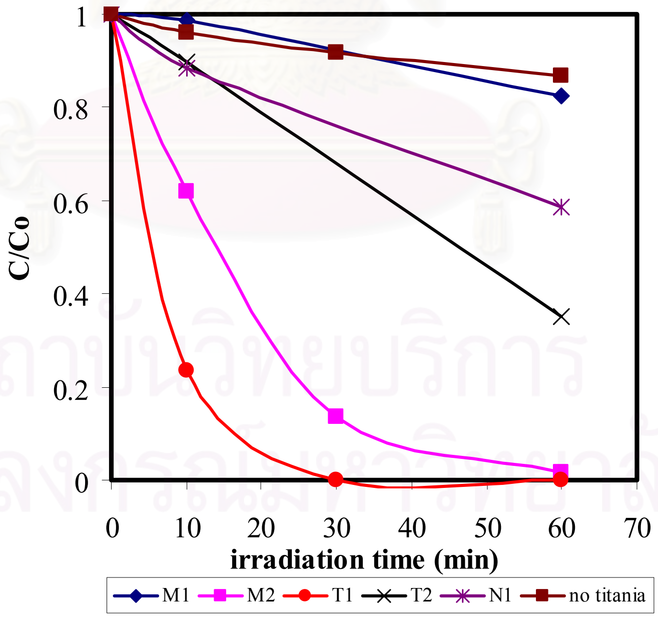


Figure 4.18. Photocatalytic removal of Black 5 with irradiation time using various types of titanium dioxide powders. C and C_0 are defined as Black 5 concentrations at specified and initial irradiation time, respectively.

4.2.3 Removal of lignin

For investigating residual concentration of lignin, a UV/Vis spectrophotometer (Jenway, 6405 UV/Vis) was used and then spectrum 282 nm, which emitted by UV lamp in UV/Vis spectrophotometer, was the suitable wavelength for observing lignin. At spectrum 282 nm, UV range, every titania or 5 titania in this research adsorbed this spectrum which emitted in UV/Vis spectrophotometer so the separation of titania from solution or water was very important. From this cause, we set the easy experiment to test the separation method in this work, centrifuging at 3800 rpm for 15 min. In the testing separation method experiment, each titania was dispersed in the demineralized water and then separated it by centrifuging at 3800 rpm for 15 min and measured this water by UV/Vis spectrophotometer. We found that these titania hard to split from water, except T1-titania. From this phenomenon, it was reasonable to conclude that T1-titania was the best photocatalyst in this work for lignin removal because, in the real treatment system, the energy used for splitting titania or recovery titania was very significant. T1-titania was then selected and applied as a catalyst for the photodegradation of coniferous wood lignin, and the results are shown in Fig. 4.19.

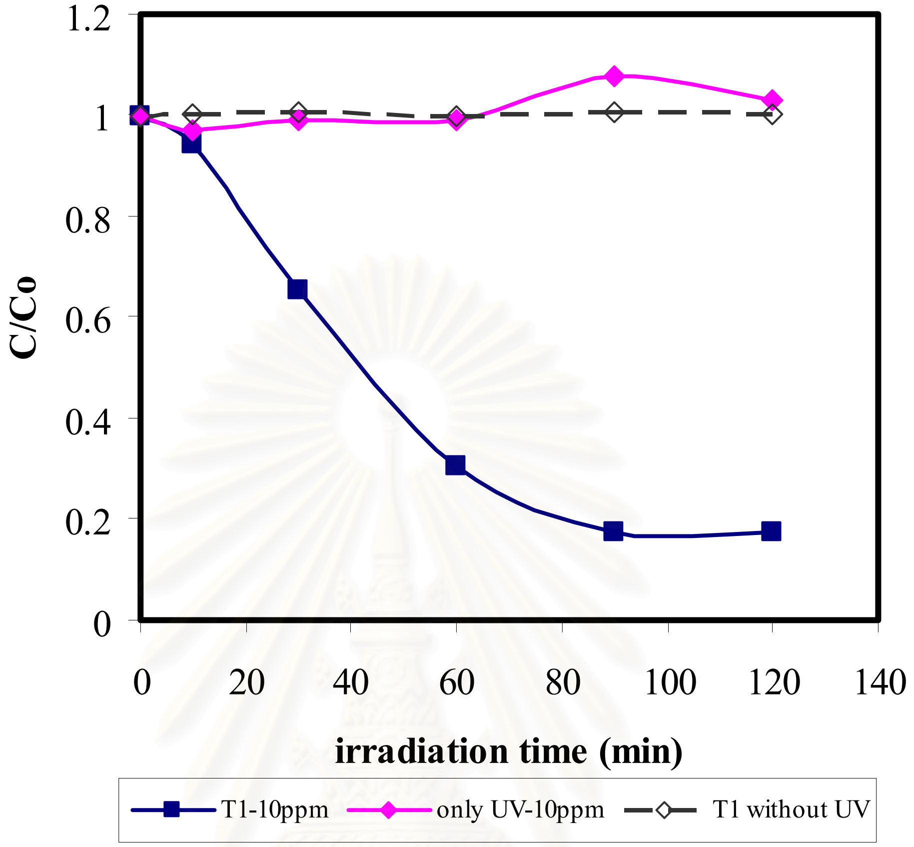


Figure 4.19. Photocatalytic removal of wood lignin with irradiation time using T1 titanium dioxide powders. C and C_0 are defined as wood lignin concentrations at specified and initial irradiation time, respectively.

4.3 Efficiencies and initial decomposition rate of the best titanium dioxide in organic compounds removal

In this research, we defined the efficiencies in 3 forms as follow adsorption efficiency, total removal efficiency, and photocatalytic decomposition efficiency which their meaning were explained in equations 4.1- 4.3.

Adsorption efficiency (%) = $(C_{b,NI}-C_{t,NI})/C_i \times 100$ (4.1)

whereas $C_{b,NI}$ is the average residual concentration (in reactors position B1 and B2 in fig. 3.3) of the colorant in the blank samples in the absence of irradiation = C_i in this case

$C_{t,NI}$ is the average residual concentration (in reactors position T1-T4 in fig. 3.3) of the colorant in the test samples in the absence of irradiation

C_i is the initial concentration of the colorant at the start of the experiment

Total removal efficiency (%) = $(C_{b,Ir}-C_{t,Ir})/C_i \times 100$ (4.2)

whereas $C_{b,Ir}$ is the average residual concentration of the colorant in the blank samples in the irradiation experiment

$C_{t,Ir}$ is the average residual concentration of the colorant in the test samples in the irradiation experiment

Photocatalytic decomposition efficiency (%) = Total removal efficiency (%) - Adsorption efficiency (%) (4.3)

From these equations, we assumed that the adsorption of organic compounds onto titania surface was constant. In the reality, only degree of organic compounds removal (adsorption + decomposition) during the process can be determined, because it was not possible to quantitatively divide between adsorption and decomposition degree (Beata et al., 2003).

The initial decomposition rate was calculated by equation 4.4. The initial concentration for this equation was the residual concentration after 10 min adsorption or after equilibrium adsorption.

$$\text{Initial decomposition rate} = (\Delta C)/(\Delta t) \qquad (4.4)$$

4.3.1 Efficiencies and initial decomposition rate of methylene blue removal

From equations 4.1-4.3, we can find the efficiencies of M2-titania and T1-titania for methylene blue removal and the results were shown in figure 4.20. The initial decomposition rate was calculated by equation 4.4. From fig. 4.20 a, the total removal efficiency of M2 (95.3%) and T1 (96.3%) was slightly different but the photocatalytic decomposition efficiency of M2 (72.6%) lower than T1 (88.1%) about 16% or the adsorption efficiency of M2 (22.8%) higher than T1 (8.2%) almost 3 times. From the result in fig. 4.17, the initial decomposition rate was obtained as follow M2 = 0.50 mg/l/min, and T1 = 0.30 mg/l/min.

From the experiment, we found that titania sludge was changed from white to bluish even though the residual concentration of methylene blue had already reached zero for 2 hours. The our assumption, the adsorption of organic compounds onto titania surface was constant, was support by this reason.

