การกำจัดยาปราบศัตรูพืชชนิดฟีนิลยูเรียออกจากน้ำโดยการแอดโซลูบิไลเซชันบนเส้นใยไทเทเนียขนาดนาโน ที่ถูกปรับปรุงด้วยสารลดแรงตึงผิว

นางสาวภมรรัตน์ จันธรรม

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REMOVAL OF PHENYL UREA HERBICIDES FROM WATER BY ADSOLUBILIZATION ON SURFACTANT MODIFIED TITANIA NANOFIBERS

Miss Pamornrat Chantam

A Thesis Submitted in Partial Fulfillment of the Requirements
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By	Miss Pamornrat Chantam
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Thesis Advisor	Assistant Professor Varong Pavarajarn, Ph.D.

Accepted by the Faculty of Engineering, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master's Degree

…………………………………….. Dean of the Faculty of Engineering
(Professor Direk Lavansiri, Ph.D.)

THESIS COMMITTEE

…………………………………………………….. Chairman
(Assistant Professor Muenduen Phisalaphong, Ph.D.)

…………………………………………………….. Thesis Advisor
(Assistant Professor Varong Pavarajarn, Ph.D.)

…………………………………………………….. Member
(Anongnat Somwangthanaroj, Ph.D.)

…………………………………………………….. Member
(Assistant Professor Okorn Mekasuwandumrong, D.Eng)

ภมรรัตน์ จันธรรม: การกำจัดยาปราบศัตรูพืชชนิดฟีนิลยูเรียออกจากน้ำโดยการแอดโซลูบิไลเซชันบนเส้นใยไทเทเนียขนาดนาโนที่ถูกปรับปรุงด้วยสารลดแรงตึงผิว (REMOVAL OF PHENYL UREA HERBICIDES FROM WATER BY ADSOLUBILIZATION ON SURFACTANT MODIFIED TITANIA NANOFIBERS) อาจารย์ที่ปรึกษา: ผศ. ดร.วรงค์ ปวราจารย์, 92 หน้า.

เทคนิคโซล-เจลและการปั่นเส้นใยด้วยไฟฟ้าสถิตได้ถูกใช้ร่วมกันเพื่อผลิตเส้นใยคอมพอสิตขนาดนาโนของไทเทเนียม (IV) ออกไซด์กับพอลิไวนิลไพโรลิโดนจากสารละลายที่ประกอบด้วยพอลิไวนิลไพโรลิโดนและไทเทเนียมเตตระไอโซโพรพอกไซด์ เมื่อนำเส้นใยคอมพอสิตไปเผา จะได้เส้นใยขนาดนาโนของไทเทเนียมที่มีขนาดเส้นผ่านศูนย์กลางเฉลี่ย 165 นาโนเมตร และมีค่าขนาดรูพรุนเฉลี่ย 50 อังสตรอม การปรับปรุงพื้นผิวของไทเทเนียด้วยสารลดแรงตึงผิวสามารถทำได้โดยการดูดซับของสารลดแรงตึงผิวโดยที่การดูดซับขึ้นอยู่กับชนิดของสารลดแรงตึงผิว สภาวะความเป็นกรด-ด่างของสารละลายสารลดแรงตึงผิว และประจุบนพื้นผิวของไทเทเนีย ไทเทเนียซึ่งถูกปรับปรุงสภาพผิวแล้วได้ถูกนำไปใช้เป็นสารดูดซับสำหรับการกำจัดยาปราบศัตรูพืชชนิดฟีนิลยูเรียอันได้แก่ ไดยูรอน ไอโซโปรทิวรอน และไลนูรอน การแอดโซลูบิไลเซชั่นของยาปราบศัตรูพืชที่เกิดขึ้นบนเส้นใยไทเทเนียซึ่งถูกปรับปรุงด้วยสารลดแรงตึงผิวสามารถช่วยเพิ่มประสิทธิภาพการกำจัดยาปราบศัตรูพืชโดยที่ความสามารถในการแอดโซลูบิไลเซชั่นนั้นขึ้นอยู่กับปัจจัยต่างๆ เช่น อุณหภูมิ, ความเป็นกรด-ด่างของสารละลายยาปราบศัตรูพืช และปริมาณของตัวดูดซับ การนำกลับมาใช้ใหม่ของไทเทเนียที่ถูกนำไปใช้แล้วด้วยกระบวนการออกซิเดชั่นด้วยแสงนั้นมีความเป็นไปได้ หากแต่ไม่สามารถกำจัดสารอินทรีย์ออกจากพื้นผิวของเส้นใยไทเทเนียได้ทั้งหมดของการทำปฏิกิริยาภายใน 6 ชั่วโมง

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สาขาวิชา วิศวกรรมเคมี ลายมือชื่ออาจารย์ที่ปรึกษา
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Sol-gel and electrospinning techniques are incorporated to produce titanium (IV) oxide/polyvinylpyrrolidone (PVP) composite nanofibers from solution containing PVP and titanium tetraisopropoxide. After calcination of the composite fibers, titania nanofibers are obtained. The average diameters of the obtained titania fibers is 165 nm with average pore size diameter of 50 Å. Surface modification of titania by surfactant can be done by adsorption of the surfactant, whereas the adsorption depends upon type of surfactant, pH of the surfactant solution and surface charge of titania. The modification was subsequently used as adsorbent in the removal of phenylurea herbicides, i.e. diuron, isoproturon and linuron. Adsolubilization of herbicide taking place on the surfactant-modified titania assists the removal efficiency. Effectiveness of the adsolubilization depends upon various parameters, such as temperature, pH of the herbicide solution and adsorbent dose. Regeneration of used titania by photooxidation is possible, but complete degradation of the adsorbed organic compounds was not achieved after 6 hours of the photooxidation.

Department Chemical Engineering
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Student's signature Pamornrat Chantam
Advisor's signature

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CONTENTS

Page

CHAPTER

Page

LIST OF TABLES

Table **Page**

LIST OF FIGURES

Figure **Page**

Figure **Page**

CHAPTER I

INTRODUCTION

Titanium (IV) oxide or titania (TiO_2) is one of the most common materials recognized in various industries. It has also been known to be an excellent catalyst in the field of photocatalysis. Titania is a wide bandgap semiconductor with many interesting properties, such as transparency to visible light, high refractive index and low absorption coefficient. Other than these properties, its eminent capability of photocatalytic decomposition of organic materials has come to utilization in the environment applications, i.e. organic pollutant treatment (Kwon et al. 2004).

The crystal of titania exists in three different forms, namely rutile, anatase, and brookite. Anatase and brookite are thermodynamically metastable and can be transformed irreversibly to the most stable and condensed rutile phase at high temperatures. Anatase titania has been used as catalyst for photodecomposition and solar energy conversion because of its high photoactivity, whereas rutile titania has been used as white pigment materials for ultraviolet light protection because of its good scattering effect. Brookite titania has a structure belonging to the orthorhombic crystal system, which is formed only under hydrothermal conditions and usually found only in minerals.

Titania can be synthesized by various procedures. Sol-gel method is one of the methods that can produce titania with extremely high surface area. The method basically consists of many steps, i.e. hydrolysis of alkoxide to form sol, gelation, gel-aging, drying and thermal stabilization. Each step can be manipulated in order to obtain product with specific characteristic, such as narrow pore size distribution and narrow particle size distribution. However, titania obtained usually contains certain amount of amorphous phase, in which their surface area decrease drastically during calcination (Fujishima et al. 1999; Payakgul 2002).

Nanocrystalline material, characterized by an ultra fine grain size (<50 nm), is a subject of current interest because of the unusual chemical magnetic, optical and electronic properties. It has been reported that nanometer-sized particles have different physical and chemical properties from bulk materials. Their catalytic activity is expected to be enhanced not only because of their increased surface area, but also because of the change of surface properties such as surface defect.

The particle size of nanocrystalline titania plays an important role in its the physical and chemical behavior because the specific surface area, the chemical stability, and the chemical reactivity of the materials are all highly correlated with particle size. It has been shown that the adsorption of organic compounds to the surface of nanocrystalline anatase is particle-size-dependent.

Phenylurea herbicides (PUHs) have been widely used throughout the world for long time. However, it has resulted in residue in crops, soil and surface water. Separation of compounds at dilute concentrations from aqueous streams is a formidable and challenging problem for the chemical, pharmaceutical industries and for environmental remediation operations. One of the few technologies currently available for dilute solution separations is adsorption onto activated carbon. It is the most frequently chosen. However, if this technology is to be economically viable, re-use or disposal of spent carbon has to be cost effective. Processes such as high temperature desorption, solvent extraction and bio-oxidation have been used for carbon regeneration. The estimated costs of these operations can be a significant percentage of the overall costs for activated carbon treatment. Hence, there is a need to use modified carbon surfaces or other adsorbents to effect dilute solution separations. This work has focused on using mineral oxide particle (titania) of high surface area to separate phenylurea herbicides from dilute aqueous solution.

In this research, the sol-gel method is combined with electrospinning technique, which is a relatively simple and versatile method for fabricating nanofibers. Titania nanofibers are then modified by adsorbing a surfactant, i.e. anionic, cationic and nonionic surfactants on the surface to enhance the adsorption capability.

The main focus of this work is an adsolubilization of complex substance, i.e. Diuron [3-(3,4-dichlorophynyl)-1,1-dimethylurea], Linuron [1-methoxy-1-methyl-3-(3,4-dichlorophenyl)urea] and Isoproturon [N-(4-isopropylphenyl)-N′,N′-dimethylurea], which are all common phenylurea herbicides, from aqueous phase on to surfactant-modified titania nanofibers. Regeneration of the surface using a photooxidation is also investigated. The results are compared with commercial available titania, i.e. Degussa P-25 from Degussa Corporation.

The objectives of this research are listed as following:

1. To study the adsorption of surfactant on surface of titania for modification of titania surface. Effects of type of surfactant, pH of solution and concentration of surfactant are investigated.
2. To investigate the adsolubilization of herbicide on surfactant-coated titania. Effects of surfactant content, temperature, initial concentration of herbicide, mass of adsorbent and pH on adsolubilization are investigated.
3. To study the photooxidation of an organic compound on surface of titania for reusing a surfactant-modified titania.

The present study is arranged as follows:

Chapter I is the introduction of this work. Chapter II describes basic theory about titania such as the general properties of titania, sol-gel process, electrospinning process and photocatalytic process. Adsorption of surfactant and adsolubilization of phenylurea herbicide are also described. Furthermore, literature reviews of the previous works related to this research are presented in this chapter as well. Chapter III shows materials, experimental systems and procedures for the titania preparation, the adsorption of surfactant, the adsolubilization of herbicide and the photocatalytic regeneration. Chapter IV presents the experimental results and discussion. In the last chapter, the overall conclusions of this research and recommendations for the future work are given.

CHAPTER II

THEORY AND LITERATURE REVIEWS

The theory relating to synthesis and properties of titania, properties of phenylurea herbicides and surfactant, adsorption and adsolubilization processes and photooxidation of organic compound will be explained in this chapter.

2.1 Physical and Chemical Properties of Titania

Titanium (VI) oxide or titania has great potential for many industrial applications. Therefore, many researches have focused on its fabrication and characterization. Titania has been used in many fields of application such as catalyst, catalyst support, electronics, cosmetic pigment and filter coating (Fox and Dulay 1993; Nishimoto et al. 1985; Tanaka et al. 1993). In recent year, main attention has been devoted to its photocatalytic activity and photoinduced superhydrophlilicity. Since titania has relatively wide band gap (3.2eV), charge carriers, i.e. electrons and holes, are produced when titania is exited. Consequently, highly reactive radicals are generated and oxidation-reduction reaction of species adsorbed on the surface of titania can occur (Zeman and Takabayashi 2003).

Titania occurs naturally in three crystalline forms: anatase which tends to be more stable at low temperature, brookite which is usually found only in minerals, and rutile which is thermally stable form of titania and frequently found in igneous rocks. All three forms of titania have been prepared artificially. However, only rutile has been obtained in the form of transparent large single crystal. A summary of the crystallographic properties of all forms are given in Table 2.1

Table 2.1 Crystallographic properties of anatase, brookite and rutile (Othmer 1999).

	Anatase	***Brookite***	***Rutile***
Crystal structure	Tetragonal	Orthorombic	Tetragonal
Density, [g/cm^3]	3.9	4.0	4.23
Hardness,[Mohs scale]	$5^{1/2}$ –6	$5^{1/2}$ –6	$7\text{-}7^{1/2}$
Unit cell	D_4a^{19} .4TiO$_2$	$D2h^{15}$ .8TiO$_2$	$D4h^{12}$ .3TiO$_2$
Lattice parameters, [nm]			
a	0.3758	0.9166	0.4584
b		0.5436	
c	0.9514	0.5135	2.953

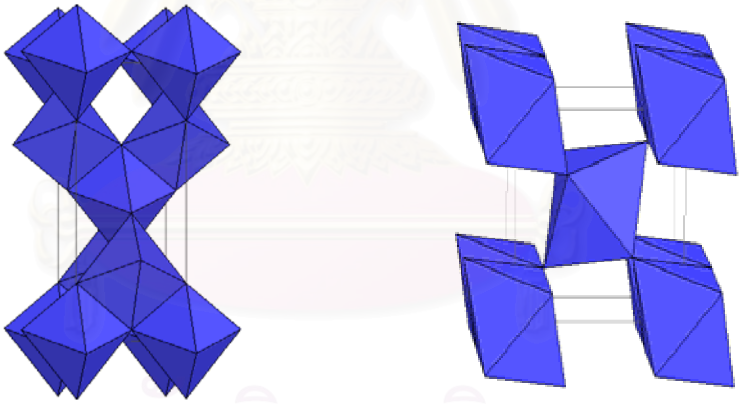


Figure 2.1 Crystal structure of TiO$_2$; Anatase (a) and Rutile (b).

The important commercial forms of titania are anatase and rutile. Both of them are tetragonal. Anatase usually occurs in near-regular octahedral. Rutile forms slender prismatic crystals, which are frequently twinned. Therefore, both anatase and rutile are anisotropic and their physical properties, e.g. refractive index, vary according to the direction relative to the crystal axes. However, in most applications, the distinction between crystallographic directions is lost because of the random orientation of large numbers of small particles.

Phase transformation from anatase to rutile is accompanied by the evolution of ca. 12.6 kJ/mol (3.01 kcal/mol). Nevertheless, the rate of transformation is greatly affected by temperature and the presence of other substances which may either catalyze or inhibit the transformation. The lowest temperature at which conversion of anatase to rutile takes place at a measurable rate is approximately 500-550^{o}C (Depero et al. 1993). The anatase to rutile transformation is not reversible since Gibb's free energy for the change is always negative.

Titania is thermally stable (mp 1855^{o}C) and has high resistance to chemical attack. When it is severely heated under vacuum, there is a chance of slight loss in oxygen atom that results in a change in composition to $TiO_{1.97}$. The product is dark blue but can be reverted to the original white color when it is heated in air (Fujishima et al. 1999).

2.2 Sol-Gel Process

Sol-gel process involves the formation of sol following by that of gel. Sol, which is suspension solid in liquid with particle size ranging from 1 nm to 1 µm, can be obtained by the hydrolysis and partial condensation of a precursor such as an inorganic salt or a metal alkoxide. Further condensation of sol particles into a three-dimensional network produces gel, which is a diphasic material with a solids encapsulating liquid or solvent. Alternatively, gel can be produced by destabilizing the solution of preformed sols. In either case, the materials are referred as aquasol (or aquagel) if water is used as a solvent, and alcosol (or alcogel) if alcohol is used. The encapsulated liquid can be removed from gel by either evaporative drying or drying with supercritical extraction (supercritical drying for short).

The single most important characteristic of the sol-gel preparation of inorganic materials is its ease of control that translates into the following advantages:

(i) the ability to maintain high purity (because of purity of staring materials);
(ii) the ability to change physical characteristics such as pore size distribution and pore volume;
(iii) the ability to vary compositional homogeneity at a molecular level;
(iv) the ability to prepare samples at low temperatures;
(v) the ability to introduce several components in a single step;
(vi) the ability to produce samples in different physical forms.

Four key steps in converting a precursor to a particular product form via sol-gel preparation are: formation of gel, aging of gel, removal of solvent, and heat treatment. The versatility of this preparative approach lies in the number of parameters that can be manipulated in each of these steps.

The precursor in sol-gel preparation can either be a metal salt/alkoxide dissolved in an appropriate solvent or a stable colloidal suspension of preformed sols. Metal alkoxides have been the most extensively used because they are commercially available in high purity and their solution chemistry has been documented. At its simplest level, sol-gel chemistry with metal alkoxides can be described in terms of two classes of reactions:

$$\text{Hydrolysis:}\quad \text{-M-OR+H}_2\text{O} \longrightarrow \text{-M-OH+ROH}$$
$$\text{Condensation:}\quad \text{-M-OH+XO-M-} \longrightarrow \text{-M-O-M- +XOH}$$

where X can either be H or R (an alkyl group).

Such a description oversimplifies the overall process because it does not correctly represent the molecular formulas of intermediates and end products, nor does it depicts the simultaneous occurrence of the two reactions. However, this oversimplification captures the key phenomenological idea that a three-dimensional gel network comes from the condensation of partially hydrolyzed species. Any parameter that affects either or both of these reactions is thus likely to have impact on the properties of the product. In fact, the important variables are the reaction rates of hydrolysis and condensation.

Because hydrolysis and condensation are both nucleophilic displacement reactions, the reactivity of metal alkoxides depends on the positive partial charge of the metal atom and its coordination number. For example, Tetraethyl orthosilicate (TEOS), which contains small positive partial charge on silicon, is the least reactive among the common alkoxides. In general, the longer and bulkier the alkoxide group attached to a particular metal atom, the less reactive that precursor is in hydrolysis and condensation. Changing the type of precursor and/or its concentration are thus effective means of controlling the reaction rates.