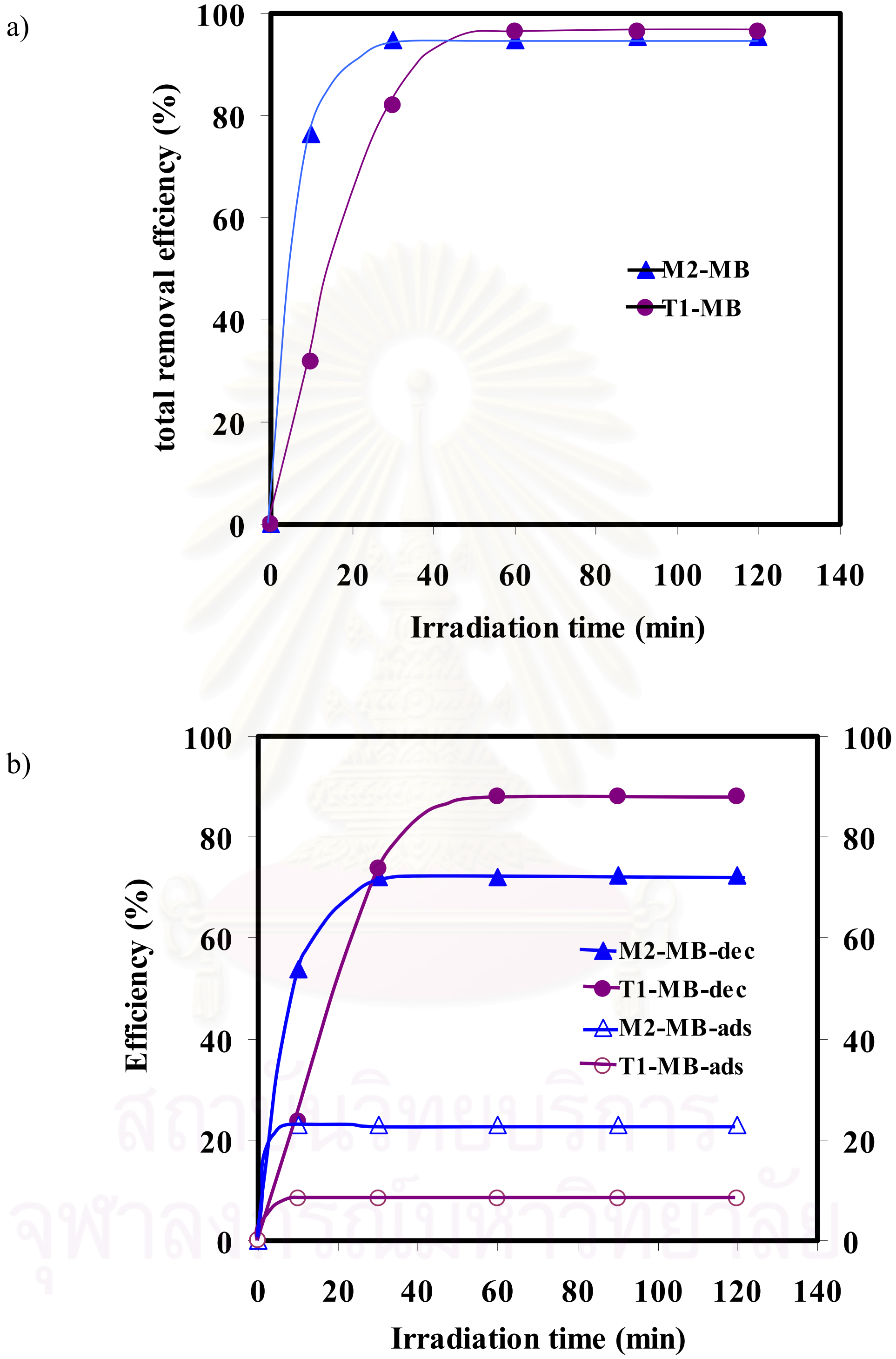


Figure 4.20. The total removal efficiency (a), adsorption efficiency and decomposition efficiency (b) vs. irradiation time of methylene blue

4.3.2 Efficiencies and initial decomposition rate of Black 5 removal

In the Black 5 removal, we found that Black 5 adsorbed onto the titania surface was insignificant so the adsorption efficiency was not obtained. From this reason, it can imply that the total removal efficiency of Black 5 removal was equal to the photocatalytic decomposition efficiency. Figure 4.21 showed total removal efficiency vs. irradiation time. The results of total removal efficiency were 83.9% for M2-titania and 92.5% for T1. The initial decomposition rate of Black 5 was solved from fig. 4.18 and shown as follow M2 = 0.39 mg/l/min and T1 = 0.79 mg/l/min.

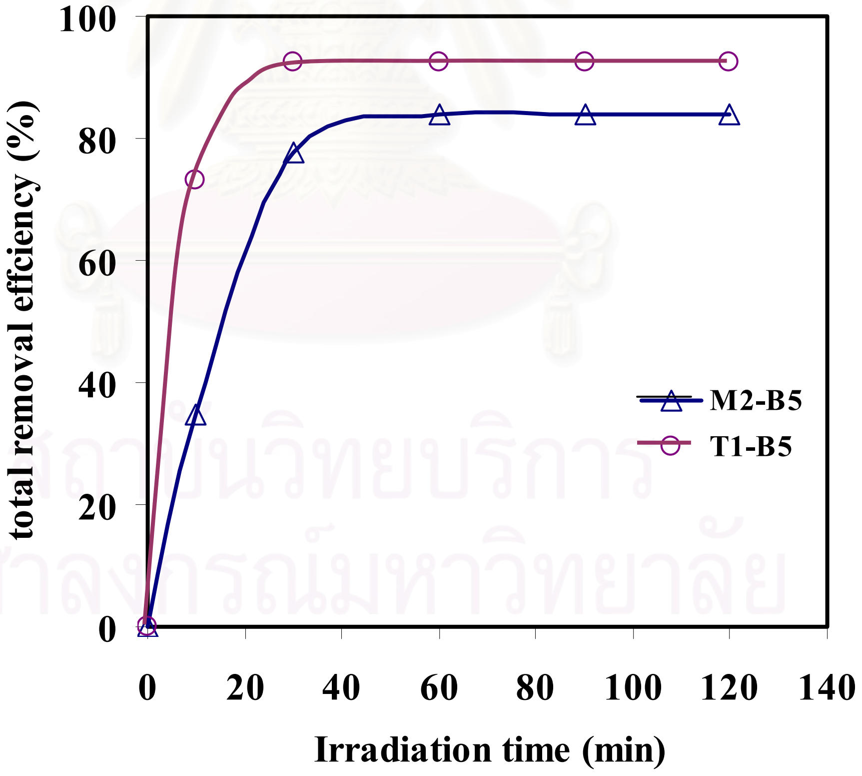


Figure 4.21. Total removal efficiency vs. irradiation time of Black 5

4.3.3 Efficiencies and initial decomposition rate of lignin removal

The best titania for lignin removal was T1-titania. Total removal efficiency of lignin removal was also similar to photocatalytic decomposition efficiency of Black 5 removal because lignin adsorption onto titania surface was obscure in this work. Other reports (Denilson et al., 1998, Chang et al., 2004, and Tanaka et al., 1999) were not performed in the dark experiment too. Total removal efficiency and/or decomposition efficiency (90.24%) vs. irradiation time was shown in fig. 4.22 and initial decomposition rate calculated by equation 4.4 was 0.06 mg/l/min.

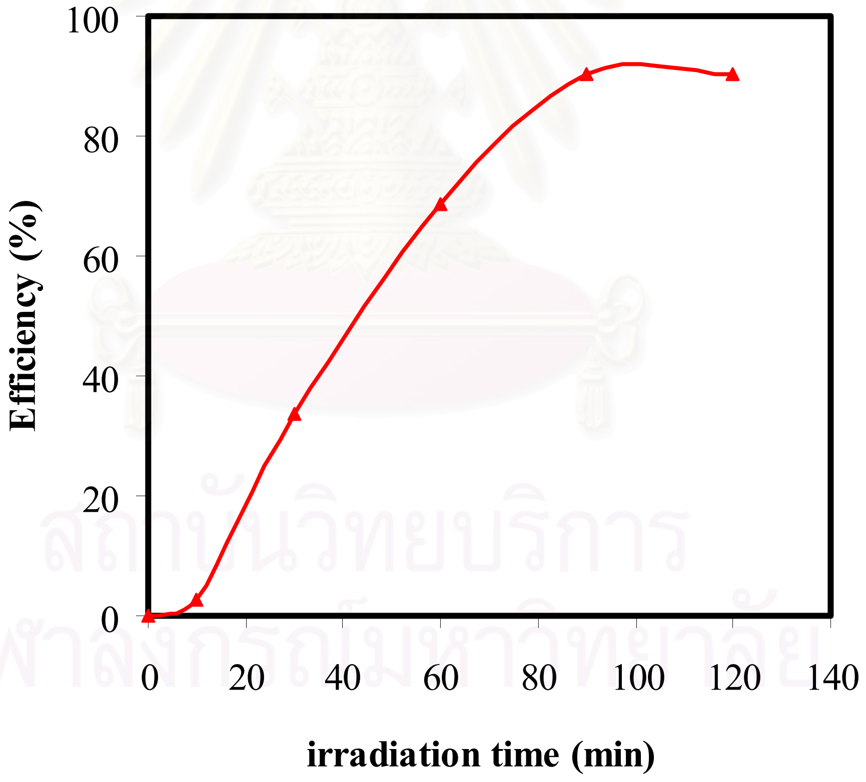


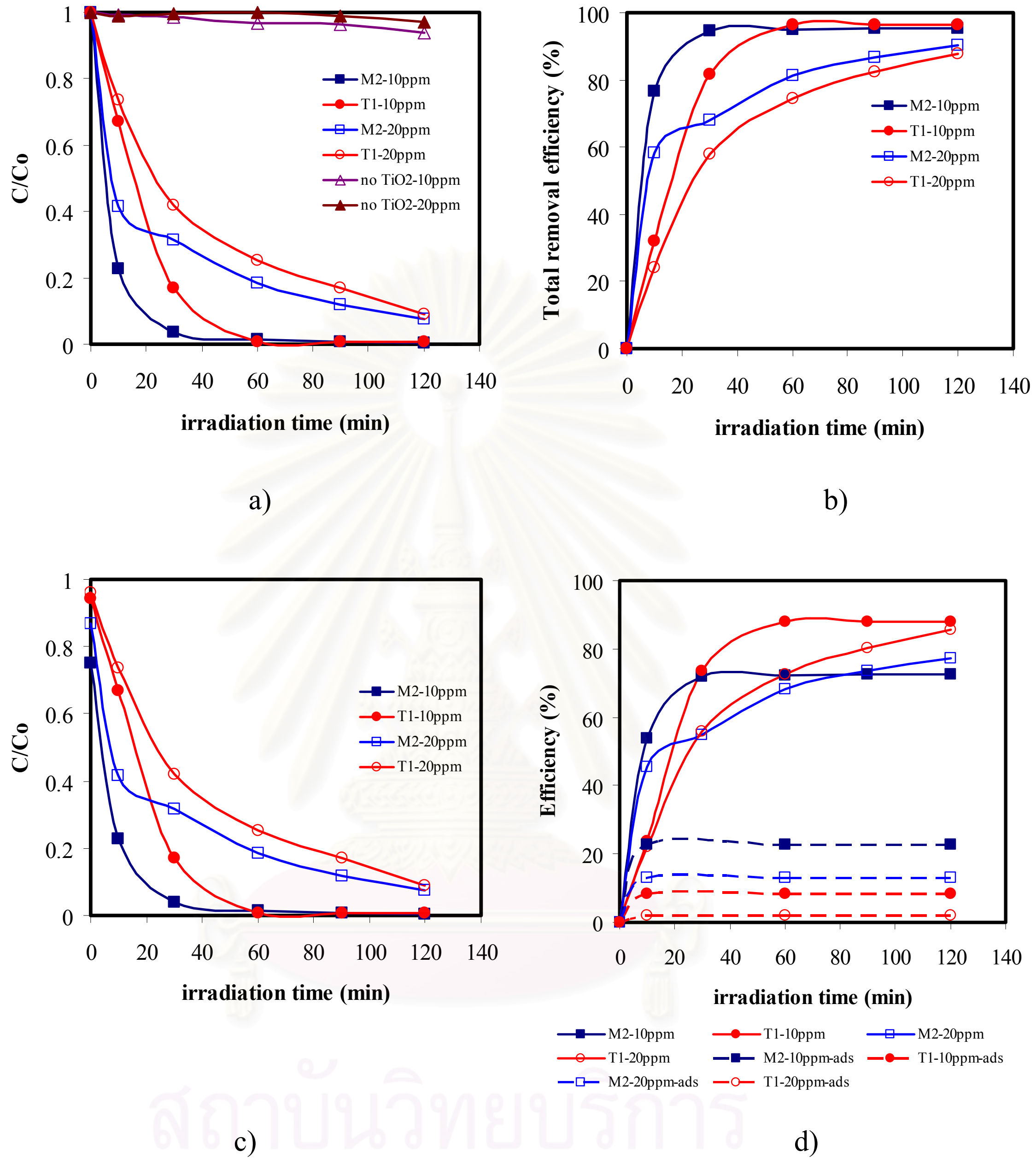
Figure 4.22. Efficiency vs. irradiation time of lignin

4.4 Effect of initial concentration on efficiencies and initial decomposition rate

At the same surrounding, the effect of increasing concentration from 10 ppm to 20 ppm was investigated in this section. In the general theory, since the initial concentration was increased, the rate of disappearance was deceased.

4.4.1 Effect of initial concentration of methylene blue

The comparison between decolorizing methylene blue 10 ppm and 20 ppm was shown in figures 4.23a -4.23d. Both the adsorption value and initial decomposition rate related with common principle. The total removal efficiency, decomposition efficiency and initial decomposition rate were decrease when the initial concentration was increase. Two reasons of this result were liquid turbidity and amount of oxygen dissolve in solution. When the liquid turbidity increase, the intensity of UV light through the quartz reactors decreased so the initial decomposition rate decreased. At the beginning of the experiment, the amount of oxygen dissolve in solution was similar. While the initial concentration increased, the oxygen was increased used for photocatalytic reaction. Thus the total removal efficiency and decomposition efficiency decreased. In the residual concentration of the blank reactor having only photolytic reaction, the 10 ppm methylene blue removal was slightly different from 20 ppm methylene blue removal. However, 20 ppm methylene blue removal was more difficult treated.



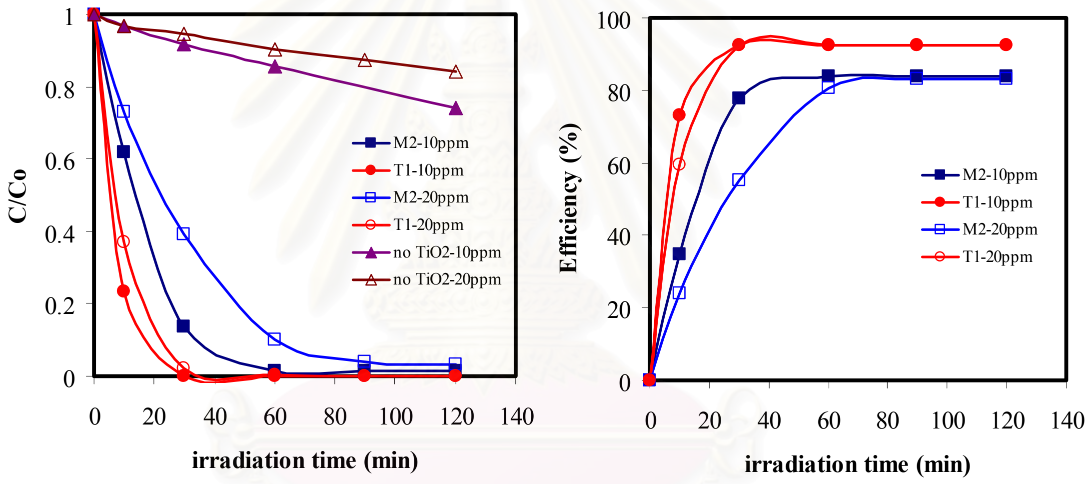
a) b)

c) d)

Figure 4.23. Total removal curves in term normalized concentration (a) and efficiency (b) and photodegradation curves in term normalized concentration (c) and efficiency (d) of methylene blue using M2 and T1 titania powders

4.4.2 Effect of initial concentration of Black 5

When initial concentration of Black 5 was increased, all trend of graph in figure 4.24 were very reasonable. The Graph in fig.4.24 had same trend as fig. 4.23 or the methylene blue removal so the reasons for describing this effect were similar to above. In the same reason, the blank sample which the colorant was eliminated by only UV (no titania) of 10 ppm was easier disappeared.

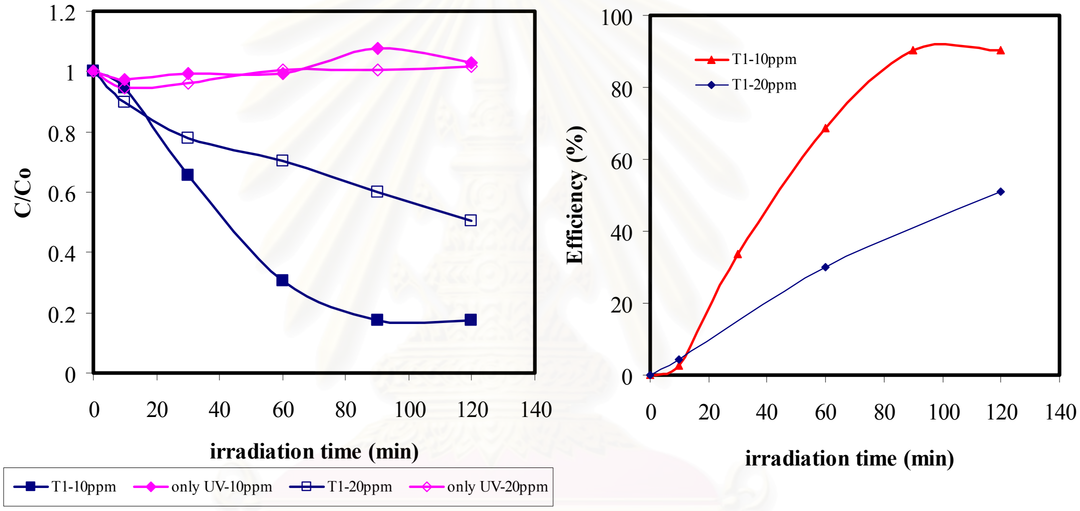


a) b)

Figure 4.24. Total removal curves and/or photodegradation curves in term normalized concentration (a) and efficiency (b) of Black 5 using M2 and T1 titania powders

4.4.3 Effect of initial concentration of lignin

Trend and reasons of lignin removal were similar to methylene blue removal and black 5 removal. Although lignin structure was different and more difficult to eliminate than other, the trend showing in fig. 4.25 was still indifferent. The result of blank sample, only UV effect, when concentration changed was small different.



a)

b)

Figure 4.25. Total removal curves and/or photodegradation curves of lignin using T1 titania powder

4.5 Effect of specific surface area of titania to remove methylene blue and Black5

In figure 4.26, the blank samples (without TiO_2) of methylene blue and Black 5 respectively indicate the level of photolytic decomposition by UV-C light. Obviously, Black 5 was more easily decomposed photolytically than methylene blue because the former had a more bulky structure. Similarly, nanosize titania is expected to photocatalytically decompose Black 5 more easily than methylene blue. In 4.24a, T1-titania decomposed Black 5 faster and better than M2-titania when little adsorption of Black 5 happened. In contrast, figure 4.23a, M2-titania initially decomposed methylene blue faster than T1-titania because the former quickly adsorbed and concentrated methylene blue on it surface. As time passed, T1-titania which adsorbed less methylene blue exhibited a higher decomposition efficiency than M2-titania because the latter (251 m^2/g) had four times the surface area of the former (56 m^2/g), thereby permanently adsorbing more methylene blue molecules.

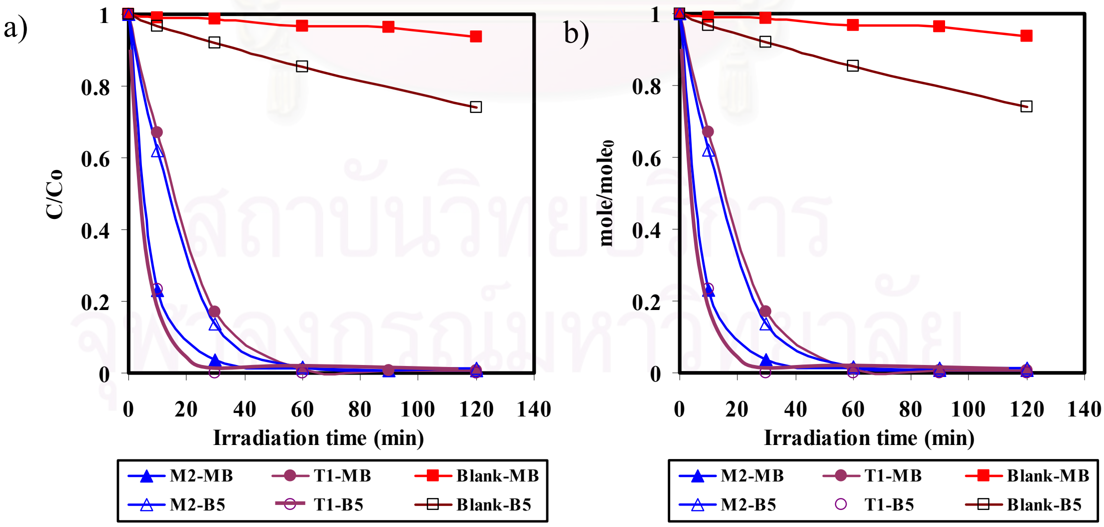
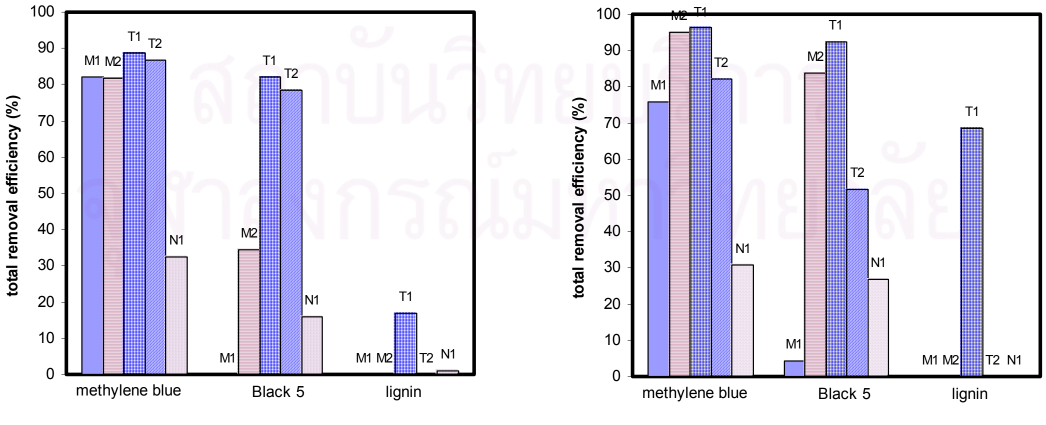