The amount of water used in sol-gel preparation and the rate by which it is added into the system also influence gel characteristics. The former is usually expressed in terms of the hydrolysis ratio h, defined as the moles of water per mole of metal alkoxide, $M(OR)_m$. There are three specific regions of interest:

(i) $h < 1$: An infinite network seldom forms due to the low functionality of the precursor towards condensation. Because there are few M-OH groups for cross-linking, gelation or precipitation cannot occur when there is no local excess of water.

(ii) $1 < h < m$: Polymeric gels can form.

(iii) $h < m$: Cross-linked polymers, particulate gels, or precipitates can form when an excess of water is added to the alkoxides.

For a given amount of water, another level of control comes from the rate of addition. Common approaches to slowly add water are: using a micropipette, absorbing moisture from a controlled humidity environment, and generating water in the solution by another chemical reaction.

Two other important sol-gel parameters are temperature and type of solvent. Both hot and cold plates are commercially available, which can be used to increase and decrease the reaction rate, respectively. Varying the temperature is most effective when it can alter the relative rate of competing reactions. Solvent can change the nature of an alkoxide through solvent exchange or can affect the condensation reaction directly. It is also possible to prepare gel without solvent as long as another mean, such as ultrasound irradiation, is used to homogenize an otherwise immiscible alkoxide/water mixture.

Using preformed sols instead of metal alkoxides as precursors is an attractive alternative in sol-gel preparation because recent advances in inorganic colloidal dispersions allow some control over the characteristic of the starting sols. Colloidal suspension of sol particles is often stabilized (i.e. prevented from flocculation) by pH adjustment. Thus, pH of the solution, which can be changed by the addition of either acid or base, is the single most important parameter in obtaining gel from preformed sols. Other parameters that influence gel quality are size and concentration of the starting sol particles.

For any of the sol-gel parameters discussed so far, its effect on gel properties can often be observed by an experimental parameter known as gel time. Gel time is defined as the time that the solution undergoes rapid rise in viscosity which is corresponding to the transition from viscous fluid to elastic gel. At the gel point, the solid phase forms a continuous structure that reflects the formation and branching of particles under specific growth condition. This particular phase is important because it is the genesis of structural evolution that takes place in all subsequent processing steps (Ertl et al. 1999).

For titania synthesis via sol-gel technique, the process starts with the mixing of titanium alkoxide with alcohol. Acid aqueous solution is subsequently added to the mixture (Jung 1999). This technique can be adapted by using ultrasonication to aid dispersion, which can result in titania with higher surface area and better thermal stability than titania prepared by using conventional stirring (Awati 2003). The average crystal size of titania synthesized by this method has been reported to be in the range of 4 – 8 nm with BET surface area in the range of 91-120 m^2/g, depending on calcination temperature. However the limit of this method is that strong reactivity of alkoxide toward water often results in uncontrolled precipitation.

2.3 Electrospinning Process

In the electrospinning process, a droplet of the polymer solution held by its surface tension at the end of a capillary tube is subjected to an electric field. Charge is induced on the liquid surface by the electric field. As the intensity of the electric field is increased, the hemispherical surface of the solution at the tip of the capillary tube elongates to form a conical shape known as the Taylor cone. When the electric field reaches a critical value at which the repulsive electric force overcomes the surface tension force, a charged jet of the solution is ejected from the tip of the Taylor cone. Since this jet is charged, its trajectory can be controlled by the electric field. As the jet travels in air, the solvent evaporates, leaving a charged polymer fiber behind which lays itself randomly on a collecting metal screen. Thus, continuous fibers are laid to form a non-woven fabric (Jayesh and Reneker 1995).

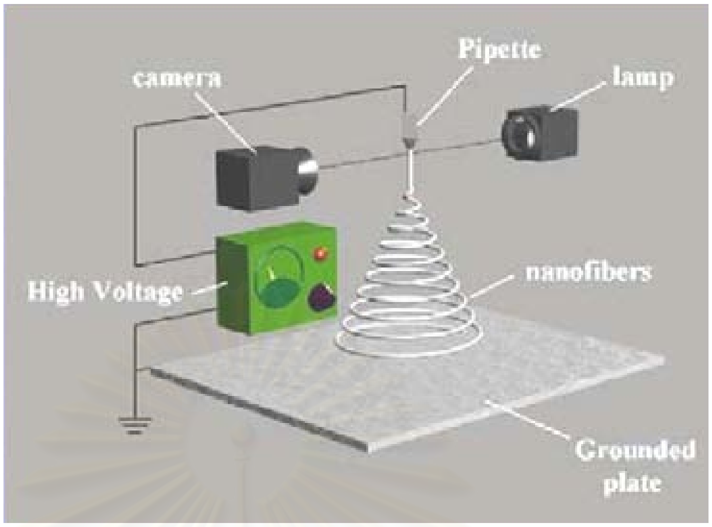


Figure 2.2 Schematic representation of the electrospinning process.

Li *et al.* (2003) studied fabrication of titania nanofibers by electrospinning with controllable diameters and porous structures. When solution containing both poly(vinyl pyrrolidone) (PVP, M_w ~ 1,300,000) and titanium tetraisopropoxide in ethanol was injected through a needle under strong electrical field, composite nanofibers made of PVP and amorphous TiO_2 were formed as a result of electrostatic jetting. These nanofibers could be subsequently converted into fibers of anatase titania without changing their morphology via calcination in air at 500^oC. The average diameter of these ceramic nanofibers could be controlled in the range from 20 to 200 nm. It was found that, after calcined at 500^oC, the nanofibers remained as continuous structures with their average diameter reduced. This size reduction could be accounted by the loss of PVP from the nanofibers and the crystallization of titania. They also reported the followings: the nanofibers increased in diameter as the PVP concentration was increased, thinner nanofibers were obtained when the strength (E) of the electric field was increased, faster feeding rate of PVP solution often resulted in thicker fibers, and the use of titanium tetraisopropoxide at lower concentration led to the formation of thinner ceramic nanofibers. Furthermore, it was suggested that the electrospinning procedure could be extended to provide a generic route to nanofibers made of other oxides such as SnO_2, SiO_2, Al_2O_3, and ZrO_2 (Li and Xia 2003).

2.4 Adsorption Process

Adsorption is a surface phenomenon. The adsorption at a surface or interface is largely a result of binding forces between atoms, molecules and ions of the adsorbate on the surface of the adsorbent (Baskaralingam et al. 2006).

Adsorption is a process that occurs when liquid or gas (called adsorbate) accumulates on the surface of a solid or liquid (adsorbent), forming a molecular or atomic film of the adsorbate. It is different from absorption, where a substance diffuses into a liquid or solid to form a "solution". The term sorption encompasses both processes, while desorption is the reverse process. Adsorption occurs in many physical, biological, and chemical systems. It is widely used in industrial applications such as activated charcoal, synthetic resins and water purification. Adsorption, ion exchange and chromatography are sorption processes in which certain adsorptives are selectively transferred from fluid phase to the surface of insoluble, rigid particles suspended in a vessel or packed in a column. Similar to surface tension, adsorption is a consequence of surface energy. However, atoms on the (clean) surface experience a bond deficiency, because they are not wholly surrounded by other atoms. Thus it energetically favors to bond with whatever happens to be available. The exact nature of the bonding depends on details of the species involved, but the adsorption is generally classified into 2 main types, i.e. physisorption and chemisorption.

In case of the adsorption of species from solution onto a solid, solute molecules are partitioned from the solution to the adsorbent leading to the change in concentration of the solution. As mentioned earlier, the adsorption phenomenon depends on the interaction between the surface of the adsorbent and the adsorbed species. The interaction may be due to:

- chemical bonding
- hydrogen bonding
- hydrophobic bonding
- Van der Waals force

The important features often investigated on the adsorption phenomenon include (i) interface characteristics, (ii) adsorption isotherm, (iii) thermodynamics of adsorption and (iv) the adsorbate–adsorbent interactions (Parida et al. 2006).

The interaction of adsorbent and adsorbate leads to the formation of adsorbed surface. To learn about molecular interaction of these two species, the major of the analysis are:

- chemical nature of the materials involved
- solution concentration
- the interaction between adsorbate and adsorbent
- lateral interaction between adsorbed species

For the majority of system involving adsorption from dilute solution, a monolayer of adsorbate on the surface of adsorbent is postulated. The analysis of adsorption isotherm also suggests. The measurements of macroscopic properties such as adsorption density, zeta potential and floatation efficiency (Allian et al. 1995; Parfitt 1983) are used for the characterization of the adsorbed surface. However, such studies, which are helpful in developing an insight the adsorption mechanism, are unable to provide any direct information on the microscopic character is tic of the adsorbed species. Spectroscopic techniques are mostly used to answer questions regarding the bonding of adsorbates onto surface sites of solid particles in molecular level.

2.5 Zeta Potential and Point of Zero Charge

Zeta potential refers to the electrostatic potential generated by accumulation of ions at the surface of a (colloidal) particle that is organized into an electrical double-layer, consisting of the Stern layer and the Diffuse layer. The Stern layer is the layer of counter ions that attach to a charge surface. These ions are temporarily bound to the surface and shield the charge of the original surface. The graphical representation of the electrical double layer is shown in Figure 2.3.

When a solid is emerged in a polar solvent or an electrolyte solution, the surface charge will be developed through one or more of the following mechanism:

1) Preferential adsorption of ions
2) Dissociation of surface charged species
3) Isomorphic substitution of ions
4) Accumulation or depletion of electrons at the surface
5) Physical adsorption of charged species onto the surface

The surface potential of the solid varies with the concentration of the ions in the surrounding solution, and can be either positive or negative. The liquid layer surrounding the particle exists as two parts; an inner region, called the Stern layer, where the ions are strongly bound and an outer region, i.e. Diffuse layer, where they are less firmly attached. Within the Diffuse layer there is a notional boundary, inside which the ions and particles form a stable entity. When a particle moves (e.g. due to gravity), ions within the boundary move with it, but any ions beyond the boundary do not travel with the particle. This boundary is called the surface of hydrodynamic shear or slipping plane. The potential that exists at this boundary is known as the zeta potential.

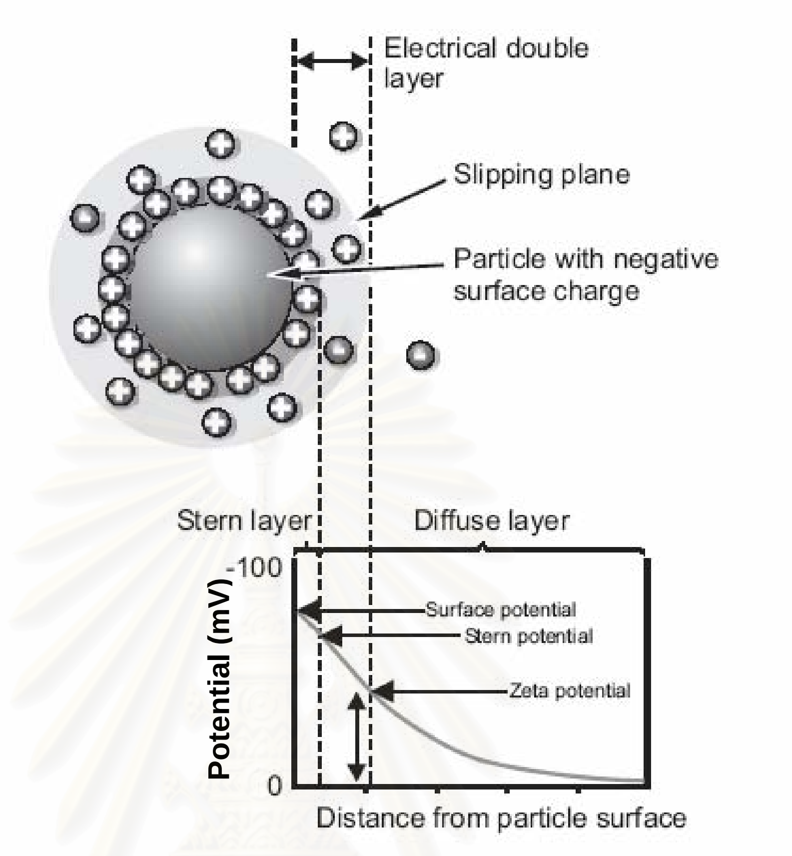


Figure 2.3 Basic description of the zeta potential.

The most important factor that affects zeta potential is pH. A value of zeta potential without a quoted pH is a virtually meaningless number. Consider a particle in suspension with a negative zeta potential, if more alkali is added to this suspension, then the particles will tend to acquire more negative charge. On the other hand, if acid is added to this suspension, a point where the negative charge is neutralized will be reached. Any further addition of acid can cause a build up of positive charge. Therefore, a zeta potential will be positive at low pH and becomes negative at high pH.

Consider a plot of zeta potential versus pH, the point where the curve passes through zero zeta potential is called the isoelectric point. This point is very important for a practical consideration. It is normally the point where the colloidal system is least stable. A typical plot of zeta potential versus pH is shown in Figure 2.4.

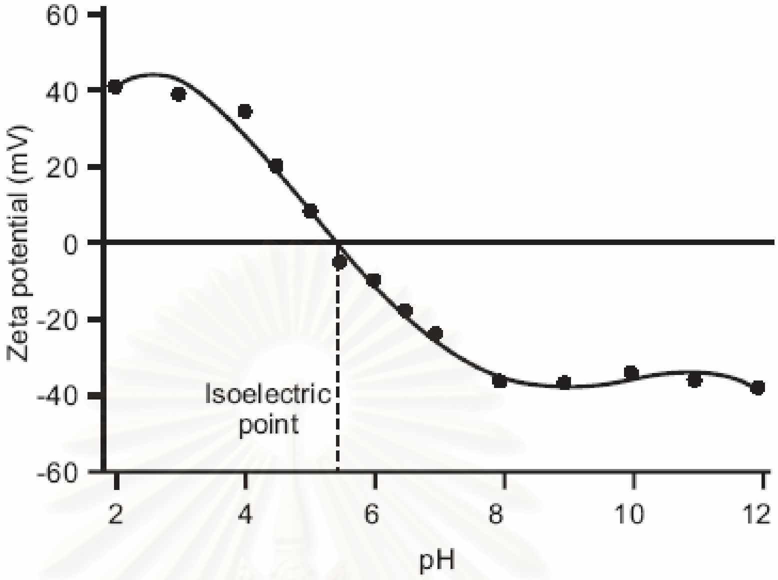


Figure 2.4 Basic definition of the isoelectric point.

The adsorption on metal oxide is pH sensitive. Below a particular pH, a metal oxide possesses a positive surface charge, whereas above that pH it has a negative surface charge. The pH at which the surface charge is zero is called “the point of zero charge”, pH_{PZC}. The surface charge in oxides is mainly derived from preferential dissolution or deposition of ions. Ions adsorbed on the solid surface determine the surface charge, and thus are referred to as charge determining ion, also known as co-ions or coions. In the oxide systems, typical charge determining ions are protons and hydroxyl groups, of which the concentration are described by pH ($pH=-\log [H^+]$). As the concentration of charge determining ions varies, the surface charge density changes from positive to negative or vice versa. The concentration of charge determining ions corresponding to a neutral or zero-charged surface is defined as a point of zero charge (p.z.c) or zero point charge (z.p.c.). At the pH > p.z.c., the oxide surface is negatively charged, since the surface is covered with hydroxyl groups, OH^-, which is the electrical determining ion. At pH < p.z.c., H^+ is the charge determining ions and the surface is positively charged (Cao 2003).

The process of adsorption is greatly influenced by pH of the solution and point of zero charge of adsorbent. (Gawade et al. 2005b) studied the adsorption of surfactant, i.e. sodium dosecyl sulfate (SDS), onto alumina for subsequent uses in wastewater treatment. The effect of pH on adsorption of SDS on alumina was studied by changing the pH. It was found that adsorption decreases as the pH increases from 2 to 11. The effective adsorption of SDS occurred at pH below p.z.c., i.e. 8.5, positive charge on alumina surface was increased. Cerovi (2006) studied point of zero charge of different carbides, such as NbC, WC, SiC and TiC powders, using a batch equilibration method. This method has been proved to be a simple and accurate method to determine point of zero charge (Cerovi 2006). In this work, the point of zero charge of titania was also determined by this technique.

2.6 Surfactant

The term surfactant is a blend of "Surface active agent". Surfactants are usually organic compounds that are amphipathic, meaning that they contain both hydrophobic groups (their "tails") and hydrophilic groups (their "heads"). Therefore, they are typically sparingly soluble in both organic solvents and water.

A micelle (micella, or micellae in plural) is an aggregate of surfactant molecules dispersed in liquid. A typical micelle in aqueous solution forms a roughly spherical or globular aggregate with the hydrophilic "head" regions in contact with surrounding solvent, sequestering the hydrophobic tail regions in the micelle center. Micelles are often globular and roughly spherical in shape, but ellipsoids, cylinders, and bilayers are also possible. Shape of micelle depends upon molecular geometry of its surfactant molecules as well as solution conditions such as surfactant concentration, temperature, pH, and ionic strength. The process of forming micelles is known as micellization.

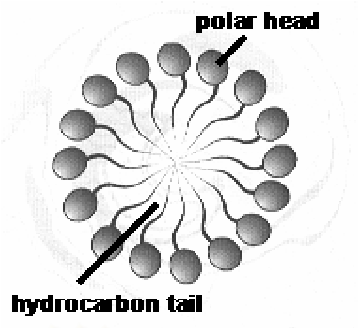


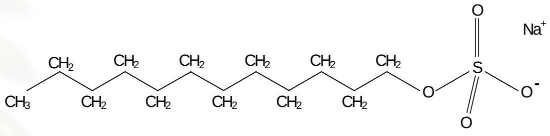
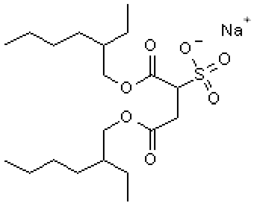
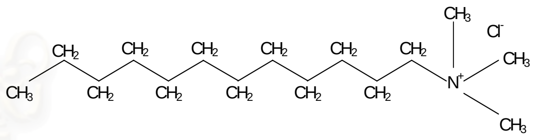
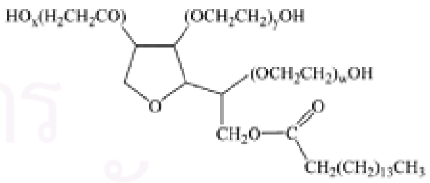
Figure 2.5 Schematic representation of micelle structure.