Figure 4.26. Total removal curves of methylene blue and Black 5 in term of normalized concentration (a) and mole (b) using M2 and T1 titania powder

4.6 Applicability of sunlight to photocatalytic decomposition

In this section, we tested the 5 titania by sunlight for methylene blue, Black 5 and lignin removal. In sunlight exposing, 5 titania used in this work can treat methylene blue colorant but M1-titania, rutile phase, could not work in Black 5 removal, however, lignin was eliminated only by T1-titania (N1-titania was very small). The result of T2 shown in figure 4.27 a) was not the same trend as using UV light source (Fig. 4.27 b) because the intensity of spectrum in sunlight was not similar to the UV light source. In figure 4.27 a, T2-titania showed the high total removal efficiency. It was possible that in sunlight had suitable spectrum for activating T2-titania. However, T1 titania still had the highest efficiency and shown the high efficiency when exposed to the UV-C light source.

This present work used fluorescent light also but the result was same as the adsorption experiment. The fluorescent light could not activate these titania because its energy was lower than excited energy which excited a electron at valence-band to conduction-band.



a) b)

Figure 4.27. Total removal efficiency at 60 min of each titania using sunlight (a) and UV-C lamps (b)

4.7 Efficiency of Black 5 removal by titanium dioxide cake layer

The efficiency of Black 5 removal in this method was about 6% but during the generating titania cake layer, T1-titania, this method can prevent titania loss 99.9% or titania loss from this method about 0.1%. Anyway this method was lower efficiency of Black 5 removal than shaking with UV light method because of 2 reasons. First, the solution at the interface between solution and titania cake layer was almost calm or mass transfer in this reaction was very low. The other method had the shaking for well transferring the substance, Black 5. Second reason, the intensity of UV light at the reaction zone (on cake layer) was lower because of the distance between UV lamp and reaction zone, amount of lamps and material of reactor. The distance between UV lamp and reaction zone of this method (12 inches) was longer than the shaking apparatus (7 inches) about two times. This method was used one UV lamp but the other had two UV lamps. The acrylic material was applied for the reactor of this method so the UV light irradiated to the reaction zone only above of the reactor.

CHAPTER V

CONCLUSIONS

5.1 Conclusions

5.1.1 Choosing the best titanium dioxide

This research used 5 titanium dioxide, M1, M2, T1, T2, and N1, as photocatalysts to decompose 3 kinds of organic compounds, methylene blue, Black 5, and lignin. The best titania which effectively decomposed methylene blue were M2 because it could provide the highest initial decomposition rate of 0.50 mg/l/min and T1 because it could provide the highest decomposition efficiency of 88.1%. For eliminating Black 5, T1-titania was the best titania providing the highest total removal efficiency or decomposition efficiency of 92.5% and initial decomposition rate of 0.79 mg/l/min. It was also found that only T1-titania was separatable from water by centrifuging with revolution of 3800 rpm for 15 minutes. In addition, T1-titania could also exhibit high potential to treat water polluted with lignin.

5.1.2 Efficiencies and initial decomposition rate of the best titanium dioxide

From sections 4.2 and 5.1.1, M2 and T1 were selected for further investigation on their efficiencies and the initial decomposition rate. Typical experimental results were listed in Table 5.1. Because the adsorption of Black 5 and lignin was negligibly low it could be assumed that total removal efficiency equaled decomposition efficiency (see definition in equation 4.4).

Table 5.1 Efficiencies and initial decomposition rate of the best titanium dioxide

Organic compound	Titania code	Efficiency (%)			Initial decomposition rate (mg/l/min)
		Adsorption	Total removal	Decomposition	
Methylene blue	M2	22.8	95.3	72.6	0.50
	T1	8.2	96.3	88.1	0.30
Black 5	T1	-	92.5	92.5	0.79
Lignin	T1	-	90.2	90.2	0.06

5.1.3 Applicability of sunlight to photocatalytic decomposition

Besides irradiation using UV light, sunlight and fluorescent light were also applied to test the performance of all titania investigated in the work. The fluorescent light was not enough energy for exciting a electron from valence-band to conduction-band. This system was possible to use outdoor because sunlight could activate titania in this work, especially T1-titania.

5.1.4 Efficiency of Black 5 removal by titanium dioxide cake layer

The new method, deposited T1-titania on the micro filter, was adapted for preventing titania loss. The result of this preventing method was very good result because it can prevent the loss of titania 99.9%. Although this method was good protection of titania loss, the removal efficiency of this method was only 6%. This low removal efficiency was caused by low mass transfer in the reaction and low intensity of UV light at the reaction zone.

5.2 Recommendation for future work

In this work, it was demonstrated that the wastewater treatment system using TiO_2 as photocatalyst was very good alternative because the investigated titania is non-toxic, inexpensive, and environmentally safe. Therefore this system will take place to conventional treatment system. However, photocatalytic oxidation system has a big problem being loss of photocatalyst. Many researches (Bhattacharyya et al., 2004; Haque et al., 2005) try to synthesize TiO_2 supported on the adsorbents such as zeolite, porous glass beads, and pure siliceous.

Thus, in the future, titania-supported using in pack-bed reactor (Arabatzis et al., 2005) or fluidized-bed reactor (Roberto et al., 2000 and 2005) will be the good choice.

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APPENDICES

APPENDIX A

Publications Resulting from This Research Work

PUBLICATIONS

International Proceedings

1. **N. Viriya-empikul**, T. Charinpanitkul, W. Tanthapanichakoon, "Photocatalytic Decomposition of Methylene Blue and Black 5 Reactive Dye Using Nanosize Titania: Effect of Phase and Size of Crystallites," *Proceedings of Regional Symposium on Chemical Engineering (RSCE 2004)*, December 1-3, 2004, Bangkok, Thailand.
2. **N. Viriya-empikul**, T. Charinpanitkul, W. Tanthapanichakoon, "Adsorption Effect on Photocatalytic Decomposition of Methylene Blue and Black 5 on Nanosize Titania," *Proceedings of International Symposium on Nanotechnology in Environmental Protection and Pollution (ISNEPP 2005),* January 12 - 14, 2005, Bangkok, Thailand.

PHOTOCATALYTIC DECOMPOSITION OF METHYLENE BLUE AND BLACK 5 REACTIVE DYE USING NANOSIZE TITANIA: EFFECT OF PHASE AND SIZE OF CRYSTALLITES

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Abstract

Four nanosize TiO_2 photocatalyst samples were used to decompose 2 types of aqueous colorants: methylene blue and Black 5. The titania nanocrystals had different average crystallite sizes (6-30 nm) and phases (anatase and rutile). Each selected aqueous solution and the titania powder of interest (100 mg/l) was poured into a 50-ml quartz photoreactor. Six reactors, including two blanks without titania, were set on a shaker and shone with two ultraviolet lamps. After the titania powder was centrifuged and separated out, the residual concentration of each aqueous colorant at a specified time was measured with UV-Vis spectrophotoscopic technique. The percent removal by simple adsorption and/or decomposition was calculated as a function of light exposure time. The experimental results were compared and discussed with respect to the phase and size of the crystallite. Applicability of natural UV light (weak sunlight source) was checked experimentally and the result compared with the cases of artificial UV-C light.

1. Introduction

In the textile dyeing industry, the pollution by effluent waste water containing residual colorants is a serious environmental problem. To treat the waste water, physical methods (adsorption etc.), biological methods (biodegradation etc.), and chemical methods (chlorination, ozonation etc.) are available [1]. In the last category, heterogeneous photocatalysis is quite promising. Titania is the one of the most popular photocatalysts because it is non-toxic, inexpensive, and environmentally safe. Titania exists in three crystalline structures (anatase, rutile, and brookite phase) which behave differently [2]. Even titania of the same morphology and phase could show different performances which depend on the specific surface area, crystallite size and porous structure.

In this work, the decomposition and adsorption efficiency of 4 different titania samples against two aqueous colorants -- methylene blue and Black 5-- were investigated experimentally and the results discussed with respect to the crystalline phase and average crystallite size of the titania samples.

2. Experimental

2.1 Materials

The chracteristics of the 4 nanosize titanium dioxide samples are listed in Table 1. The experimental unit consists of 6 quartz-tube photoreactors (each with 50 ml effective volume), 4 of which contain 2 mg each of the nanosize titania of interest dispersed in 20 ml of aqueous solution containing 10 ppm of either Methylene Blue (MB) or Black 5 [3] (refer to Fig. 1) The remaining two blank reactors contain only the colorant without any titania. The quartz photoreactors are set on a shaker and shone at by two 30-Watt UV-C lamps (Philips G30T8) at room temperature (Fig. 2). Placed in two different locations in the shaker, the blanks are used to estimate the average photolytic effect, if any, of UV light.

2.2 Experimental Procedure

Four types of experiments were carried out as follows.

Type 1. Tests to find out the photocatalytic decomposition plus adsorption efficiency of each of the nanotitania listed in Table 1 against the colorant (methylene blue or Black 5) after exposure to UV light for either 10 or 60 min. with shaking.

Type 2. Tests to find out photocatalytic decomposition plus adsorption efficiency of each of the nanotitania listed in Table 1 against the colorant (MB or Black 5) after exposure to UV light for either 10 or 60 min. without any shaking.

Type 3. Tests to find out the adsorption efficiency of each of the nanotitania against the colorant (MB or Black 5) without any exposure to light for either 10 and 60 min.

Type 4. Tests to find out the photocatalytic decomposition plus adsorption efficiency of each of the nanotitania against the colorant (MB or Black 5) after exposure to sunlight for 60 min. In this experiment, all four different nanotitania were irradiated simultaneously by the same sunlight.