Surfactants are classified into four types. Surfactants having a negative or positive charge on the hydrophilic group are called “anionic” or “cationic” surfactants, respectively. Surfactants containing both positive and negative charges are called “zwitterionic”. The last type consists of surfactant molecules with no apparent charge on the hydrophilic group. They are called “nonionic” surfactants.

Adsorption of surfactant onto solid particles has been extensively studied theoretically and applicably (Parfitt 1983). One of the interesting properties is the fact that the surfactant adsorbed layer exhibits hydrophobic property, similar to a micellar core. Accordingly, incorporation of water-insoluble compounds in the surfactant adsorbed layer is possible. This process is referred to as ‘adsolubilization’. Surfactant-modified sorbents have been proposed for applications in removal of organic compounds from aqueous solution. Surfactants were tested for their sorptive behavior onto different sorbents such as alumina, silica, titania, zeolite, clay and activated carbon (Gawade et al. 2005a; Karapanagioti et al. 2005; Yuan et al. 2000). Gawade et al. (2005a) modified alumina surface by adsorption of an anionic surfactant, i.e. sodium dodecyl sulfate (SDS), for the removal of herbicide from water. It resulted that the alumina surface changed its characteristics from hydrophilic to hydrophobic upon adsorption of anionic surfactant at pH less than point of zero charge (pH_{PZC}) and the surfactant-treated alumina was found to have greater adsorption capacity for herbicide (isoproturon) than untreated alumina (Gawade et al. 2005b).

In this work, sodium dodecyl sulfate (SDS), sodium di(2-ethylhexyl) sulfosuccinate (AOT or Aerosol OT), dodecyltrimetyl ammonium chloride (DTAC) and polyoxyethylene (20) sorbitan monopalmitate (Tween-40 or Tw-40) are selected as representatives of surfactant to be adsorbed on the surface of titania nanofibers. Properties of these surfactants are shown in Table 2.2.

Table 2.2 Properties of surfactants used in the study.

Surfactant	Type	MW	CMC (mg l^{-1})	Chemical structure
Sodium dodecyl sulfate (SDS) $CH_3(CH_2)_{11}OSO_3Na$	Anionic	288.8	2310.4[a]	
Sodium di(2-ethylhexyl) sulfosuccinate (AOT or Aerosol OT) $C_{20}H_{37}O_7SNa$	Anionic	444.56	700[b]	
Dodecyltrimetyl ammonium chloride (DTAC) $C_{15}H_{34}NCl$	Cationic	263.89	5349.05[c]	
Polyoxyethylene (20) sorbitan monopalmitate (Tween-40 or Tw-40) $C_{16}H_{31}O_2C_6H_{11}O_4(CH_2CH_2O)_{20}$	Nonionic	1282	29[d]	

[a](Yuan et al. 2000) [b](Karapanagioti et al. 2005) [c](Nowakowska et al. 2003) [d](Shen et al. 2007)

2.7 Adsolubilization Process

Adsolubilization is the preferential partitioning of solutes into surfactant aggregates (admicelles) adsorbed on the surface. It is the surface analog of solubilization in micelles. Adsolubilization has also been referred to as surface solubilization and coadsorption. It has been extensively studied over the last two decades. It is a fundamental part of various processes including admicellar polymerization, pharmaceutical applications and surfactant enhanced environmental remediation. In spite of the number of current and potential applications, little work has been done to provide basic understanding of the phenomenon (Tan and O'Haver 2004).

The adsorbed surfactant aggregates, called as either admicelles or hemimicelles, may serve to solubilize solutes. Although adsolubilization was reported as early as 1955, it was not systematically studied until in the mid-1980s. Since then, many methods have been used to study the nature and structure of these adsorbed aggregates. The results have shown that admicelles assume a variety of shapes including, monolayers, bilayers, spheres and cylinders (Grant et al. 1998; Patrick et al. 1997; Tiberg et al. 1999). The admicelle internal structure has been compared to that of micelles, divided into three different regions (core, palisade, and head group) based on increasing polarity. It has been hypothesized that solutes with different polarities and structures will preferentially partition into different regions within the admicelle according to their hydrophobicity and structure. Additionally, several partition coefficients have been defined by different groups and used to examine adsolubilization behavior.

The adsolubilization has applications in many fields such as paints, drugs, cosmetics and waste-water treatment. Until now, the adsolubilization of dyes (Adak et al. 2005), alcohols (Adak et al. 2006), monomers, aromatic compounds (Valsaraj et al. 1998; Yuan et al. 2000) and steroids has been reported using hydrophilic particles. The adsolubilization method is one of the effective ways for lowering concentration of low soluble organic pollutants from effluent. Recently, the adsolubilization of contaminants has been examined for environmental problem.

A major body of this work has been directed toward modifying and testing titanium dioxide nanofiber to identify ways to increase process efficiency and to improve the adsolubilization of herbicide on surfactant-treated titania nanofiber.

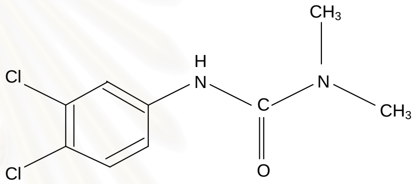
2.8 Phenylurea Herbicides

In the present day, tropical countries of the world still use herbicide in agriculture. It is the major cause of many problems about toxic contaminant in environment. Phenylurea herbicide is one group of herbicide which has been widely used throughout the world to eliminate general weed for several crops such as citrus, asparagus and bush fruit (Pena et al. 2002). Phenylurea herbicide functions as photosynthesis inhibitor. However, only less than 1% of total applied herbicide reaches the target plant. The vast majority being dispersed ends up contaminating land, air and mainly water. Examples of herbicide in this group are diuron, isoproturon, linuron, monuron and fenuron. In this work, diuron, isoproturon and linuron are selected as representatives for an investigation of phenylurea adsolubilization on surfactant-modified titania nanofibers.

2.8.1 Diuron

Diuron [3-(3,4-dichlorophenyl)-1,1-dimethylurea) or N´-(3,4-dichlorophenyl)-N,N-dimethyl urea] is a herbicide, which is largely used in agriculture for selective control of germinating grass and broad-leaved weed in many crops. It is also used for total weed control in non-cultivated area (Tomlin 2000). It has shown to inhibit plant photosynthesis by blocking light reaction (Cawse 1980). Physical properties of diuron are shown in Table 2.3.

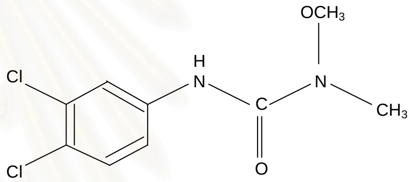
Table 2.3 Physicochemical properties of Diuron

Chemical structure	
Molecular weight	233.10
Molecular formula	$C_6H_{10}Cl_2N_2O$
Melting point	158 – 159°C
Vapor pressure	0.0041 Pa at 30°C
Appearance	White crystalline solid
Synonyms	Cekiuron, Crisuron, Dailon, Diater Di-on, Derex4L, Diurex, Diurol Dynex, etc.
Solubility	42 ppm in water at 25°C
Toxicity	The concentrated material may cause irritation to the eyes and mucous membrane. But a 50% water paste is not irritating to the intact skin of mammal
Half-life	Over 300 days in soil

2.8.2 Linuron

Linuron [3-(3,4-dichlorophenyl)-1-methoxy-1-methyl urea or N´-(3,4-dichlorophenyl)N´-methoxy- N´-methyl urea] is a selective herbicide belonging to the phenylurea group with pre- and post-emergence activity. It is widely used in different types of cultivation. Linuron tends to be strongly absorbed by soil and therefore its mobility is low (Sfinchez-Martfn et al. 1996). Linuron is used to control weed in many vegetations including potatoes, peas, carrot, bean, wheat, celery, parsnip and parsley. Its properties are shown in Table 2.4.

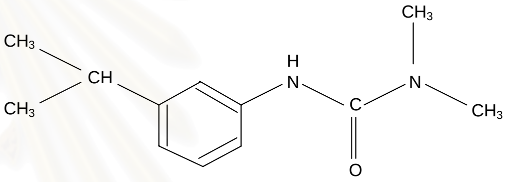
Table 2.4 Physicochemical properties of Linuron

Chemical structure	
Molecular weight	249.17
Molecular formula	$C_9H_{10}Cl_2N_2O_2$
Melting point	85 – 94°C
Vapor pressure	0.0020 Pa at 24°C
Appearance	White crystalline solid
Synonyms	Afalon, Lorox, Linex, Linurex, Markman1, Rotalin, etc.
Solubility	75 ppm in water at 25°C
Toxicity	Excessive exposure to Linuron may affect the blood, and may cause cancer, vary to aquatic organism and likely to be harmful to other wildlife, low toxicity herbicide
Half-life	3-4 months in most soils

2.8.3 Isoproturon

Isoproturon [(3-(4-isopropylphenyl)-1,1-dimethylurea or 3-p-cumenyl-1,1-dimethylurea] is a selective herbicide acting by inhibition of photosynthesis (Tomlin 1994). It has been used for pre-and post-emergence control of annual grass, wild oats, annual meadow grass and many broad leaf weeds, etc. Isoproturon can be mobile in soil and has been detected in both surface water and ground water. In water, its half-life is about 30 days.

Table 2.5 Physicochemical properties of Isoproturon

Chemical structure	
Molecular weight	206.29
Molecular formula	$C_{12}H_{18}N_2O$
Melting point	155 – 156°C
Vapor pressure	0.003 mPa at 20°C
Appearance	White crystalline solid
Solubility	72 ppm in water at 20°C
Toxicity	Low toxic, acute oral to mouse is over 10000 mg/kg
Half-life	30 days in water , 6.5 to 30 days in soil

2.9 Photooxidation

Atoms have discrete energy levels for their electrons. For a semiconductor such as titania, the highest filled band is termed the valence band (VB), and the lowest unoccupied level is the conduction band (CB). The separation between the top of the valence band and the bottom of the conduction band is called band gap.

The photocatalytic reaction starts with an exposure of photocatalyst to light. After light is absorbed by the photocatalyst, two types of carriers, i.e. electron (e^-) and holes (h^+), are generated. Semiconductor oxides such as TiO_2, ZnO, $SrTiO_3$, K_4NbO_2, Fe_2O_3 and SnO_2 are good photocatalyst because of the long life for both of these carriers are used in photocatalytic process. For titania, anatase has been long known to be more photoactive than rutile. One of the reasons may lie in the difference in their so-called energy band structures. The band gap of a semiconductor is the minimum energy of light required to make the electrons excited enough to get moving. When a photon of energy higher or equal to the band gap energy is absorbed by a semiconductor particle, an electron from the valence band is promoted to the conduction band with simultaneous generation of an electronic vacancy or "hole" (h^+) in the valence band. For anatase titania, this energy is 3.2 electron volts (eV), which corresponds to UV light (wavelength of 388 nanometers), while the band gap for the rutile is 3.0 eV, corresponding to violet light (wavelength of 413 nanometers). The hole can react with water to produce the highly reactivity hydroxyl radical (OH^-). Both the holes and the hydroxyl radicals are very powerful oxidants and can be used to oxidize most organic materials.

The VB energies for anatase and rutile are both similar, which is very low in the energy diagram. It means that, for both materials, the VB holes (and the hydroxyl radicals) have great oxidizing power. The CB energy for rutile is close to the potential required to electrolytically reduce water to hydrogen gas, but that for anatase is higher in the energy diagram, which means that it has higher reducing power. Therefore, it can drive the very important reaction involving the electrolytic reduction of molecular oxygen (O_2) to superoxide (O_2^-). Superoxide is found to be almost as important as the holes and hydroxyl radicals in breaking down organic compounds (Fujishima et al. 1999).

As mentioned earlier, the primary photocatalytic process occurs upon irradiation of a semiconductor catalyst. Figure 2.6 shows the primary steps in the photoelectrochemical mechanism on titania (Hoffmann et al. 1995):

(1) formation of charge carriers by 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.

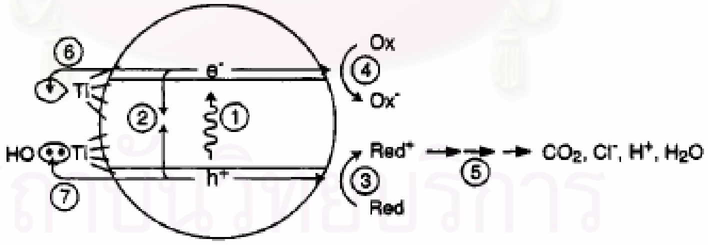


Figure 2.6 Primary steps in the photoelectrochemical mechanism (Hoffmann et al. 1995).

Among the new oxidation methods or advanced oxidation processes (AOP), heterogeneous photocatalysis on titania appears as an emerging destructive technology leading to the total mineralization of most of the organic pollutants, following the usually proposed mechanism (Ammar et al. 2001).

1. Absorption of efficient photons ($h\nu \geq E_G$ = 3.2 eV) by titania

$$(TiO_2) + h\nu \longrightarrow e^-_{CB} + h^+_{VB} \qquad (1)$$

2. Oxygen ionosorption (first step of oxygen reduction; oxygen's oxidation degree passes from 0 to .1/2)

$$(O_2)ads + e^-_{CB} \longrightarrow O_2^{\bullet -} \qquad (2)$$

3. Neutralization of OH^- groups by photoholes which produces $OH^\bullet$ radicals

$$(H_2O \rightleftharpoons H^+ + OH^-)ads + h^+_{VB} \longrightarrow H^+ + OH^\bullet \qquad (3)$$

4. Neutralization of $O_2^{\bullet -}$ by protons

$$O_2^{\bullet -} + H^+ \longrightarrow HO_2^\bullet \qquad (4)$$

5. Transient hydrogen peroxide formation and dismutation of oxygen

$$2HO_2^{\bullet -} \longrightarrow H_2O_2 + O_2 \qquad (5)$$

6. Decomposition of H_2O_2 and second reduction of oxygen

$$H_2O_2 + e^- \longrightarrow OH^\bullet + OH^- \qquad (6)$$

7. Oxidation of the organic reactant via successive attacks by $OH^\bullet$ radicals

$$R + OH^\bullet \longrightarrow R'^\bullet + H_2O \qquad (7)$$

8. Direct oxidation by reaction with holes

$$R + h^{+} \longrightarrow R^{+\bullet} \longrightarrow \text{degradation products} \qquad (8)$$

As an example of the last process, holes can react directly with carboxylic acids generating CO_2

$$RCOO^{-} + h^{+} \longrightarrow R^{\bullet} + CO_2 \qquad (9)$$

Separation of dilute concentrations of organic compounds from industrial and agricultural process water requires the use of advanced treatment methods. Most of the processes only concentrate the contaminant from water onto a solid substrate. Therefore, subsequent separation process is required to remove the solute and regenerate the solid for re-use. Yuan et al. (2001) studied reusable adsorbents for dilute solution separation by photodegradation of organic compounds on surfactant-modified titania. The photoreactions on TiO_2 occur with the molecule adsorbed on the surface of titania or molecules within a few monolayers around the catalyst particle, since the radicals involved in the photooxidation do not migrate far from the surface. The increased surface concentration of organic compounds will lead to an increase in the rate of photocatalysis of organic compounds as well. The photodegradation of hydrophobic organic compounds are in Figure 2.7.

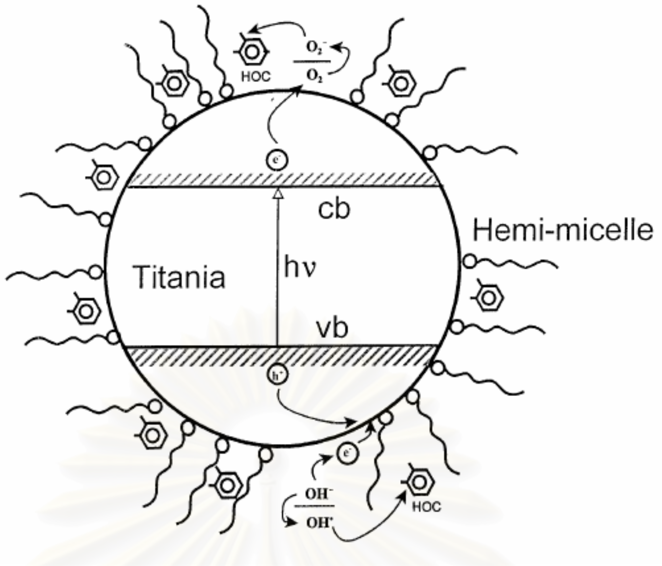


Figure 2.7 Schematic of the photodegradation of hydrophobic organic compounds on surfactant-modified titania (Yuan et al. 2001).

CHAPTER III

EXPERIMENTAL

3.1 Preparation of Titania Nanofibers

3.1.1 Materials

1. Titanium tetraisopropoxide (TTIP) 97% was purchased from Sigma-Aldrich Chemical Company and used as received.
2. Poly vinylpyrolidone (PVP), $M_w \approx 1{,}300{,}000$, was purchased from Sigma-Aldrich Chemical Company and used as received.
3. Ethyl alcohol 98 % and acetic acid were purchased from Sigma-Aldrich Chemical Company and used as received.

3.1.2 Electrospinning Apparatus

The schematic of the electrospinning apparatus used in this work is shown in Figure 3.1. The components of the apparatus and their functions are described as follows.