2.3 Analyses

Before each analysis, TiO_2 powder in the aqueous sample was centrifuged (4000 rpm, 15 min) and separated out. The concentration of either Methylene Blue or Black 5 in the supernatant liquid was measured with a UV-Vis spectrophotometer (Jan Way, 6405 UV/Vis) at wavelength 660 nm or 595 nm, respectively.

2.4 Efficiency

The measured concentration values from each experiment were averaged (see equations 1 and 2) and used to calculate the % removal by adsorption (see equation 3) and % removal by phoytocatalytic decomposition (see equation 4). The average concentration of the colorant in the blank tubes was computed from:

$$C_b = (C_{B1}+C_{B2})/2 \qquad (1)$$

where C_b is the average residual concentration of the colorant in the blank tubes (without photocatalytic reaction), C_{B1} and C_{B2} are the residual concentrations of the colorant in the blank tubes (without photocatalytic reaction) placed at positions B1 and B2, respectively. The average concentration of the colorant in reactor tubes was computed from

$$C_t = (C_{T1}+C_{T2}+C_{T3}+C_{T4})/4 \qquad (2)$$

where C_t is the average residual concentration of the colorant in the photoreactor tubes (after photocatalytic reaction), C_{T1},C_{T2}, C_{T3}, and C_{T4} are the residual concentrations of the colorant in the tubes (after photocatalytic reaction) placed at positions T1, T2, T3, and T4, respectively.

2.4.1 Adsorption Efficiency

The % removal efficiency by adsorption (shown in Table 2) was computed from the avearge concentrations of the colorant in type 3 experiment as follows:

$$\% \text{ removal} = (C_b-C_t)/C_i \times 100 \qquad (3)$$

where C_i is the initial concentration. The results shown in the column 'Average adsorption (without light source)' of Table 2 were the average values obtained from the % removal at 10 min. and 60 min. because the adsorption of the colorant on the nanotitania surface was found to take place rapidly and the values at 10 min and 60 min differed insignificantly.

2.4.2 Photocatalytic Decomposition Efficiency

The % removal efficiency calculated from equation (3) includes the effect of both photocatalytic decomposition and adsorption. Therefore, the % removal efficiency by decomposition only is given by:

$$\% \text{ removal by decomposition} = \% \text{ removal (eq.3)} - \% \text{ removal by adsorption} \qquad (4)$$

3. Results and discussion

3.1 Adsorption Efficiency

3.1.1 Adsorption of Methylene Blue

In Table 2 the values of % removal of MB by adsorption are the average of those at 10 min. and 60 min. because they were found to differ only slightly. This means that adsorption equilibrium was essentially reached after only 10 min. from the start. The finding is consistent with J-M Herrmann et al. who reported that adsorption equilibrium was reached within 1 h, whatever the initial concentrations [1]. The adsorption results are as follows:

M1 34.81% > T2 28.43% > M2 22.99% > T1 8.32%

As expected, M1 with the rutile phase was the best adsorbent for MB. Among the 3 nanocrystals with the anatase phase, T2 could adsorb more MB than M2 and T1 because T2 possesses the highest specific surface area.

3.1.2 Adsorption of Black 5

In this adsorption experiment, we observed that the titania powder separated out by centrifugation retained its white color. This phenomenon was consistent with the finding that the adsorption of Black 5 on the four nanotitania was negligible because Black 5 molecule is much more bulky than MB.

3.2 Photocatalytic Decomposition

In this work, the decomposition experiements encompassed both types 1 and 2. The reported % decomposition efficiency of eq. 4 is the average of types 1 (with shaking) and 2 (without shaking) at the same reaction time because in the real world the photocatalytic treatment of industrial waste water can be expected to take place in diverse flow situations such as turbulent flow, laminar flow and no flow in the system.

3.2.1 Decomposition of Methylene Blue

Table 2 revealed that after the first 10 min., M2 was the most active at 55.88%. When the photocatalytic reaction was continued up to 1 h, T1 became the most active at 83.61%. By the way, S. Wongnawa *et al.* [2] and J-M Herrmann *et al.* [1] investigated the bleaching of methylene blue by Degussa P25 titania having comparable size as T1. They reported that more than 80% of MB could be degraded after 2 h. Since P25 was a mixture of anatase (~ 80%) and rutile phase (~20%), their result is deemed consistent with ours because T1 has 98% anatase.

3.2.2 Decomposition of Black 5

In the photocatalytic decomposition of Black 5, T1 was found to be the most active at both reaction times (10 and 60 min).

3.2.3 Decomposition of Methylene Blue vs. Black 5

At 10 min. the corresponding photocatalytic decomposition efficiency of MB by M1, M2, and T2, respectively, was higher than that of Black 5 because of the enhancement effect of MB adsorption. At 60 min., however, the decomposition of Black 5 by the same photocatalysts was higher than that of Methylene Blue with the exception of M1 which is of rutile phase. The photocatalytic decomposition of Black 5 happened more easily because its molecular structure is bulkier than MB, thereby requiring less energy for breaking the chemical bonds.

3.3 Checking applicability of photocatalytic decomposition in normal situation

If possible, sunlight should be used as the light source for the above photocatalytic reaction because it is widely and freely available and plentiful during daytime. Therefore we decided to test the performance of these nanotitania with respect to sunlight. Our preliminary results show that sunlight was less effective for the decomposition of MB by T1 and T2 (less than 65%) than Black 5 (more than 80%) after 60-minute exposure to weak sunlight. As mentioned above, MB is harder to decompose than Black 5.

4. Conclusion

M1 is a better adsorbant but poorer photocatalyst than the other 3 because M1 is of ruitle phase. The adsorption effect of the nanotitania is more pronounced for the smaller molecule, MB, but the decomposition effect is greater for the larger molecule, Black 5. Though sunlight is less effective for the decomposition of MB than Black 5, it is a useful source of clean abundant energy.

In any case, the present photocatalytic method still faces a serious problem of nanotitania loss by elution. This problem would be solved if the nanosize titania can be immobilized on certain highly mesoporous materials [4].

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Table 1 Physical characteristicss of titania samples

Code name	Crystal phase	TiO$_2$ w% content	Average crystallite size (nm)	Crystal shape	Specific surface area (m^2/g)
M1[+]	Rutile	99.9	40x10Ø	cylinder	122-170
M2[+]	Anatase	99.9	15	sphere	220-229
T1[Δ]	Anatase	98	30	sphere	52-59
T2[Δ]	Anatase	20 (in water)	6	sphere	260[*]

[+] Titania samples and their properties are provided by MODERN DYESTUFFS & PIGMENTS CO., LTD

ΔTitania samples and their properties are provided by Prof. Yasushige Mori, Doshisha University

* Estimated from the average crystal size and morphology

Table 2 % Removal of **methylene blue**

Code name	Average decomposition by UV (at 10 min)	Average decomposition by UV (at 60 min)	Average adsorption (without light source)	Decomposition by sunlight (at 60 min)
M1	19.52	39.19	34.81	48.60
M2	55.88	71.40	22.99	60.19
T1	28.32	83.61	8.32	51.41
T2	32.09	56.28	28.43	59.83

Table 3 % Removal of **black 5**

Code name	Average decomposition by UV (at 10 min)	Average decomposition by UV (at 60 min)	Decomposition by sunlight (at 60 min)
M1	~ 0.00	7.23	~ 0.00
M2	23.70	79.13	37.65
T1	42.34	88.28	82.56
T2	27.99	77.13	99.92

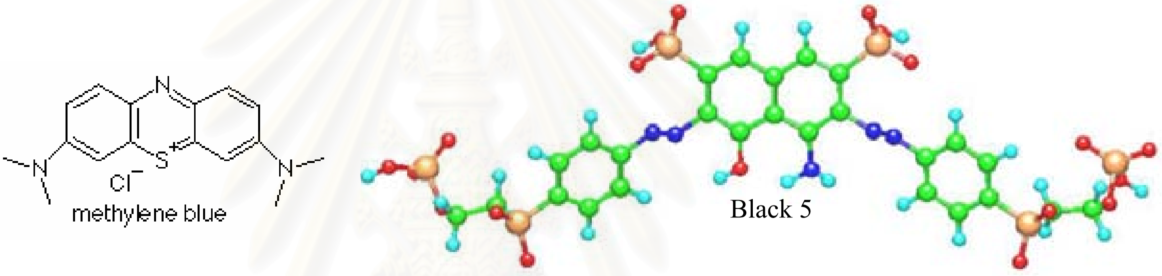

Fig.1. Structures of methylene blue and Black 5

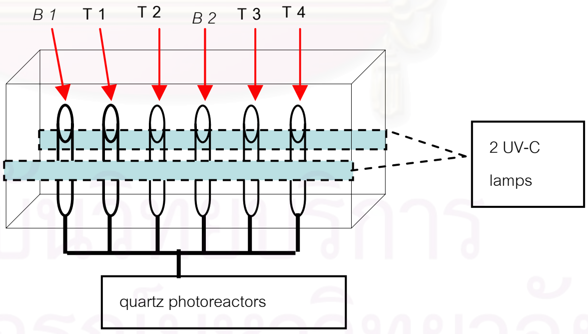

Fig.2. Arrangement of reactors and lamps in the cyclic shaker

ADSORPTION EFFECT ON PHOTOCATALYTIC DECOMPOSITION OF METHYLENE BLUE AND BLACK 5 ON NANOSIZE TITANIA

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Abstract

Two nanosize TiO_2 photocatalysts, with the same anatase phase but different average crystallite size and specific surface area, were used to photocatalytically decompose 2 types of dyes: aqueous methylene blue and black 5. M-Titania and T-Titania nanocrystals have average crystallite sizes of 15 and 30 nm, respectively. Twenty milliliters of each aqueous dye solution containing 2 milligrams of the individual titania powder (100 mg/l) was poured into six identical quartz photoreactors. The reactors, including two blanks without titania, were set on a mechanical shaker and shone with two 30-Watt UV-C lamps (Philips G30T8). Similar experiments were also carried out without shaking during illumination. The residual concentration of the aqueous solution against time was measured with UV-Vis spectroscopic technique. The normalized concentration, and removal efficiency based on pure adsorption and overall removal efficiency were obtained as a function of illumination time. The rates of decomposition of the two colorants were compared and discussed with respect to the adsorption effect. It was found that adsorption significantly enhances the overall removal efficiency.