- A high voltage power supply (ES30PN, Gamma High Voltage Research Inc., Ormond Beach, Florida) is used to generate either positive or negative DC voltage up to 30 kV, with very low electrical current of 166 microamperes.
- A 5 ml syringe is used as a container for electrospinning solutions. The syringe is built by a plastic structure and is set in vertical orientation.
- A stainless steel needle (gauge number 20, the outside diameter of 0.90 mm) is used as a nozzle and as an electrode to conduct the electrical energy from the power supply to the solutions. The tip of the needle is cut into a flat shape and the length of the needle is 2 cm.
- Aluminum foil and stainless steel 40 meshes (3cm x 3cm) are used as a ground collector which is covered on the plastic stand.

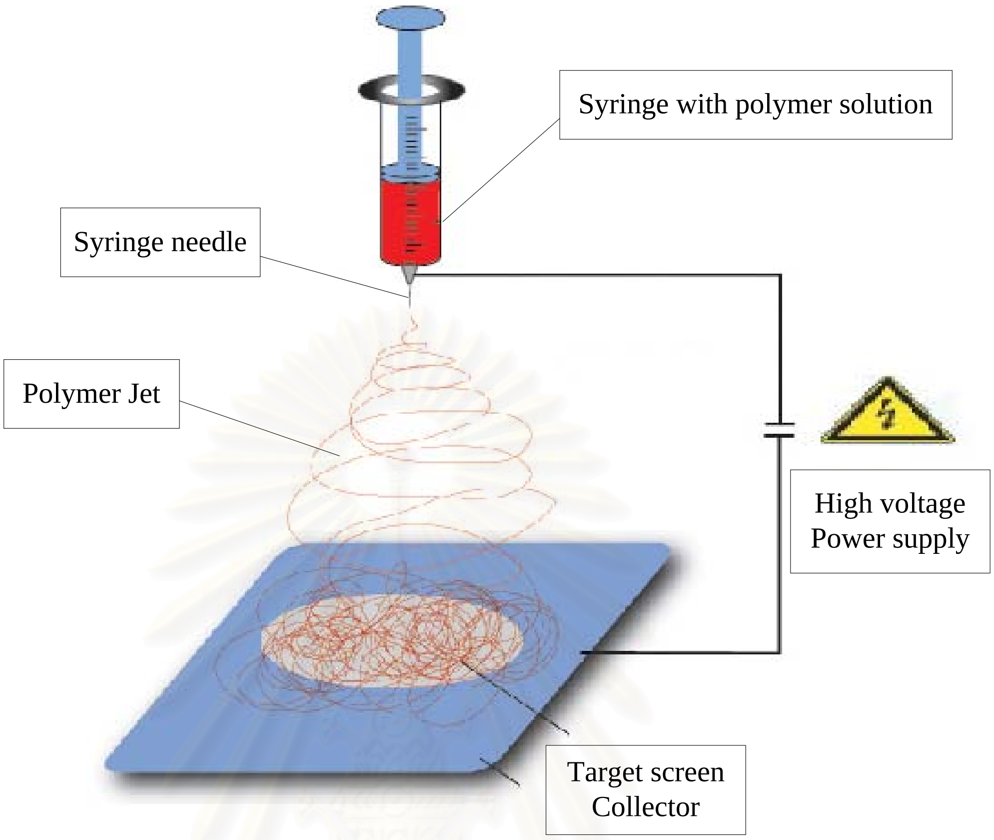


Figure 3.1 Experimental set up for electrospinning process.

3.1.3 Preparation Procedures

3.1.3.1 Preparation of spinning solution

In a typical procedure, 1.5 g of titanium tetraisopropoxide (TTIP) was mixed with 3 ml of acetic acid and 3 ml of ethanol. The solution was rest for 10 min before being added into 7.5 ml of polyvinylpyrolidone (PVP, $M_w \approx 1{,}300{,}000$) solution in ethanol. The concentration of the PVP solution was 13 wt.% and the resulting mixture was constantly stirred for 10 min. The mixture was constantly stirred for another hour. The as-prepared solution was referred to as the spinning solution.

3.1.3.2 Spinning process

The spinning solution was immediately loaded into a plastic syringe. A blunt-ended 20-gauge stainless steel needle was used as the nozzle. The emitting electrode from a Gamma High Voltage Research ES30PN power supply capable of generating DC voltages up to 30 kV was attached to the needle. The grounding electrode from the same power supply was attached to a piece of aluminum foil or stainless steel 40 mesh (3cm x 3cm) which was used as the collector plate and was placed approximately 7 cm below the tip of the needle. Upon the application of a high voltage (15 kV) across the needle and the collective plate, a fluid jet was ejected from the nozzle. As the jet accelerated towards the collector, the solvent evaporated, leaving only ultrathin fibers on the collector. The as-spun fibers were left exposed to moisture for approximately 24 hours to allow complete hydrolysis of TTIP. The obtained fibers were TiO_2/PVP composite fibers.

3.1.3.3 Calcination of the TiO_2/PVP composite fibers

The electrospun TiO_2/PVP composite fibers were subjected to heat treatment at 500°C in air for 3 hours and heating rate of 10°C/min by using a box furnace to remove residual PVP. The sample was heated from room temperature at the rate of 10°C/min.

3.1.4 Characterizations of Titania Fibers

3.1.4.1 X-ray Diffraction (XRD)

The crystalline phases of the obtained TiO_2 fibers were identified by using a Siemens D5000 X-ray diffractometer at the Center of Excellence on Catalysis and Catalytic Reaction Engineering, Chulalongkorn University. The measurement was carried out by using Ni-filtered CuKα radiation, operated in the 2θ range of 20-80 degree at the scan step of 0.04 degree. The crystallite size was estimated from line broadening of the main XRD peak, according to the Scherrer equation, using α-Al_2O_3 as standard.

3.1.4.2 Scanning Electron Microscopy (SEM)

Surface morphology and size of the resulting electrospun fibers were observed by a JSM 5800 Scanning Electron Microscopy (SEM), which was operated at 20 kV, at the Scientific and Technological Research Equipment Center (STREC), Chulalongkorn University. Samples were coated by thin film of gold prior to the analysis.

3.1.4.3 Surface area measurement

The BET surface area of pure TiO_2 fibers were measurement by a Pulse Chemisorption System: Micrometrics Chemosorb 2750 at the Center of Excellence on Catalysis and Catalytic Reaction Engineering, Chulalongkorn University. Using nitrogen as the adsorbate. The operating conditions are as follows:

Sample weight	~ 0.05 g
Degas temperature	200^oC
Vacuum pressure	< 10 mmHg

3.1.4.4 Fourier Transform Infrared Spectroscopy (FTIR)

Functional groups of the as-prepared fibers and calcined fibers were identified by a Nicolet 6700 Fourier transform infrared spectrophotometer. Infrared spectra were recorded between wave number of 400 and 4000 cm^{-1}, resolution 2 and data spacing 0.964 cm^{-1}.

3.1.4.5 Thermogravimetric and Differential Thermal Analysis (TG/DTA)

The as-spun titania fibers were subjected to thermogravimetric and differential thermal analysis (Diamond Thermogravimetric and Differential Thermal Analyzer, TG-DTA, Perkin-Elmer) to determine the temperature of possible PVP decomposition and phase change. Mass of the adsorbed surfactant on titania was determined by this analysis technique.

3.1.4.6 Point of zero charge determination

The point of zero charge, pH_{pzc}, of bare titania as well as the modified titania was determined by solid additional method(Mishra et al. 2003). Batch experiments were performed in a series of 125-ml Erlenmeyer flasks. The pH_{pzc} was determined in 0.001, 0.01 and 0.1 mol dm^{-3} KNO_3 solution. 50 ml of KNO_3 solution was transferred to the flask. The initial pH of the solution was adjusted to the predetermined value, in the range from 2 to 10, by adding either 0.1 N HNO_3 or NaOH to the solution. The initial pH value of the solution was accurately noted. Then, one gram of titania was added to the solution and the flask was securely capped immediately. The suspensions were allowed to equilibrate for 48 hours, during which constantly shaking was applied. After that, the pH value of the supernatant liquid was noted. The same procedure was repeated with different value of the initial pH. Finally, the difference between initial and final pH values (ΔpH) was plotted against the initial pH. The point of intersection, at which $\Delta pH=0$, gave the pH_{pzc}. This procedure was repeated for all concentrations of KNO_3.

3.2 Adsorption of Surfactants

3.2.1 Surfactants

1. Sodium dodecyl sulfate (SDS) ≥99% was purchased from Fluka Chemical Company and used as received.
2. Sodium di(2-ethylhexyl) sulfosuccinate (AOT or Aerosol OT) 98% was purchased from Sigma-Aldrich Chemical Company and used as received.
3. Dodecyltrimetyl ammonium chloride (DTAC) ≥99% was purchased from Fluka Chemical Company and used as received.
4. Polyoxyethylene (40) sorbitan monopalmitate (Tween 40) was purchased from Fluka Chemical Company and used as received.

3.2.2 Adsorption Procedures

For the process of titania modification, 5 g of titania was mixed with 50 ml of aqueous solution of surfactant, SDS, DTAC, Tween40 and AOT, in the predetermined concentration in the range of 0.02 to 2 wt%. The mixture was stirred for 24 h at room temperature, during which pH was adjusted to the desired value by using either 1 N of H_2SO_4 or 1 N of NaOH solution. In this work, pH for the surfactant adsorption is in the range from 2 to 10. Then, the surfactant-modified titania was carefully separated from the solution by centrifugation, after which the surfactant-treated titania was dried at 60^oC for 24 hours and used as an adsorbent for herbicide removal. The extent of adsorption, i.e. the amount of surfactant adsorbed on the surface of titania, was determined by thermogravimetric and differential thermal analysis.

3.3 Adsolubilization of Phenylurea Herbicides

3.3.1 Herbicides

1. Diuron [3-(3,4-dichlorophenyl)-1,1-dimethylurea) or N´-(3,4-dichlorophenyl)-N,N-dimethyl urea], 98% was purchased from Sigma-Aldrich Chemical Company.
2. Isoproturon [(3-(4-isopropylphenyl)-1,1-dimethylurea or 3-p-cumenyl-1,1-dimethylurea], 99% was purchased from Chem Service.
3. Linuron [3-(3,4-dichlorophenyl)-1-methoxy-1-methyl urea or N´-(3,4-dichlorophenyl)N´-methoxy- N´-methyl urea], 99% was purchased from Chem Service.

3.3.2 Adsolubilization Procedures

For the adsolubilization experiments, 0.03-0.3 g of the surfactant-modified titania was mixed with 300 ml of aqueous solution of phenylurea herbicide (concentration of herbicide was varied between 1 and 10 ppm) at temperature in the range of 30 to 60°C. The pH of herbicide solution was adjusted to the desired value in the range of 3 to 8 using either 1 N of H_2SO_4 or 1 N of NaOH solution. The mixing was done by means of sonicator. Amount of herbicide in the solution was periodically monitored by using reverse-phase liquid chromatography system, with UV detector (HPLC-UV, Agilent Technologies, series 1200) and C-18 column (ZORBAX SB-C18, 5µm particle size, 4.6x150mm). The solution of 70% acetronitrile-30% water was used as mobile phase (flow rate 1.5 ml/min). The sample injection volume was 20 µl.

3.4 Photocatalytic Regeneration

After the adsolubilization process, herbicide and surfactant-coated titania was separated from the solution by centrifugation. The titania powder was dried at 60^{o}C for 24 hours. For the photocatalytic regeneration experiments, 25 mg of dried titania was mixed with 250 ml of distilled water in a pyrex® beaker. The mixture was stirred and kept in the dark for 2 hours to allow the complete desorption of the physisorbed herbicide on the surface of surfactant-coated titania. The photocatalytic regeneration was initiated by exposing the beaker to light from UV lamps (PHILIPS TLD 15W/05). The sample were periodically taken from the system and analyzed for organic compounds by reverse-phase liquid chromatography. The diagram of the equipment setup for photocatalytic regeneration is shown in Figure 3.2.

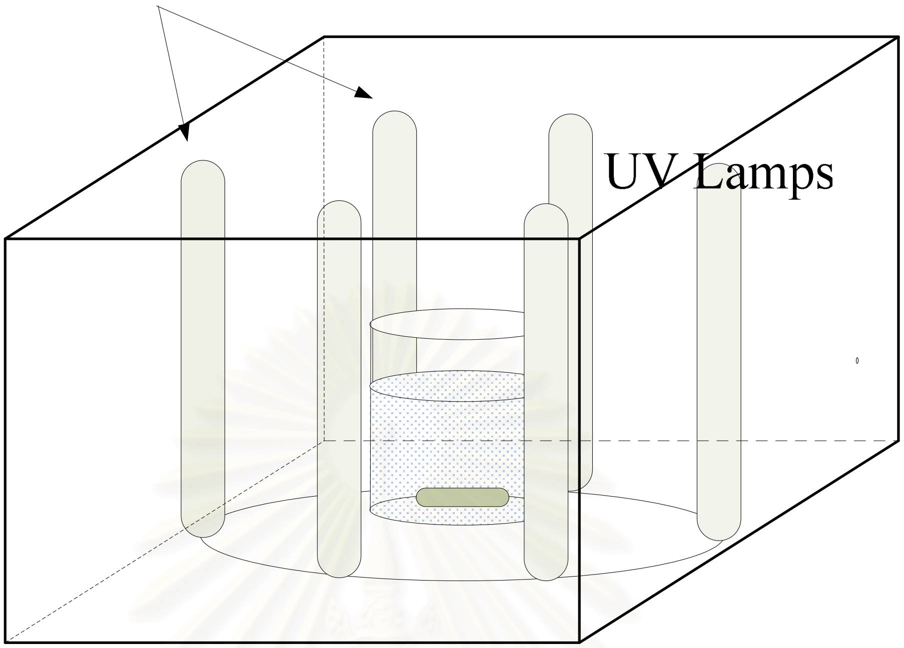


Figure 3.2 Diagram of the equipment setup for the photocatalytic regeneration.

CHAPTER IV

RESULTS AND DISCUSSION

Adsolubilization on surfactant-modified titania nanofibers can be applied to remove many organic compounds from wastewater. In this study, titania nanofibers was prepared by combination of electrospinning technique and sol-gel method. The surface of titania nanofibers was modified by adsorbing surfactant and then used as adsorbent on the adsolubilization of herbicides. Finally, photooxidation of herbicides on the surface of titania nanofibers was also investigated.

4.1 Properties of Titania Nanofibers

Titania/PVP composite nanofibers were prepared from the spinning solution containing TTIP, PVP, acetic acid and ethanol according the procedures previously described. After electric field with field strength of 15 kV was applied across the distance between the injection orifice and the collector, which was kept at 7 cm, the electrospinning of the fibers occured. Then, these nanofibers were subjected to calcination in air at 500^{o}C for 3 hours. BET surface area of the obtained titania nanofiber was found to be 33 m^2/g.

4.1.1 Thermal Analysis

The TG/DTA thermodiagrams for the obtained TiO_2 nanofibers are shown in Figure 4.1. According to the TG analysis results, mass of the as-spun fibers are sharply decreased at temperature up to 500^{o}C and slowly decrease from 500 to 1000^{o}C. The DTA analysis also shows the exothermic peak at 330 and 440^{o}C. The peak at 330°C is corresponding to the decomposition of PVP and the residual hydroxy group, while the peak at 440°C corresponds to the crystallization of amorphous phase into the anatase titania (Hong et al. 2003). Above 500°C, it can be assumed that the product completely transforms into the anatase phase because there is no significant change in either TG or DTA signal. It is clear from the TG curve that all the PVP and organic content are completely removed at 500°C, resulting in pure TiO_2 nanofibers. This conclusion is also confirmed by the thermodiagram of the fibers after calcined at 500°C for 3 hours, which shows no significant mass loss for the whole rage of the analysis temperature.