1. Introduction

Pollution is a serious problem of the world. Wastewater from the textile industry is a dramatic source of esthetic pollution, of eutrophication and of perturbation in the aquatic life (Jean-Marie Herrmann et. al., 2001 and 2002). Many treatment methods were used to remove aqueous organic pollutants such as adsorption (P.B. Dejohn and R.A. Hutchins, 1976), biological methods (S.S. Patil and V.M. Shinde, 1988 and A.T. More et. al., 1989) and chemical methods (chlorination, ozonation) (Y.M. Slokar and A.M. Le Marechal, 1998). These methods had several disadvantages, for example, long reaction time, sludge formation, corrosion, and even toxic substances. UV/TiO_2 photocatalytic method was a good candidate because of TiO_2 is non-toxic and environmentally safe. In this method, the hydroxyl radicals ($OH^{\cdot}$) and hydroperoxyl radicals ($HO_2^{\cdot}$) were produced (Eqs. a-f) for eliminating organic pollutants (Hoeben W. F. L. M., 2000).

$$2H_2O + 4h^+ \rightarrow 4H^+ + O_2 \tag{a}$$

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2 \tag{b}$$

$$H_2O + h^+ \rightarrow OH^{\cdot} + H^+ \tag{c}$$

$$OH^- + h^+ \rightarrow OH^{\cdot} \tag{d}$$

$$O_2 + e^- \rightarrow O_2^- \tag{e}$$

$$O_2^- + H^+ \rightarrow HO_2^{\cdot} \tag{f}$$

while h^+ is a hole on TiO_2 surface and e^- is an excited electron on TiO_2 surface. The photocatalytic intermediate products of Black5 besides CO_2 and H_2O were unknown. However Jean-Marie Herrmann et. al., 2001 and 2002 investigated and reported 7 types of intermediates from methylene blue. After 6 hours, these intermediates did not completely disappear.

In this article, UV/TiO_2 method was investigated to see the effect of adsorption of two different organic dyes on the decomposition of methylene blue and Black 5 on various nanotitania.

2. Experimental

2.1 Materials

An artificial aqueous solution of methylene blue or Black 5 (fig.1) was decomposed by two nanotitania, whose properties are shown in table 1.

2.2 Photoreactor and light source

Six photoreactors were made of 50-ml quartz tubes, of which 4 photoreactors contained 20 ml dye solution and 2 mg nanotitania. The remaining two blank reactors contained only the dye solution without any titania, for checking the photolysis effect. All quartz photoreactors were set on a shaker and shone at by two 30-watt UV-C lamps (Philips G 30T8) at room temperature (fig. 2). Similarly the adsorption of the dye (methylene blue or black 5) on the nanosize titania was investigated using the same procedure but without any irradiation.

2.3 Analyses of residual concentration

Before each analysis, TiO_2 powder in the aqueous sample was centrifuged (3500 rpm, 15 min) and separated out. The residual concentration of either methylene blue or black 5 in the supernatant liquid was measured with a UV-Vis spectrophotometer (Jan Way, 6405 UV/Vis) at wavelength of 660 nm or 595 nm, respectively.

2.4 Efficiency

2.4.1 Total removal efficiency

The total removal efficiency of the dye from the solution by the titania at any time θ was determined from the change in the residual dye concentration in the blank and the test samples after UV irradiation. This efficiency excludes the photolytic decomposition due to UV irradiation.

$$\text{Total removal efficiency (\%)} = (C_{b,Ir}-C_{t,Ir})/C_i \times 100 \qquad (1)$$

whereas $C_{b,Ir}$ is the average residual concentration (in reactors B1 and B2 in fig. 2) of the colorant in the blank samples in the irradiation experiment

$C_{t,Ir}$ is the average residual concentration (in reactors T1-T4 in fig. 2) of the colorant in the test samples in the irradiation experiment

C_i is the initial concentration of the colorant at the start of the experiment

2.4.2 Adsorption efficiency

Similarly, the adsorption efficiency of the dye on the titania was obtained as above but in the absence of irradiation. The adsorption efficiency at time θ was calculated from

$$\text{Adsorption efficiency (\%)} = (C_{b,NI}-C_{t,NI})/C_i \times 100 \qquad (2)$$

whereas $C_{b,NI}$ is the average residual concentration of the colorant in the blank samples in the absence of irradiation = C_i in this case

$C_{t,NI}$ is the average residual concentration of the colorant in the test samples in the absence of irradiation

2.4.3 Photocatalytic decomposition effciency

The apparent photocatalytic decomposition efficiency of the titania at time θ was determined as the difference between the total removal efficiency and the adsorption efficiency

3. Results and discussion

3.1 Methylene blue removal

The completion of methylene blue removal was obtained after about 30 min for M-Titania and 1 hr for T-Titania when the residual concentration equals zero. Jean-Marie Herrmann et. al. (2001 and 2002) and Chamnan R. et. al. (2004) showed that the complete removal of methylene blue by P-25 titania was obtained after 1 hour and more than 8 hours, respectively. In figures 3 and 4, M-Titania exhibited higher methylene blue adsorption capacity than T-Titania. However the equilibrium adsorption of methylene blue in this work was reached within 10 min. Jean-Marie Herrmann et. al. (2001 and 2002) reported that equilibrium adsorption of methylene blue was reached within 1 hr. While Chamnan R. et al. (2004) reported that the adsorption of methylene blue took place almost instantly. When we calculated the specific surface areas of M-Titania and T-Titania by assuming non-porous and spherical shape, the calculated values equaled 104 and 52 m^2/g, respectively. However specific surface areas of M-Titania and T-Titania obtained from BET measurement equaled 229 and 59 m^2/g, respectively. From the big difference in the specific surface area, it is reasonable to assume that M-Titania had non-spherical irregular shape resulting in higher adsorption area. During the experiment, we found that both titania could significantly adsorb methylene blue because the color of both titania was changed from white to bluish even though the residual concentration of methylene blue had already reached zero for 2 hours. This means that some adsorbed methylene blue molecules were not decomposed on the titania surface because methylene blue could form H-bonds on the titania surface thus preventing methylene blue from contacting the active site on the titania. Fig.4 reveals that the final catalytic decomposition efficiency of T-titania was higher than M-titania.

3.2 Black 5 removal

Complete Black 5 removal happened after about 1 hr and 30 min for M-Titania and T-Titania, respectively (figures 3 and 4). This result was contrary to the methylene blue removal. Since black 5 molucules are more bulky than methylene blue, both titania could not effectively adsorb Black 5, and the removal of Black 5 was mainly caused by photocatalytic decomposition. Fig.4 confirms that T-Titania had higher decomposition efficiency than M-Titania.

3.3 Photocatalytic decomposition of methylene blue versus Black 5

In figure 3a, the blank samples (without TiO_2) of Black 5 and methylene blue indicate the level of photolytic decomposition by UV-C light. Obviously, Black 5 was more easily decomposed photolytically than methylene blue because the former had a more bulky structure. Similarly, nanosize titania is expected to photocatalytically decompose Black 5 more easily than methylene blue. In fig.3(b), T-titania decomposed Black 5 faster and better than M-titania when little adsorption of Black 5 happened. In contrast, M-titania initially decomposed methylene blue faster than T-titania because the former quickly adsorbed and concentrated methylene blue on it surface. As time passed, T-titania which adsorbed less methylene blue exhibited a higher decomposition efficiency than M-titania because the latter had four times the surface area of the former, thereby permanently adsorbing more methylene blue molecules.

4. Conclusion

Having a higher specific surface area, M-titania is a better methylene blue adsorbent but poorer photocatalyst than T-Titania. Since UV-light without photocatalysts can decompose Black 5 better than methylene blue, it can be concluded that the bulkier Black 5 breaks down more easily. Interestingly, a portion of the adsorbed methylene blue molecules would not be decomposed on both M-Titania and T-Titania. According to Fig.1, either end of a methylene blue molecule can form H-bonds with the oxygen atoms on the titania surface. Once anchored at both ends by H-bonds, the rest of the methylene blue molecule could be restricted in its movement and is prevented from contacting the active sites on the titania surface. This phenomenon is not observed in Black5 because it was not absorbed by either titania. Though photocatalysis can decontaminate colored wastewater, more investigation into the degradation intermediates is necessary.

Acknowledgement

The authors are grateful to MODERN DYESTUFFS & PIGMENTS CO., LTD and Prof. Mori Yasushige Doshisha University for providing the nanotitania samples. Partial financial support from TRF-RTA Project of W.T. is acknowledged. Useful discussion with Mr. Kajornsak Faungnawakij is acknowledged.

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Table 1 Physical characteristicss of titania samples

Code name	Crystal phase	TiO_2 w% content	Average crystallite size (nm)	BET surface area (m^2/g)
M^+	Anatase	99.9	15	229
T^Δ	Anatase	98	30	59

$^+$Titania samples and their properties are provided by MODERN DYESTUFFS & PIGMENTS CO., LTD

$^\Delta$Titania samples and their properties are provided by Prof. Yasushige Mori, Doshisha University