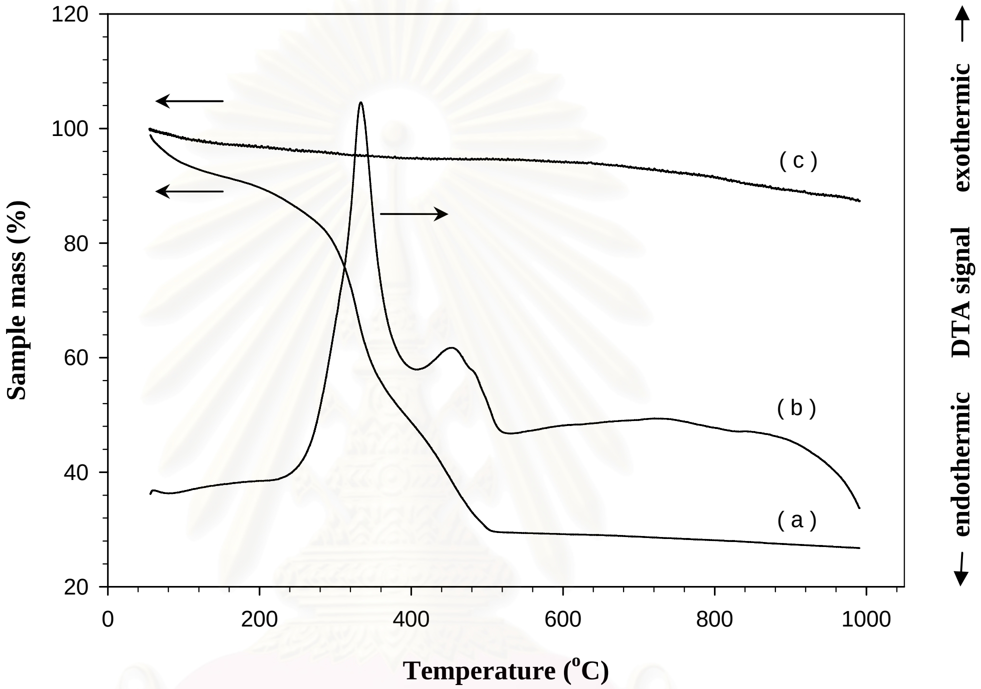
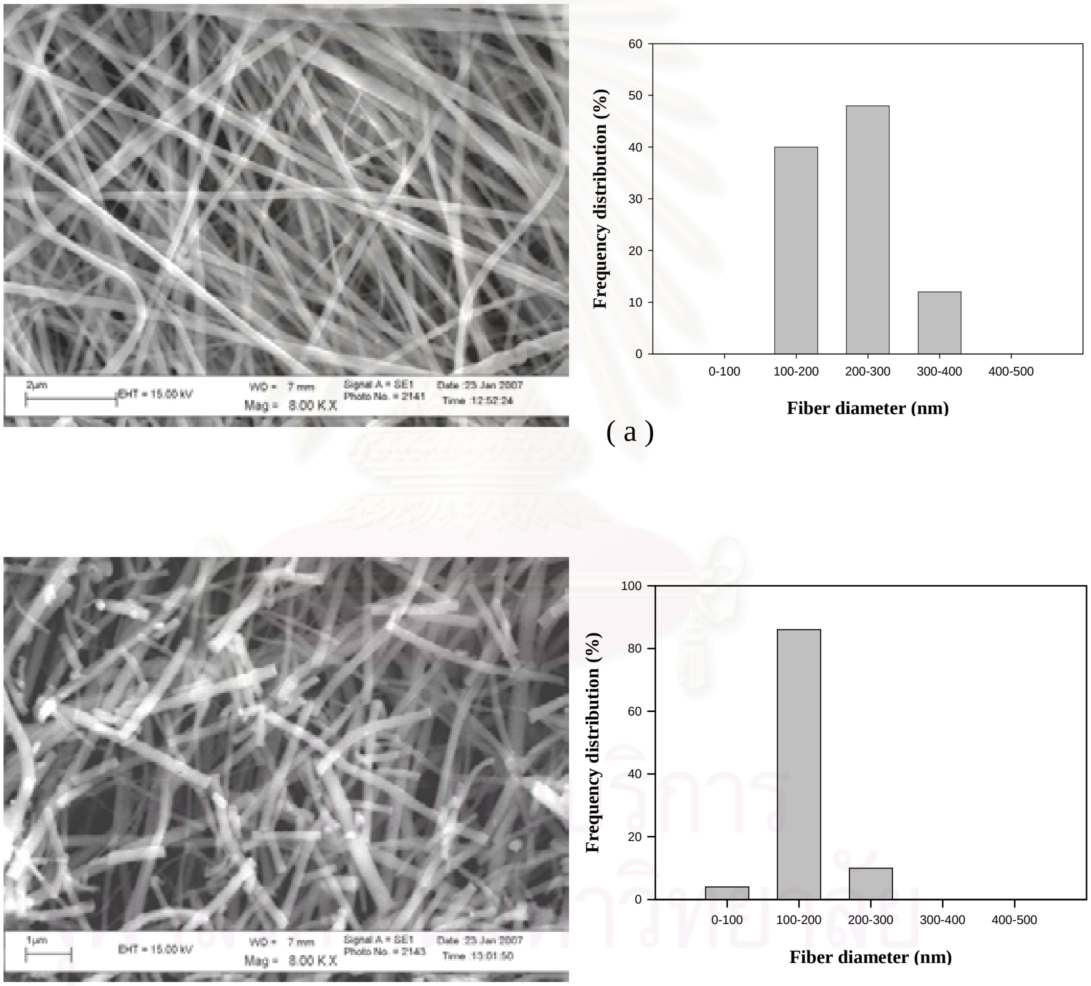


Figure 4.1 TG/DTA thermodiagrams for the titania nanofibers: (a) and (b) as-spun fibers, (c) fibers calcined at 500°C.

4.1.2 Morphology of Titania Fibers

The SEM micrographs of the fibers are shown in Figure 4.2. It can be seen that surface of the as-spun (pre-calcined) fibers is smooth according to amorphous nature of TiO_2/PVP composite fibers, (see Figure 4.2(a)). Crystallization takes place during the calcination. The titania fibers obtained after calcination at 500°C (Figure 4.2(b)) exhibit significant shrinkage as well as a reduction in fiber diameter due to the removal of both PVP and organic content from the fiber, which has already been proved by TG/DTA analysis. Shrinkage of the fibers also results in fibers that are no longer straight, as well as the breakage of the fibers into short fibers. The frequency distributions for diameter of both as-spun and calcined fibers are also determined from SEM image analysis program and shown in Figure 4.2. The results confirm visual observation, regarding the reduction in fiber diameter. Before the calcination, the average diameter of the TiO_2/PVP composite fibers is 229 nm. The average diameter decreases to 165 nm, after calcination.



(a)

(b)

Figure 4.2 SEM micrographs and frequency distribution of fiber diameter: (a) as-spun fibers, (b) fibers calcined at 500°C.

4.1.3 X-ray Diffraction Analysis

The XRD patterns of the as-spun TiO_2/PVP composite fibers, titania fibers after calcination at 500°C for 3 hours and the reference titania (Degussa P25 from the Deggussa corporation) are shown in Figure 4.3. XRD analysis indicates that the as-spun fibers prior to calcination are amorphous (Figure 4.3(a)). After calcination at 500°C for 3 hours (Figure 4.3(b)), the major phase of the fiber is anatase titania with a trace of rutile. Increasing calcination temperature would result in higher content of rutile phase. Only rutile phase is obtained if the calcination is conducted at 800°C (Watthanaarun et al. 2005). On the other hand, if the fibers are calcined at temperature lower than 500°C, the removal of PVP from the fibers is not completed, according to the thermal analysis reported earlier. Residual PVP can deteriorate activity of titania surface.

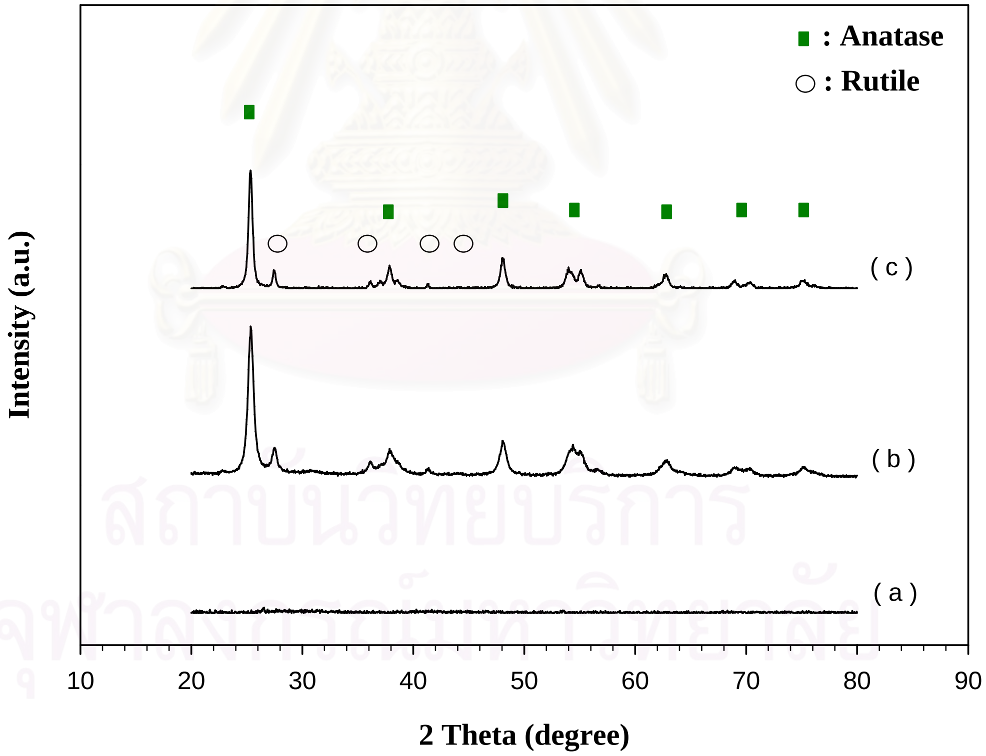


Figure 4.3 XRD patterns of as-spun fibers (a), fibers calcined at 500°C for 3 hours (b), and the commercial titania (Degussa P-25) (c).

4.2 Surfactant-Modified Titania Nanofibers

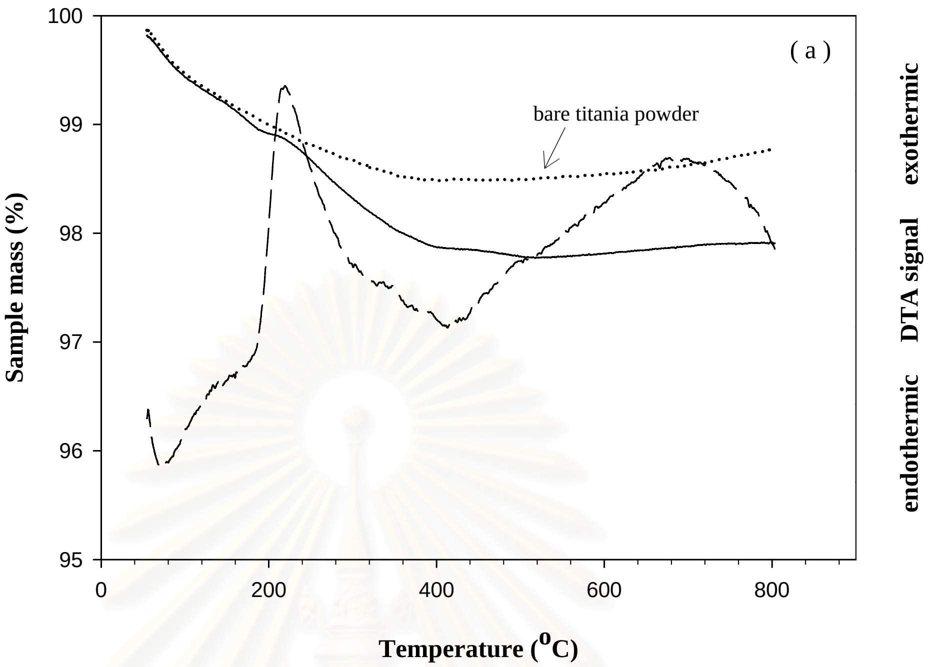
In order to enhance the adsorption of herbicide, which is hydrophobic organic compound, onto the surface of titania nanofibers, the major idea of this work is to make the surface more hydrophobic by surfactant adsorption. Three types of surfactant, i.e. anionic, cationic and nonionic, were used for titania surface modification. Interaction between surface of adsorbent and adsorbate species are investigated.

4.2.1 Effects of Type of Surfactant

There are many parameters that can affect adsorption of the surfactant on titania particle. One of important parameter is type of the surfactant. In this work, anionic, cationic and nonionic surfactants are studied. In the first portion of this section, adsorption capacity of the surfactant is investigated, by using commercial titania powder (Degussa P-25). Adsorption on the synthesized titania nanofibers is discussed in the later part of this section.

4.2.1.1 Anionic surfactant

Sodium dodecyl sulfate (SDS) and sodium di(2-ethylhexyl) sulfosuccinate (AOT) were used as representatives for anionic surfactant in this work. SDS-modified titania and AOT-modified titania were produced by adsorption on the titania particles (concentration of SDS and AOT aqueous solution employed in the surface modification process was fixed at 2wt%.). The pH of surfactant solution was not controlled in this section and it was found to be about 6.45 and 6.5 for SDS and AOT solution, respectively. Products from the adsorption process were analyzed by TG/DTA technique. The mass change of the sample was determined during thermal treatment at a ramp rate of 20^{o}C/min. For SDS coated-titania, the thermodiagram shows slight decrease in sample mass within the temperature range around 193-475^{o}C (Figure 4.4(a)), which is the same range for the decomposition of pure SDS shown in the Figure 4.4(b). According to the TG/DTA result, amount of SDS adsorbed on titania particles was found to be 0.59wt%. For AOT coated-titania, mass of the sample decreases in the range of temperature around 225-528^{o}C (Figure 4.5(a)), which corresponds to mass of AOT adsorbed on titania. The amount of AOT adsorbed is 2.85wt%. From the data obtained from TG analysis, number of mole of SDS and AOT adsorbed on titania is found to be 2.23×10^{-2} and 6.96×10^{-2} mole per gram of titania, respectively. This result implies that molecule of AOT can adsorb on the surface of titania more effectively, although AOT molecule is bulkier than SDS. The possible reason may lie on the structure of AOT, which contains carbonyl functional group. Oxygen atom in the carbonyl group may enhance the interaction between AOT and titania, whereas such functional group is not present in SDS. Nevertheless, further detailed study is needed to elucidate the adsorption mechanism of AOT.



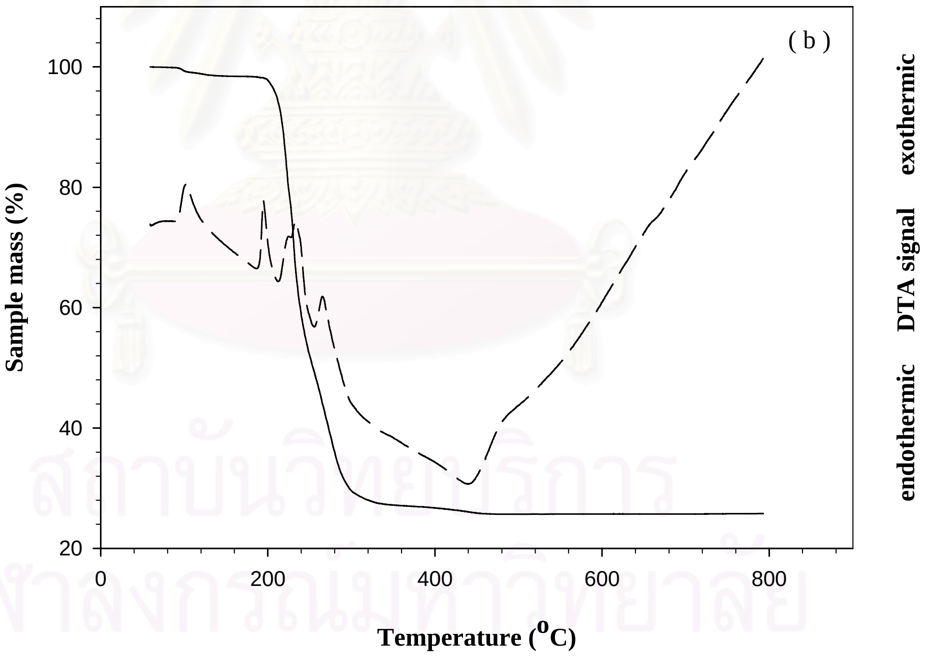


Figure 4.4 TG/DTA thermodiagrams for titania powder modified with SDS (a) and pure SDS (b); TG signal (——), DTA signal (−−−).

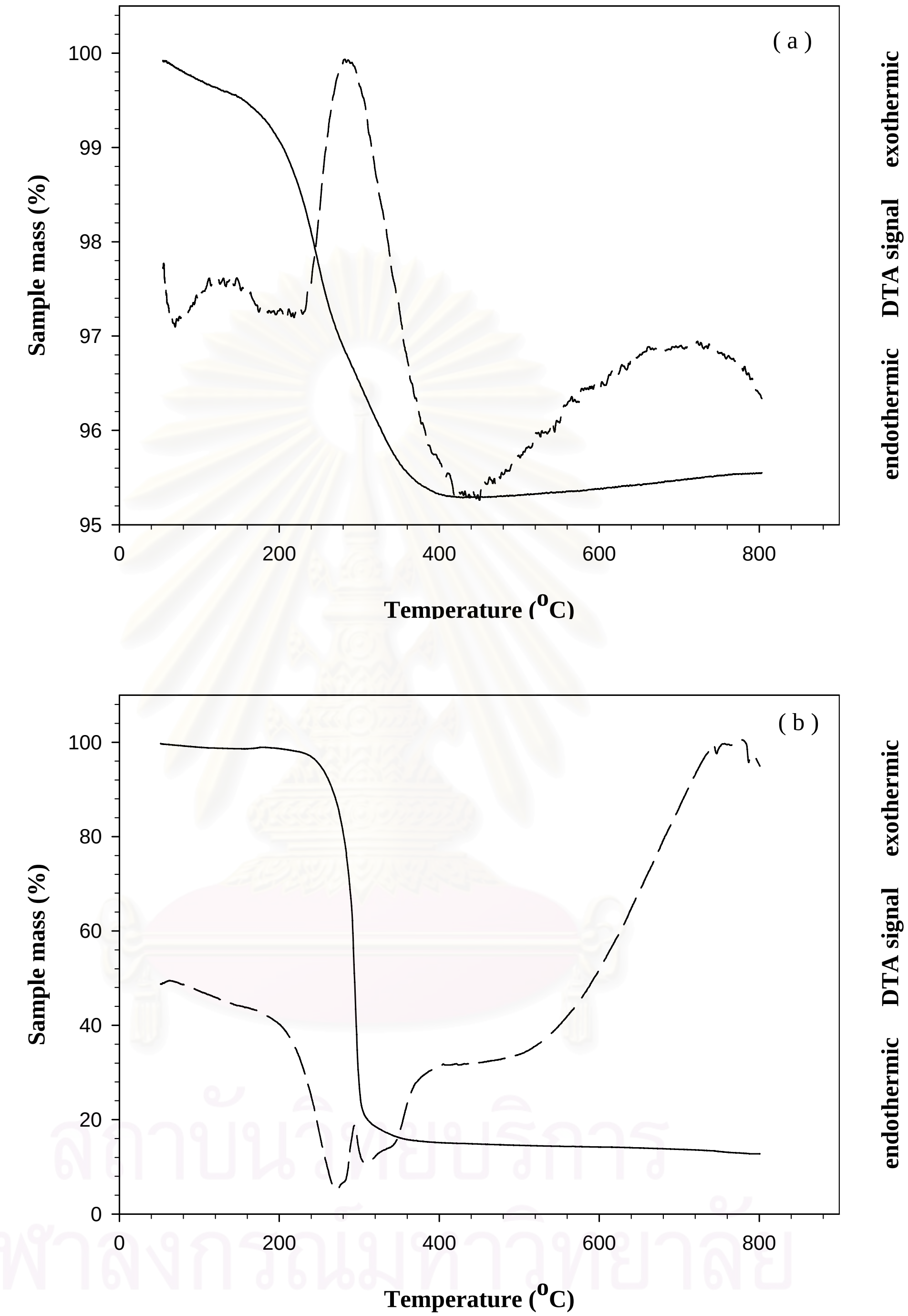


Figure 4.5 TG/DTA thermodiagrams for titania powder modified with AOT (a) and pure AOT (b) ; TG signal (——), DTA signal (–––).

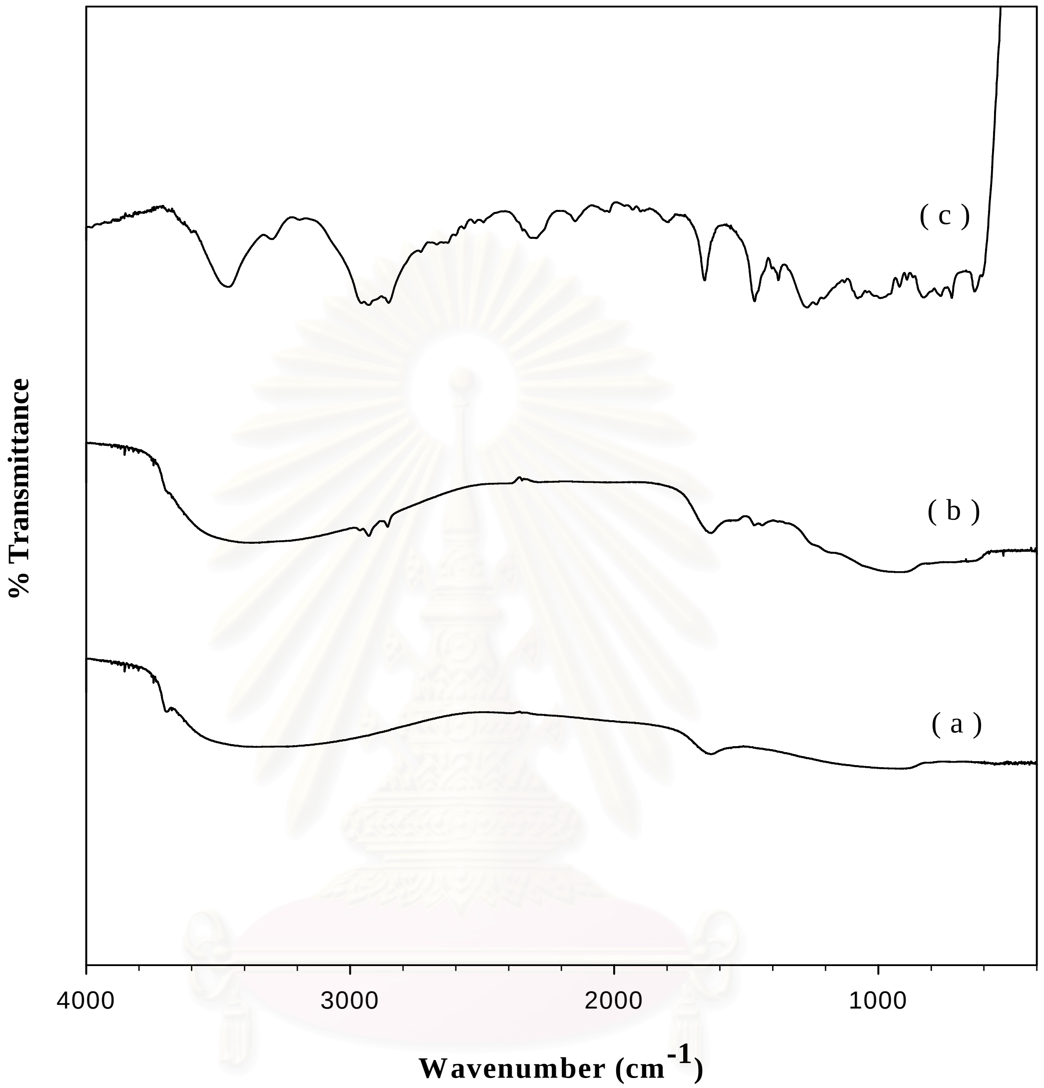


Figure 4.6 FT-IR spectra of bare titania powder (a), titania powder modified with SDS (b) and pure SDS (c).

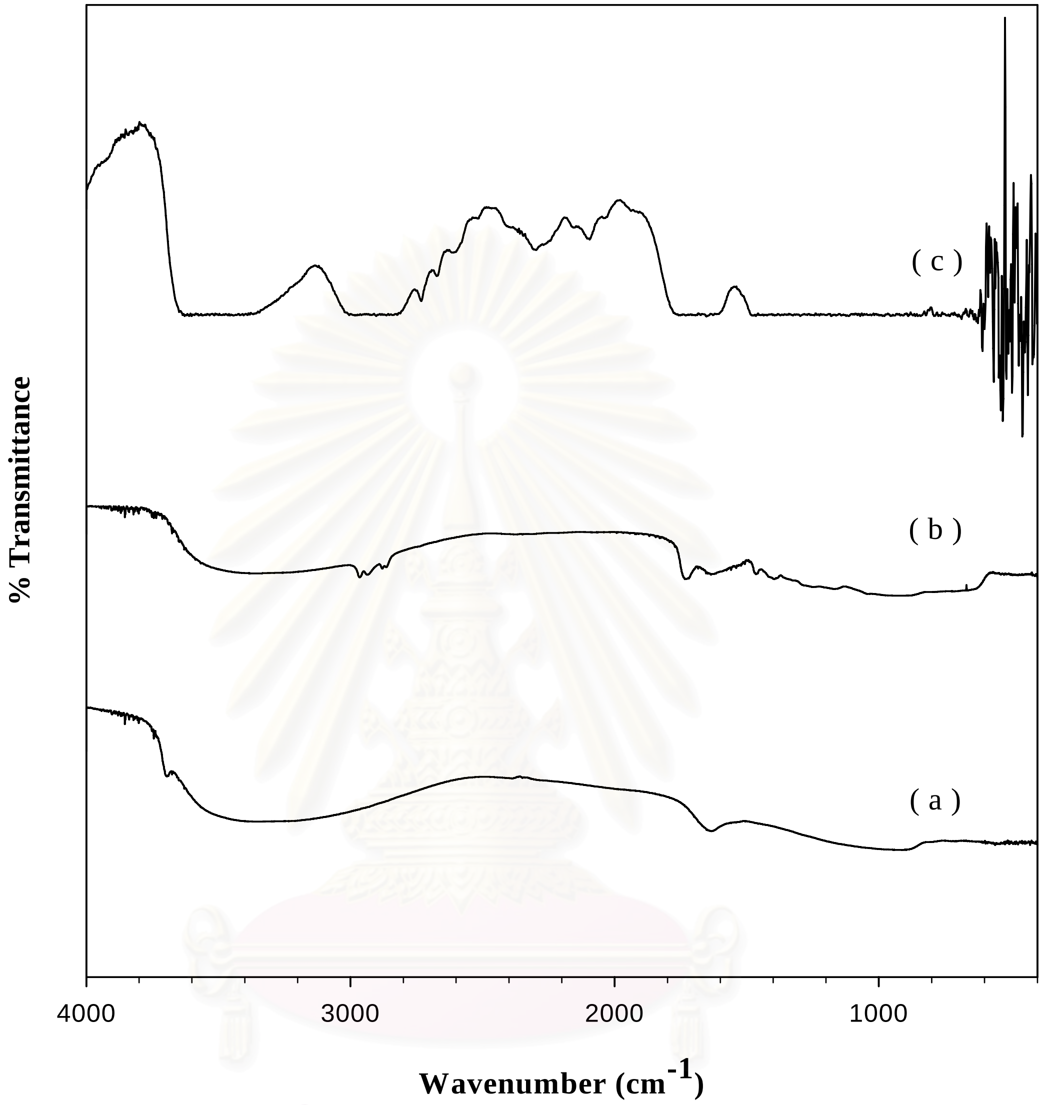


Figure 4.7 FT-IR spectra of bare titania powder (a), titania powder modified with AOT (b) and pure AOT (c).

To further confirm that SDS and AOT were successfully coated on the surface of titania particles after the adsorption, the solid particles from adsorption were characterized by FT-IR, from which the results are shown in Figure 4.6 and 4.7, respectively. It should be noted that wavenumber of around 1050-1120 cm^{-1} and 1220-1300 cm^{-1} are assigned as the vibrational stretching bands of the sulfate groups, while wavenumber in the range of 2960-2850 cm^{-1} corresponds to the stretching vibration of CH_2 and CH_3 groups (Rungruang et al. 2006). According to the FT-IR analysis, all distinct bands of the surfactant are present in the modified titania. Therefore, it is confirmed that the surfactant can be adsorbed onto the surface of titania by the technique employed in this work.

4.2.1.2 Cationic surfactant

DTAC or dodecyltrimetyl ammonium chloride was used as cationic surfactant to be adsorbed on titania surface in this work. In the similar manner as previously described, adsorption capacity of DTAC on the surface of titania was found to be 0.94wt%, based on the observed mass loss at temperature in a range of 225-467^{o}C in TG/DTA analysis (Figure 4.8).

FT-IR analysis was conducted to confirm that the surface of titania particles was modified by DTAC. The spectra of the modified titania (Figure 4.9(b)) shows the broad absorption band at the wavenumber around 2960-2850 cm^{-1}, which relates to a stretching vibration of CH_2 and CH_3 groups in DTAC structure. The results suggest the presence of DTAC on the surface of titania after the modification process.

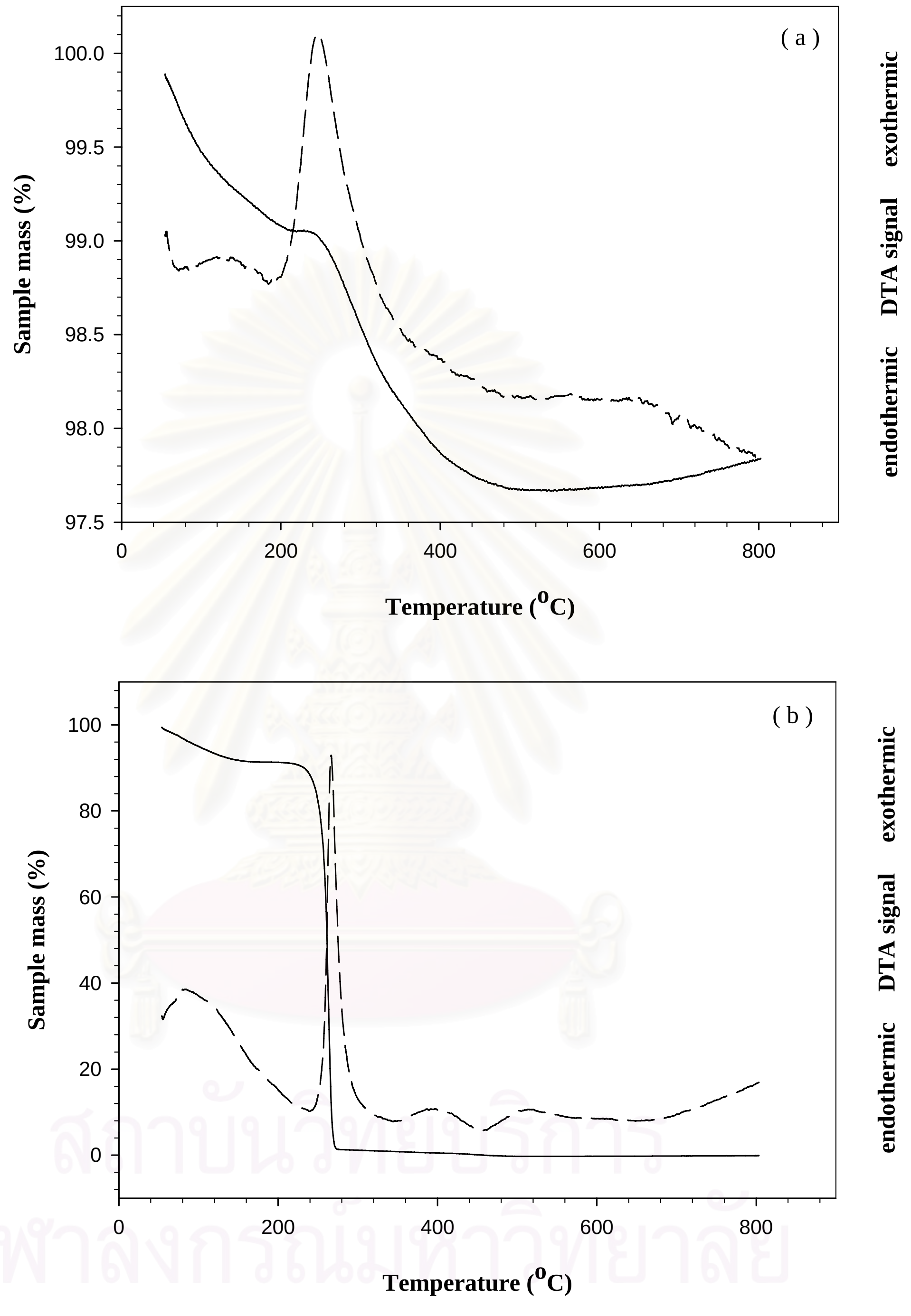


Figure 4.8 TG/DTA thermodiagrams for titania powder modified with DTAC (a) and pure DTAC (b) ; TG signal (——), DTA signal (−−−).

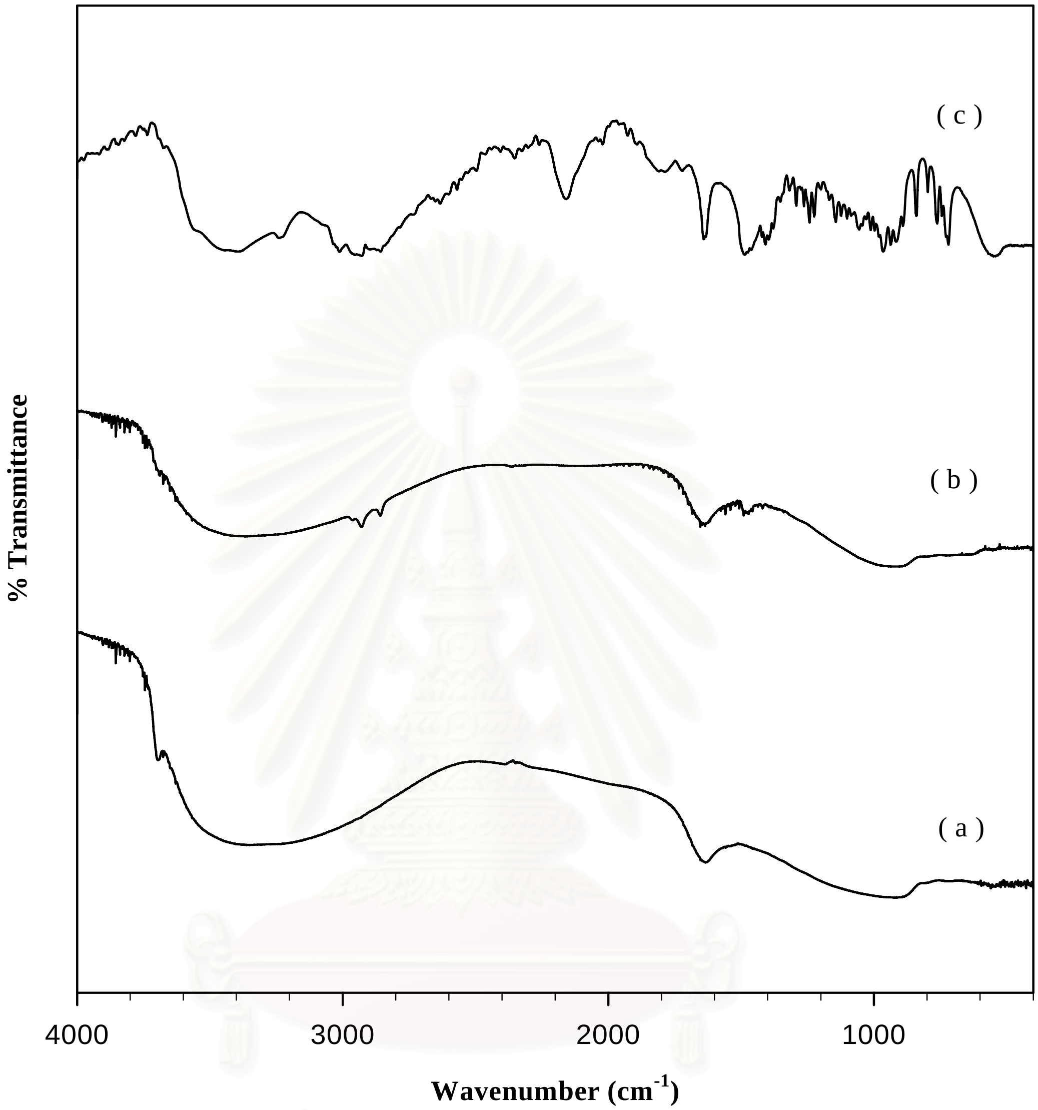


Figure 4.9 FT-IR spectra of bare titania powder (a), titania powder modified with DTAC (b) and pure DTAC (c).

4.2.1.3 Nonionic surfactant

Tween40 was used as nonionic surfactant to be adsorbed on titania surface. The TG/DTA analysis result for the modified titania in Figure 4.10(a) shows mass loss about 1.33wt%. in the temperature range corresponding to the decomposition of Tween 40 (164-489^{o}C). However, the FT-IR spectra of the Tween40-modified titania (Figure 4.11) does not reveal any significant absorption band associated with Tween40. This inconsistency has not been resolved, since Tween40-modified titania was later found to be ineffective in the removal of herbicides from water. Detailed discussion will be given in the next section.