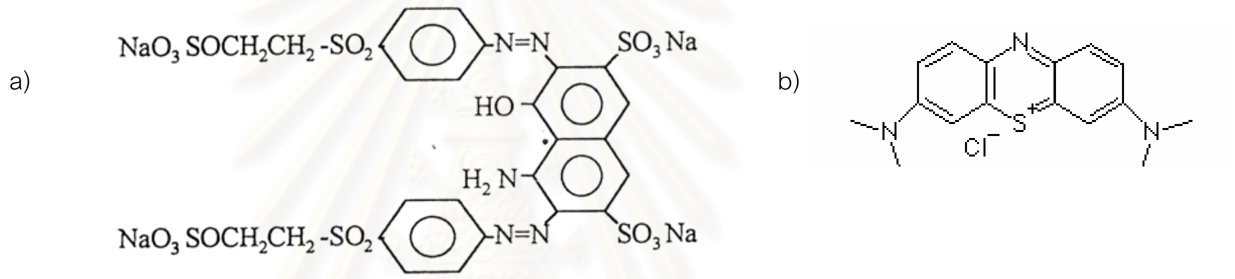


Fig.1. Structures of dyes: a) Black 5 and b) methylene blue

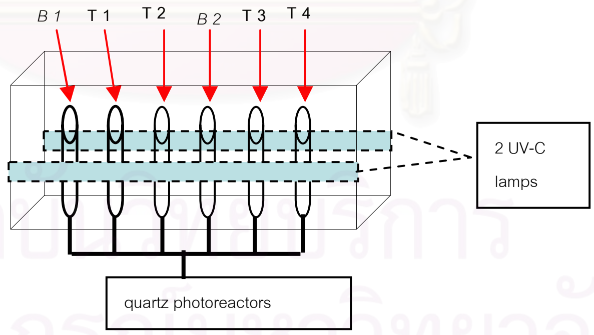


Fig.2. Arrangement of reactors and lamps in the shaker

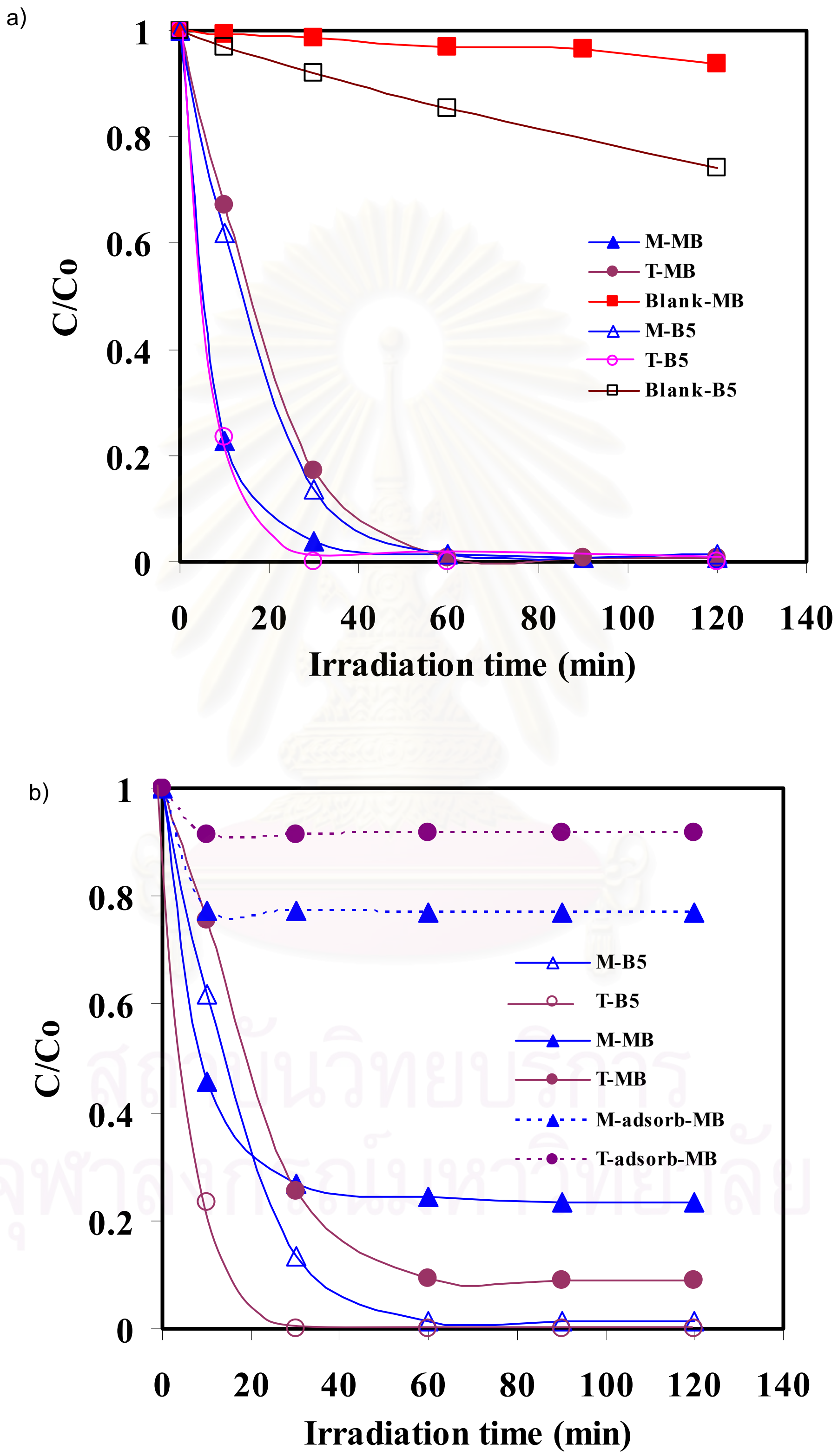


Fig.3. Normalized residual concentration vs. irradiation time a) combined adsorption and decomposition effect b) individual effect

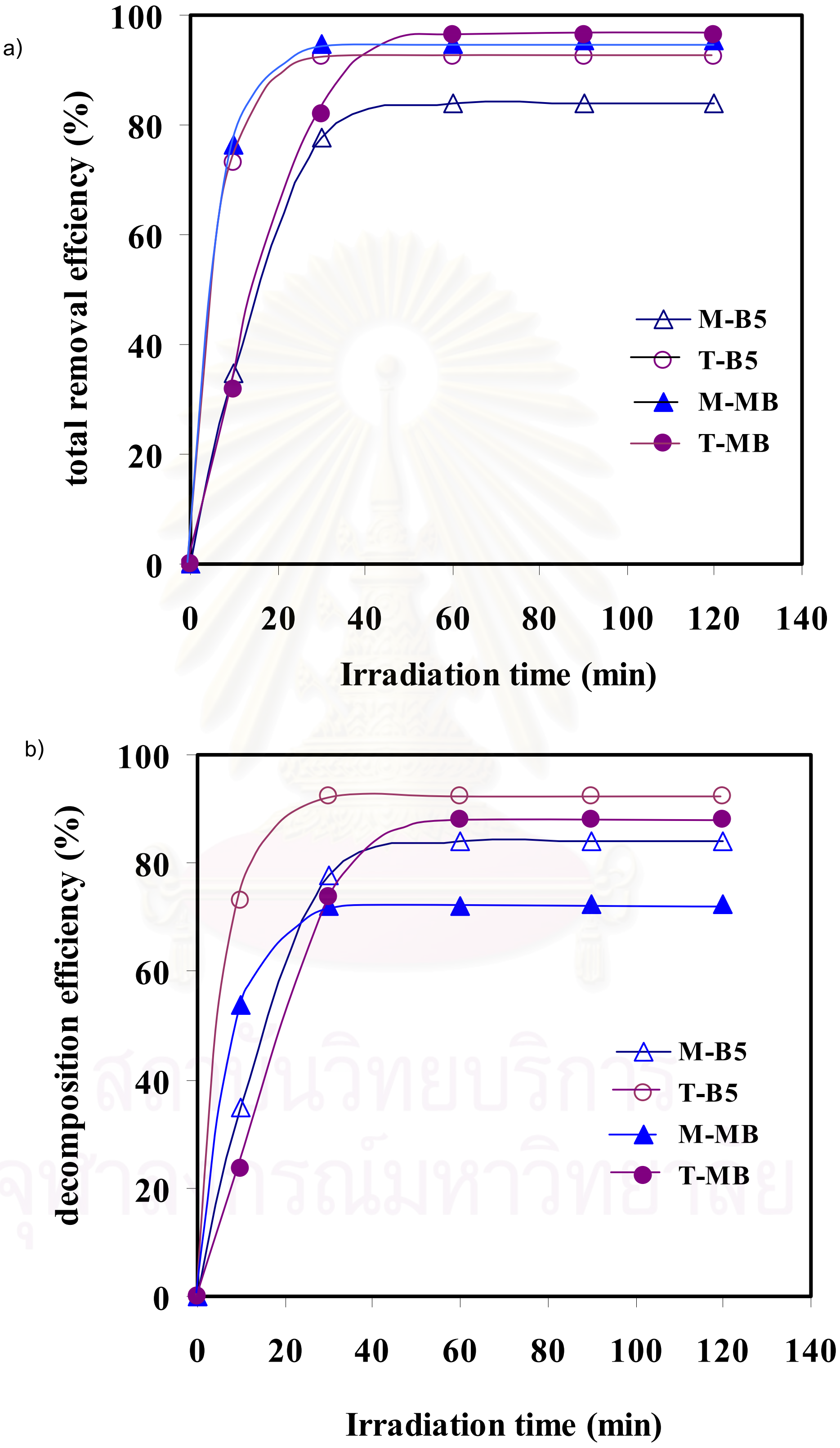
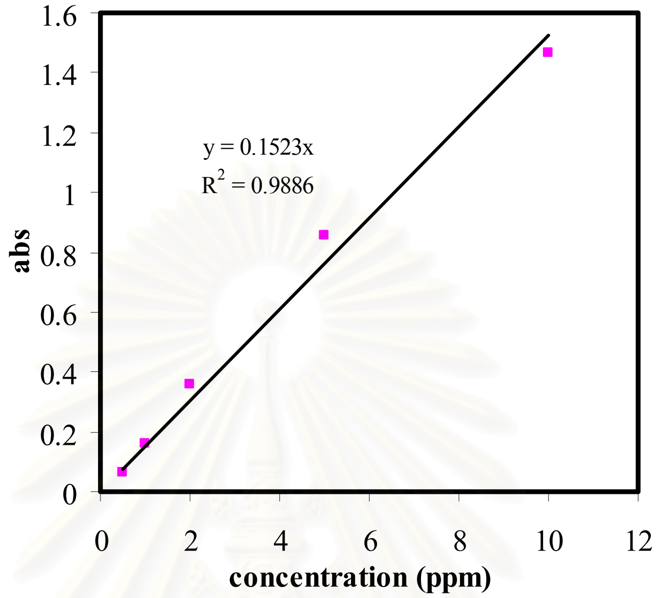