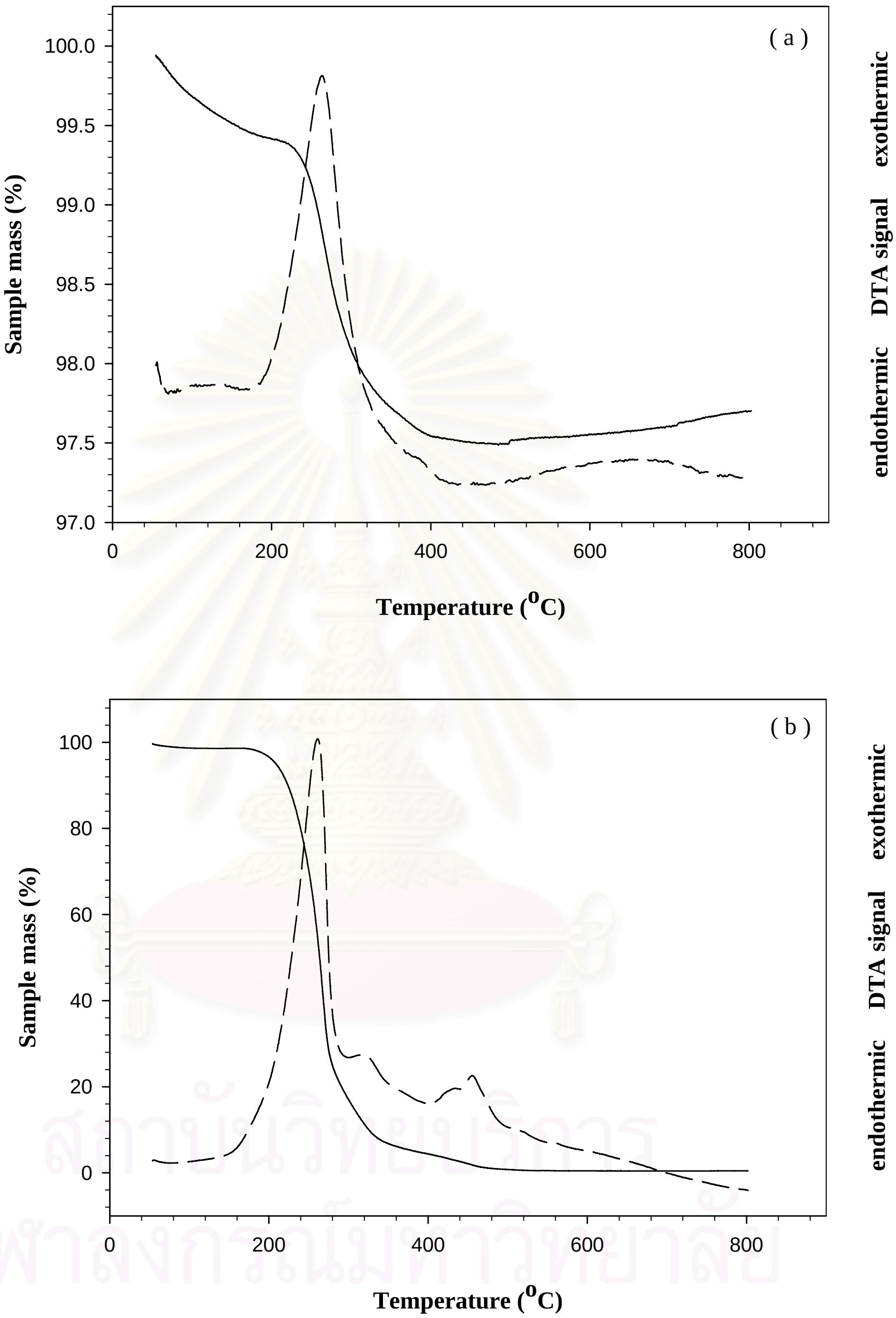


Figure 4.10 TG/DTA thermodiagrams for titania powder modified with Tween40 (a) and pure Tween40 (b) ; TG signal (——), DTA signal (– – –).

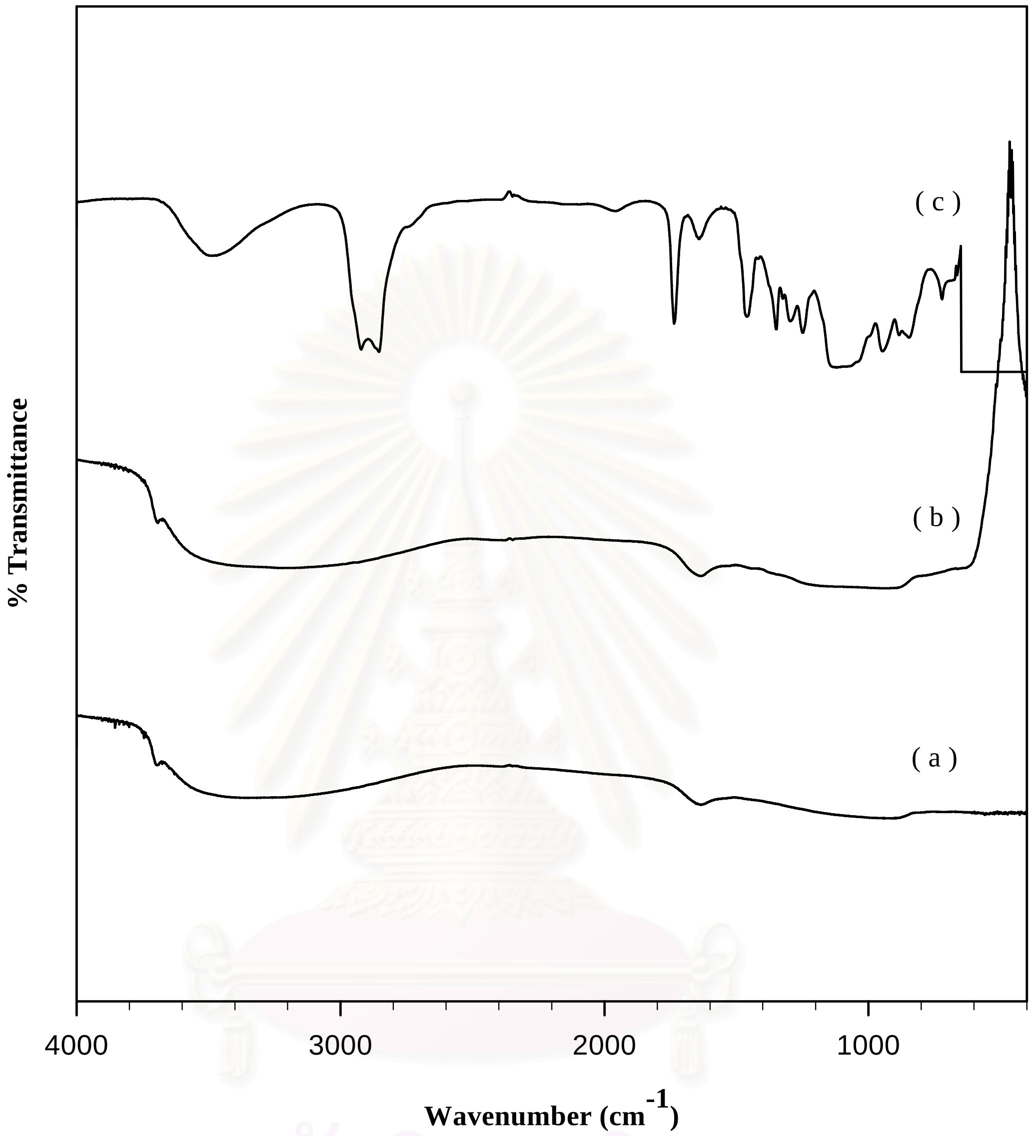


Figure 4.11 FT-IR spectra of bare titania powder (a), titania powder modified with Tween40 (b) and pure Tween40 (c).

4.2.1.4 Adsorption of surfactant on titania nanofibers

After the test for the adsorption of various surfactants on titania powder, it is applied to the synthesized titania nanofibers. The amount of surfactant adsorbed on titania nanofibers is determined from TG analysis result and compared with that obtained from titania powder. The results are shown in Figure 4.12.

According to Figure 4.12, it is clear that both AOT and DTAC can adsorb onto the surface of titania nanofibers in the greater amount than the surface of titania powder, while amount of SDS adsorbed on titania nanofibers and powder are not significantly different. The possible reason is point of zero charge, which was found to be 3.5 and 5 for titania nanofiber and powder, respectively. Since the pH of the solution used for DTAC adsorption was not controlled and found to be 5.5 titania nanofibers, which has lower point of zero charge, would have more negative surface charge than titania powder. Therefore, DTAC, which is cationic surfactant, is adsorbed in higher amount on titania nanofiber.

For SDS and AOT, the reason that the surfactant can adsorb on to the titania nanofibers better than titania powder may involve the accessibility of the surfactant molecule to titania surface. Although titania powder has higher BET surface area than the synthesized fibers (54.74 m^2/g versus 47.12 m^2/g), the surface of the nanofiber is easier to access than the surface of agglomerated powder. It should be pointed out that the BET surface area measurement was done by using nitrogen gas, which is significantly smaller than the surfactant molecule (Figure 4.13 shows pore size distribution for synthesized titania fibers and titania powder). Nevertheless, the significant increase in the amount of AOT adsorbed on titania nanofibers may also associate with the molecular structure of AOT as mentioned in the proceeding section.

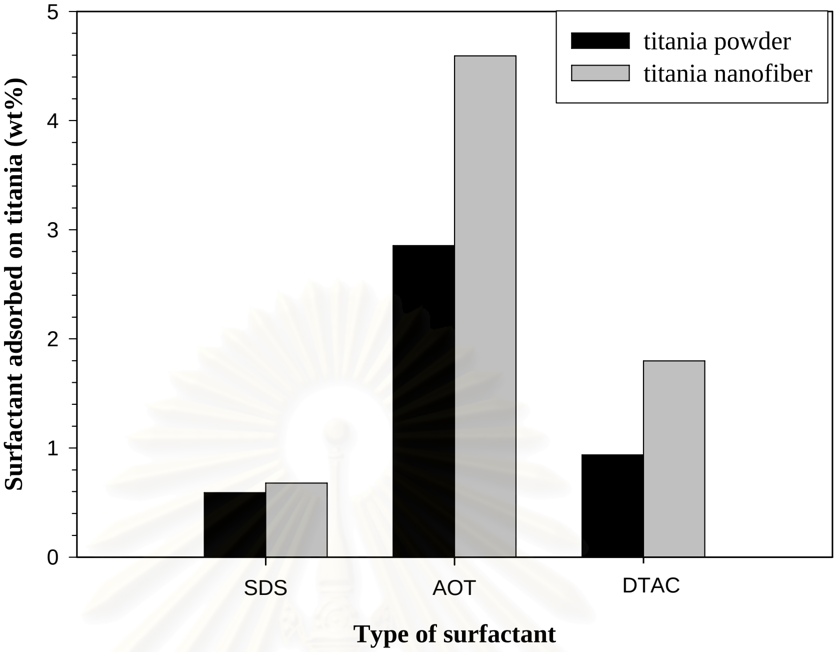


Figure 4.12 Amount of adsorbed surfactant on titania powder and titania nanofibers.

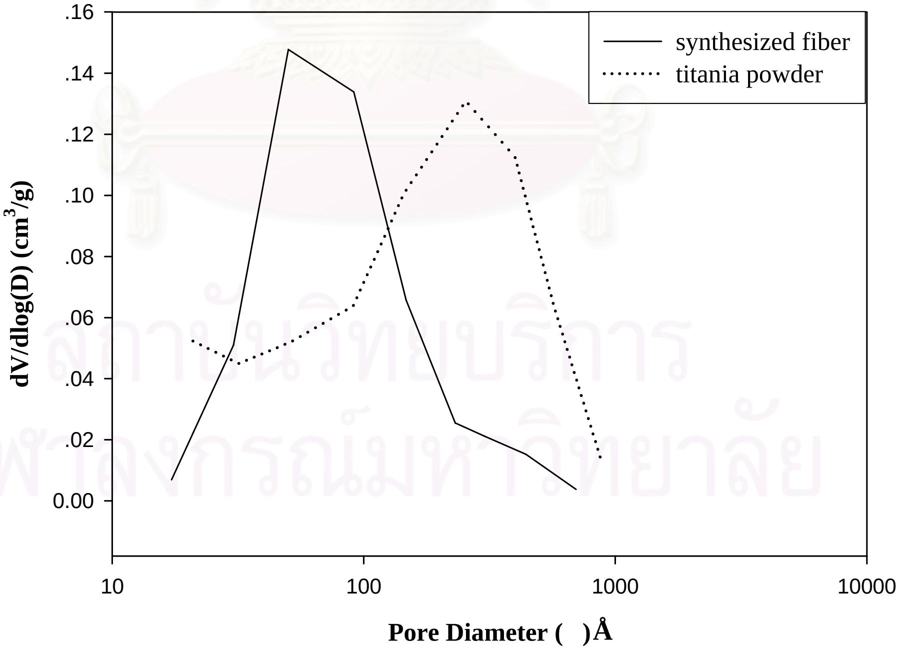


Figure 4.13 Pore size distribution of powder titania and synthesized titania nanofibers.

4.2.2 Effects of pH for the Modification of Titania

When pH of system is changed, the potential determining ions for titania surface may change from H^+ to OH^-, and vice versa. Figure 4.14 illustrates the comparison of SDS adsorption on the P25 titania powder at pH 2.84, 6.45 and 10.06, respectively. It should be noted that the concentration of surfactant employed in this study was fixed at 2 wt%. These data suggest that SDS has greater affinity for the titania surface in solution at pH 2.84 than other pH values. Since the point of zero charge ($pH_{p.z.c.}$) of the P25 titania powder was found to be at pH 5 as shown in Appendix A, when pH of the solution is greater than $pH_{p.z.c.}$, the titania surface is negatively charged, most probably due to the increased number of OH^- ions covering on the surface. These ions subsequently cause an increase in electrostatic repulsion between SDS molecules (negatively charged surfactant) in the solution and the surface of titania, i.e. SDS has less probability to overcome this energy barrier and adsorb on titania. On the other hand, DTAC which is a positively charged surfactant (i.e. cationic surfactant) can adsorb onto the surface of titania better at pH higher than $pH_{p.z.c.}$

Figure 4.15 and 4.16 show thermodiagrams of titania nanofibers modified with SDS and AOT, respectively, both of which are anionic surfactant. For SDS, the adsorption behavior, regarding the effect of pH, on the synthesized titania nanofibers is the same as observed in the commercial titania powder. In case of AOT, however, the effect of pH is less pronounced. In fact, the effect of pH on AOT adsorption is reversed from that observed from that observed in case of SDS, even though both species are anionic surfactants. This result confirms that the adsorption of AOT on titania involves mechanism other than electrostatic interactions. On the other hand, for the adsorption of DTAC on titania nanofibers (Figure 4.18), it is found that DTAC can adsorb on the surface more effectively at pH higher than $pH_{p.z.c.}$ of titania, as observed earlier on titania powder. The summary for amount of surfactant adsorbed on titania at different conditions are given in Table 4.1.

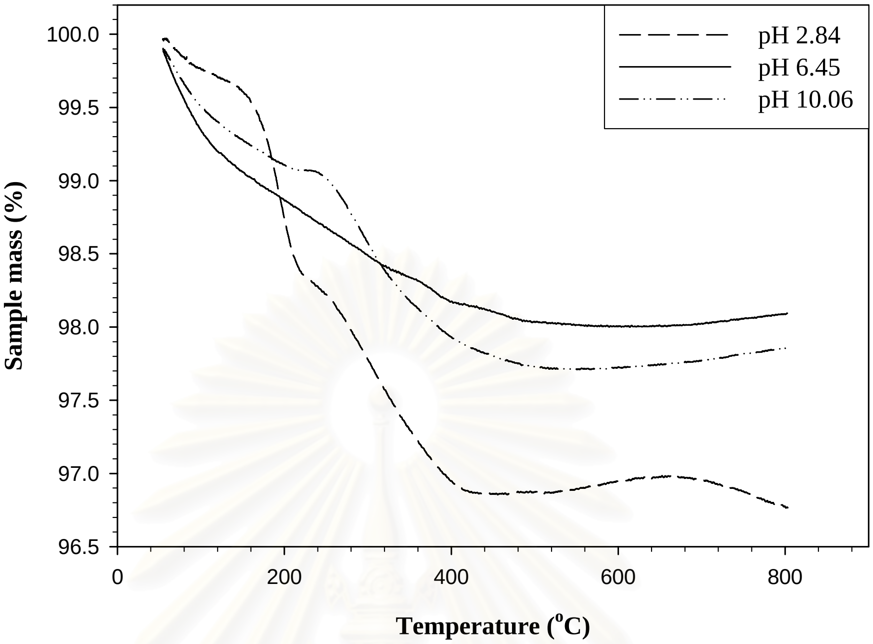


Figure 4.14 TG/DTA thermodiagrams for titania powder modified with SDS at different pH.