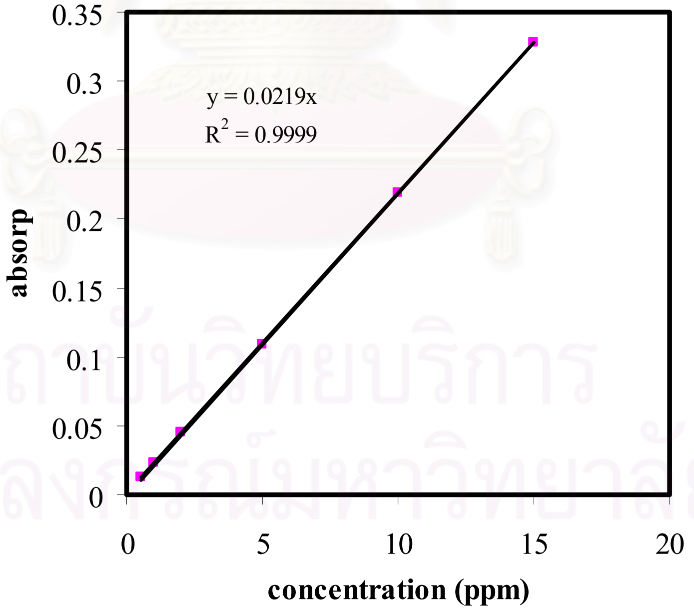
Fig.4. Total removal efficiency (a) and decomposition efficiency (b) vs. irradiation time

APPENDIX B

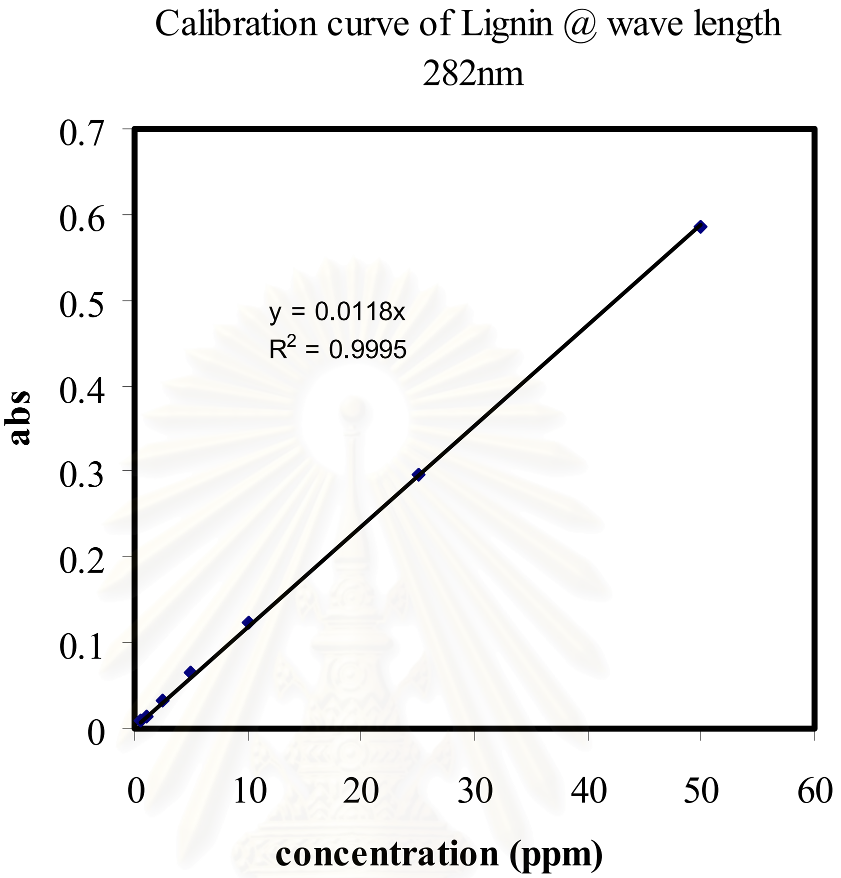
Experimental Results



Calibration curve of methylene blue @660nm



Calibration curve of Black 5 @ wave length 595nm



Average Residual concentration of **methylene blue** using titania exposed to UV-C

name/code	position						[initial]
	1(blank)	2	3	4(blank)	5	6	
M1 @10 min	9.55	4.74	4.44	9.58	4.24	4.14	9.68
M1 @30 min							
M1 @60 min	9.52	2.35	2.44	9.51	2.47	2.54	9.72
M2 @10 min	9.51	1.97	2.21	9.53	2.17	2.40	9.59
M2 @30 min	9.49	0.33	0.39	9.49	0.35	0.38	9.63
M2 @60 min	9.20	0.10	0.17	9.26	0.13	0.14	9.59
T1 @10 min	9.60	6.17	5.86	9.59	6.15	6.23	9.70
T1 @30 min	9.44	1.35	1.49	9.46	1.90	1.79	9.55
T1 @60 min	9.33	0.07	0.05	9.29	0.12	0.09	9.59
T2 @10 min	9.52	3.95	3.77	9.60	3.83	3.81	9.62
T2 @30 min							
T2 @60 min	9.47	1.68	1.45	9.46	1.46	1.21	9.62
N1 @ 10 min	9.51	8.07	8.06	9.53	8.15	8.03	9.67
N1 @ 30 min							
N1 @ 60 min	9.43	6.42	6.19	9.43	6.41	6.41	9.67

Residual concentration of **methylene blue** using titania without light source

name/code	position						[initial]
	1(blank)	2	3	4(blank)	5	6	
M1 @10 min	9.57	6.39	6.57	9.71	6.03	6.15	9.72
M1 @60 min	9.68	6.26	6.20	9.69	6.68	6.45	9.72
M2 @10 min	9.65	7.58	7.64	9.64	7.45	7.14	9.70
M2 @60 min	9.68	7.35	7.43	9.65	7.67	7.34	9.76
T1 @10 min	9.57	8.77	8.80	9.63	8.84	8.78	9.67
T1 @60 min	9.68	8.83	8.91	9.66	8.96	8.83	9.72
T2 @10 min	9.68	6.47	7.10	9.69	7.64	6.43	9.76
T2 @60 min	9.68	6.60	6.91	9.59	7.12	7.20	9.76
N1 @ 10 min	9.53	8.79	8.69	9.53	8.72	8.75	9.56
N1 @ 60 min	9.52	8.71	8.70	9.55	8.82	8.75	9.56

Average Residual concentration of **Black 5** using titania exposed to UV-C

name/code	position						[initial]
	1(blank)	2	3	4(blank)	5	6	
M1 @10 min	9.75	10.32	10.25	9.82	10.11	10.14	10.34
M1 @30 min							
M1 @60 min	9.00	8.56	8.31	8.90	8.72	8.49	10.34
M2 @10 min	9.95	6.39	6.30	9.95	6.35	6.44	10.27
M2 @30 min	9.45	1.51	1.46	9.45	1.19	1.46	10.37
M2 @60 min	8.86	0.18	0.18	8.86	0.14	0.14	10.37
T1 @10 min	9.95	1.74	2.79	9.91	2.10	3.01	10.27
T1 @30 min	9.54	0.00	0.00	9.63	0.00	0.00	10.37
T1 @60 min	8.86	0.00	0.00	8.86	0.00	0.00	10.37
T2 @10 min	10.05	9.36	9.38	10.00	9.11	9.43	10.39
T2 @30 min							
T2 @60 min	9.43	3.72	3.36	9.45	3.75	3.72	10.39
N1 @ 10 min	9.95	9.25	9.16	9.95	9.22	9.22	10.41
N1 @ 30 min							
N1 @ 60 min	8.93	6.05	6.12	8.88	6.00	6.30	10.41

% abs of methylene blue using titania, M1, exposed to UV-C + shaking

code name	% abs	avg. % abs
P1	1.421	1.4265
P2	1.432	
C1	0.280	0.314
C2	0.348	
int1	1.462	1.464
int2	1.466	

** P = photolysis
C = photocatalysis
int = initial

concentration of methylene blue using titania, M1, exposed to UV-C + shaking

code name	concentration (ppm)	COD (mg/l)
P	9.42	27.4
C	1.94	19.6
int	9.67	23.5

** P = photolysis
C = photocatalysis
int = initial

Residual concentration of **methylene blue** using titania exposed to UV-C

name/code	position						[int]	[GF/A]1	[GF/A]2
	1(blank)	2	3	4(blank)	5	6			
M2 @60 min	9.61	0.40	0.33	9.68	0.36	0.38	9.70	0.14	0.27
%abs	1.455	0.084	0.074	1.466	0.079	0.082	1.469	0.045	0.065
avg. residual concentration from centrifuge 4000 rpm 15 min	0.37	%removal MB	95.61						
avg. residual concentration which was filtrated by glass microfiber (pore=1.6 micron)	0.20	%removal MB	97.33						

Residual concentration of black 5 using titania exposed to UV-C

name/code	position						[int]	[GF/A]1	[GF/A]2
	1(blank)	2	3	4(blank)	5	6			
M2 @60 min	9.63	1.97	1.69	9.63	2.56	1.78	10.27	3.48	4.17
%abs	0.211	0.044	0.038	0.211	0.057	0.04	0.225	0.077	0.092
avg. residual concentration from centrifuge 4000 rpm 15 min	2.00	%removal black 5	74.25						
avg. residual concentration which was filtrated by glass microfiber (pore=1.6 micron)	3.83	%removal black 6	56.50						

Table pH of MB and B5

	pH	C
deminerialize water	5.84	0
MB @ 10 ppm	5.81	9.65
B5 @ 10 ppm	6.21	10.27
B5 @ 20 ppm	5.96	20.18

After adsorption @ 10 ppm

	pH	C
MB	6.24	7.453
B5	6.48	10.27

After decomposition by only UV @ 10 ppm

	pH	C	t (min)
MB @ 0 min	5.81	9.65	0
MB @ 10 min	6.20	9.58	10
MB @ 60 min	6.14	9.288	60
B5 @ 0 min	6.21	10.27	0
B5 @ 10 min	6.11	9.95	10
B5 @ 60 min	6.11	8.77	60

After decomposition by UV/TiO2 @ 10 ppm

	pH	C	t (min)
MB @ 0 min	5.81	9.65	0
MB @ 10 min	6.07	2.2	10
MB @ 60 min	6.05	0.136	60
B5 @ 0 min	6.21	10.27	0
B5 @ 10 min	6.00	6.37	10
B5 @ 60 min	5.83	0.16	60

VITA

Mr. Nawin Viriya-empikul was born on March 21, 1980 in Bangkok, Thailand. He studied in primary and secondary educations at Assumption College. In 2003, he received the Bachelor Degree of Engineering (Chemical Engineering) from Chulalongkorn University. After that, he gained admission to Graduate School of Chulalongkorn University and he graduated in 2005 with the thesis entitled “Decomposition of Organic Compounds Using Nanosized Titania”.