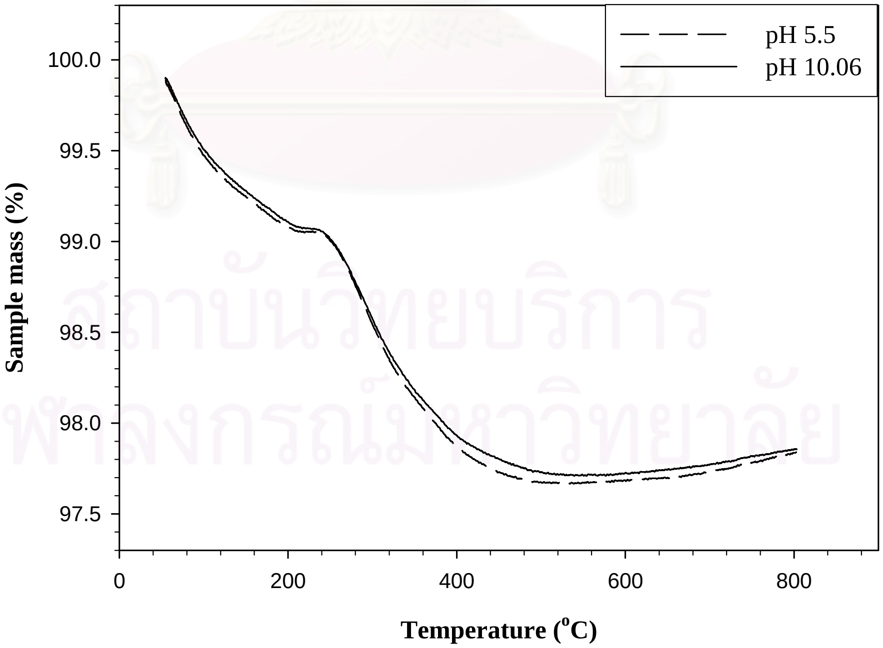


Figure 4.15 TG/DTA thermodiagrams for titania powder modified with DTAC at different pH.

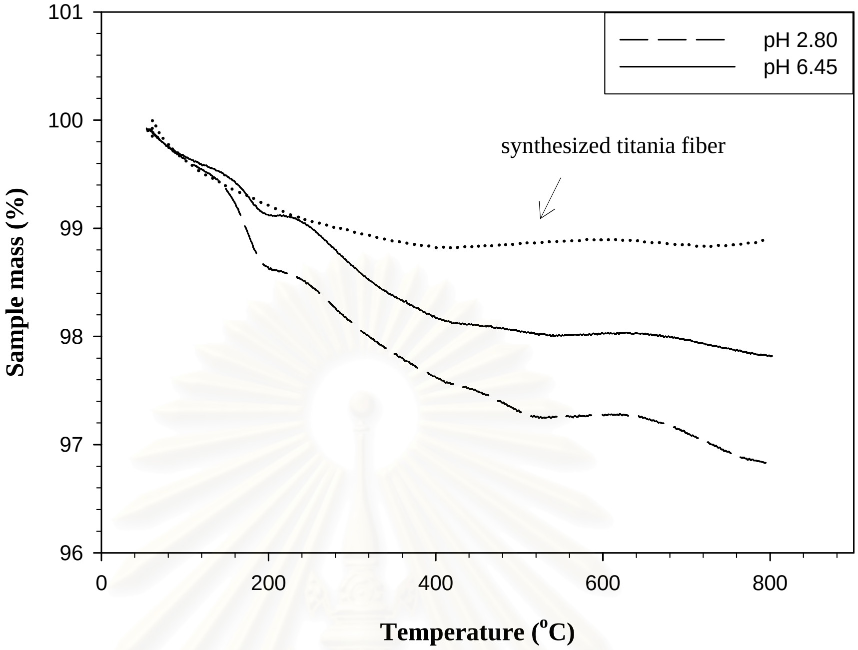


Figure 4.16 TG/DTA thermodiagrams for titania nanofibers modified with SDS at different pH.

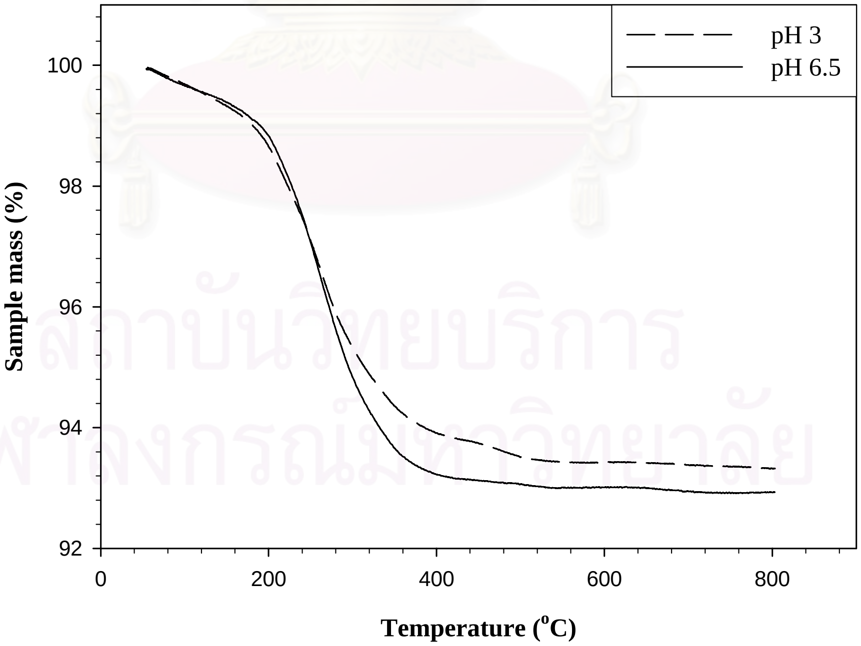


Figure 4.17 TG/DTA thermodiagrams for titania nanofibers modified with AOT at different pH.

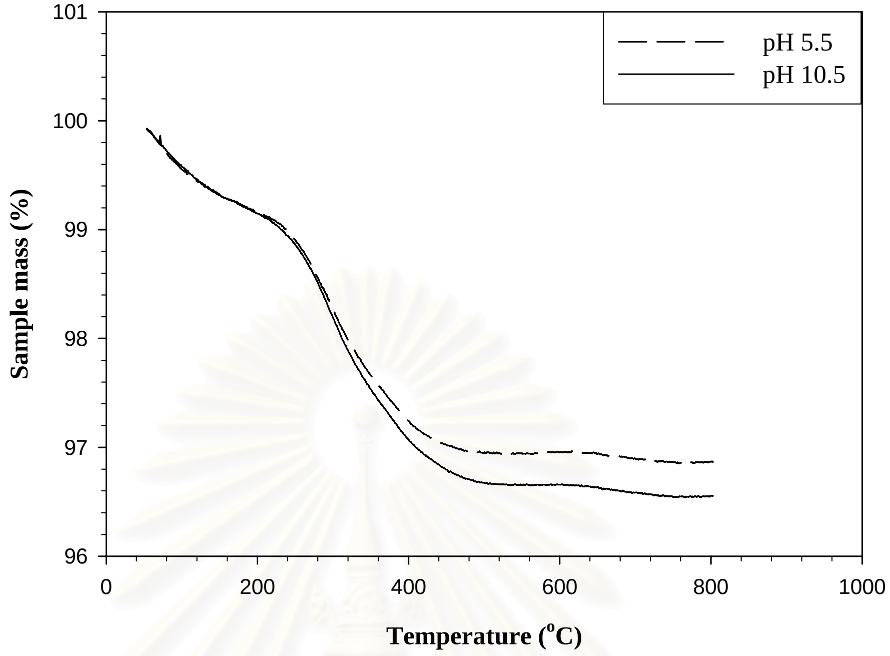


Figure 4.18 TG/DTA thermodiagrams for titania nanofibers modified with DTAC at different pH.

Table 4.1 Content of surfactant adsorbed onto titania at different pH.

Titania molecule	Type of surfactant	Adsorption pH	%wt. of adsorbed
P25	anionic : SDS	2.84	1.529
	SDS	6.45	0.590
	SDS	10.06	0.831
	AOT	6.50	2.854
	cationic : DTAC	5.50	0.938
	DTAC	10.50	1.898
synthesized fibers	anionic : SDS	2.80	0.889
	SDS	6.45	0.679
	AOT	3.00	3.770
	AOT	6.50	4.593
	cationic : DTAC	5.50	1.798
	DTAC	10.06	2.004

4.2.3 Effect of Surfactant Concentration

In order to investigate the effect of surfactant concentration on the effectiveness of the adsorption, SDS-modified titania powder was prepared by using solution containing SDS in different concentrations ranging from 0.02-2 wt%. From Figure 4.18, it is noticed that, with the increase of SDS concentration, the adsorption of surfactant increases. Amount of SDS adsorbed is found to be 0.30, 0.36 and 0.59 wt% when the concentration of SDS solution used is 0.02, 0.2 and 2 wt%, respectively. Nevertheless, it should be noted that the critical micelle concentration (CMC) of SDS is about 2310.4 mg/l (Yuan et al. 2000). Therefore, the results from 0.02 and 0.2 wt% SDS solution are not significantly different.

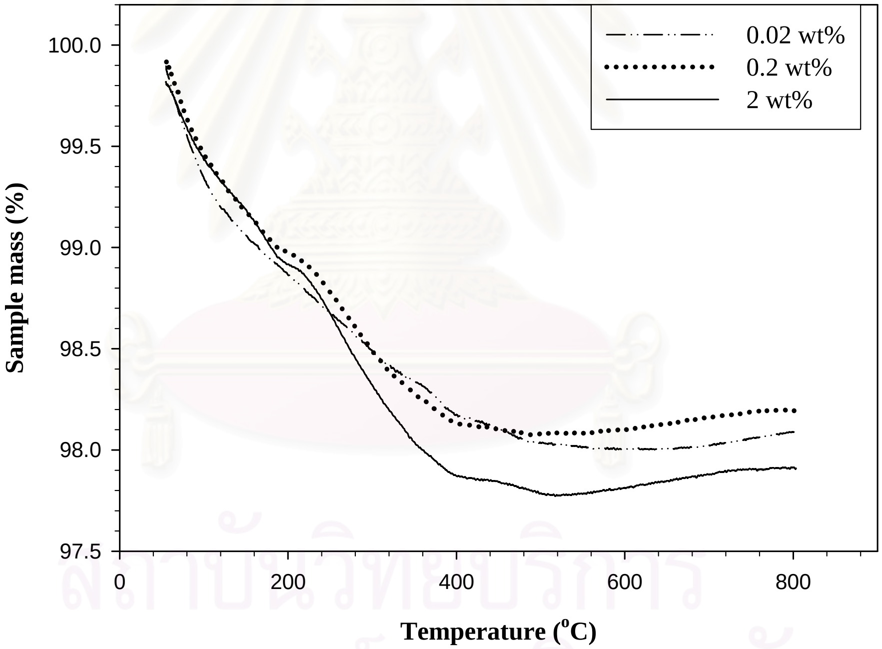


Figure 4.19 TG/DTA thermodiagrams for titania powder modified with SDS at different concentration.

It is confirmed by the results from FT-IR analysis that the surface of titania particles, in all samples, are modified by SDS. The spectra in Figure 4.20 show the broad absorption bands appearing at the wavenumber 2960-2850 cm^{-1}, which corresponds to a stretching vibration of CH_2 and CH_3 groups in SDS.

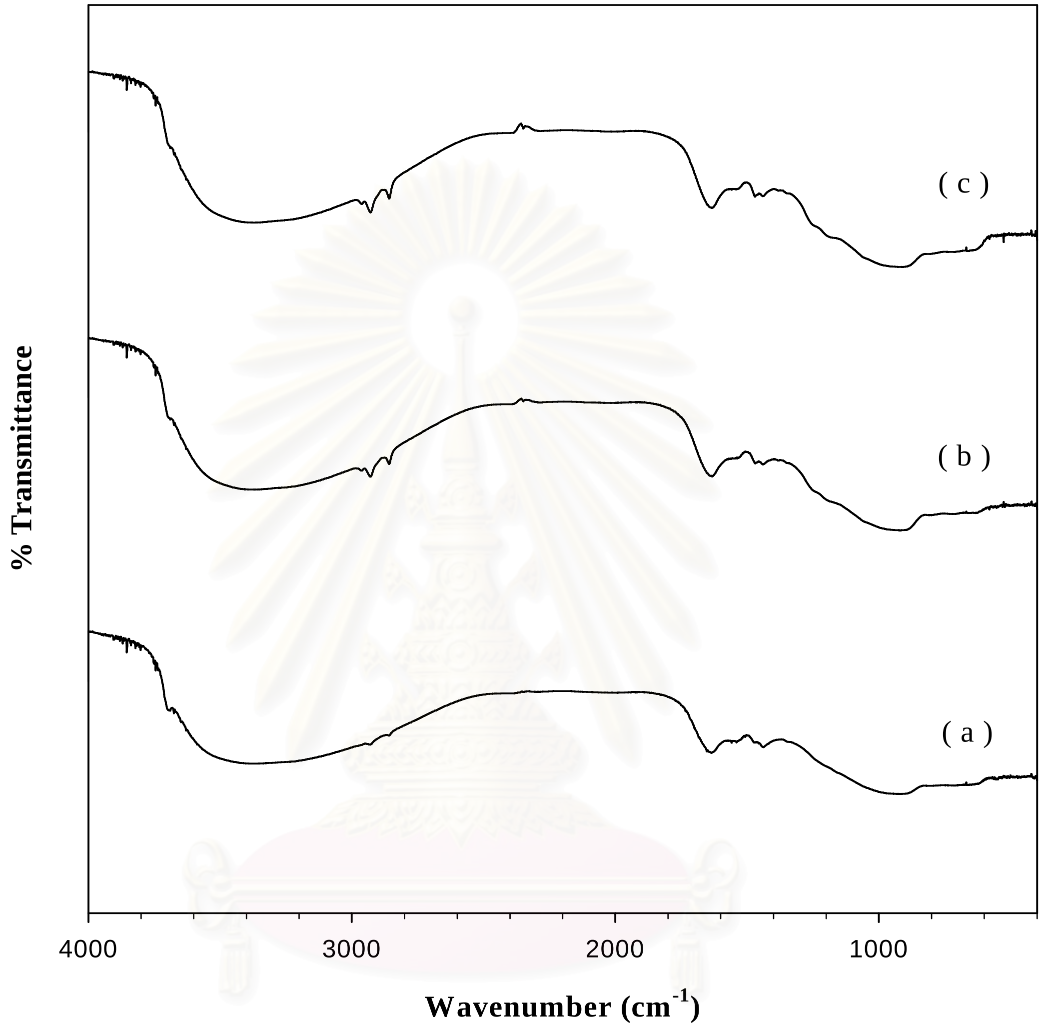


Figure 4.20 FT-IR spectra of titania powder modified with SDS at different concentration: (a) 0.02 wt%, (b) 0.2 wt% and (c) 2 wt%.

4.3 Adsolubilization of Herbicides on Surfactant-Modified Titania

4.3.1 Adsorption of Herbicides on Titania

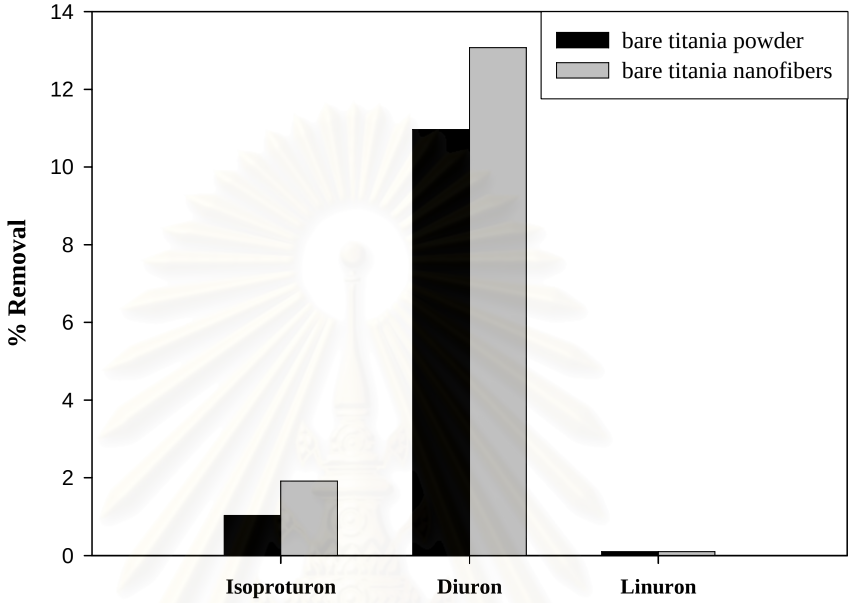


Figure 4.21 Herbicide removal efficiency of bare titania powder and titania nanofibers.

As preliminary experiment for the adsolubilization of various herbicides on titania, bare titania, in both powder and nanofiber form, was immerse into an aqueous solution of isoproturon diuron and linuron (concentration of 10 ppm). Amount of titania employed was 10 mg/10ml. The mixture was constantly agitated by the aid of ultrasonic both for 40 minutes, which has been reported to be long enough for the adsorption to reach equilibrium (Klongdee et al. 2005). The results, regarding herbicide removal efficiency, are shown in Figure 4.21.

According to the Figure 4.21, it is found that the amount of herbicide removed by bare titania nanofibers is generally higher than titania powder. It should be noted that, in the case of bare titania, the removal of herbicide from water is done solely by adsorption of herbicide onto surface of titania. Therefore, the results shown in Figure 4.21 can be explained in the same manner as those for the difference in adsorption capacity of surfactants on titania powder and nanofibers (Figure 4.12).

Figure 4.21 also shows that different herbicide can be adsorbed onto titania differently, although all herbicides investigated are in the same family. Among these herbicide, diuron can adsorb onto titania surface better than isoproturon and linuron. About 13% of diuron can be removed by bare titania nanofibers and 11% by titania powder. On the contrary, isoproturon and linuron show almost no adsorption, even after 40 minutes. Therefore, in the following section, diuron will be used as herbicide to test adsolubilization capability of the modified titania, since changes in concentration of either isoproturon or linuron might be in the same order of magnitude as the measurement errors.

Kinetic studied were also conducted to find out the equilibrium time required for diuron uptake by bare titania powder and bare titania nanofibers, depicted in Figure 4.22. It is confirmed that the contact time of 40 min is sufficient to attain the equilibrium. In fact, the adsorption takes place very quickly. About 80% of the equilibrium adsorption capacity is achieved within a period less than 10 minutes. Comparing of removal efficiency between bare titania powder and titania nanofibers, it is found that the adsorption of diuron on bare titania nanofibers is a bit higher than that of the commercial titania powder, which agrees with the results in Figure 4.21. Nevertheless, the adsorption characteristic of diuron on both types of titania are very similar.

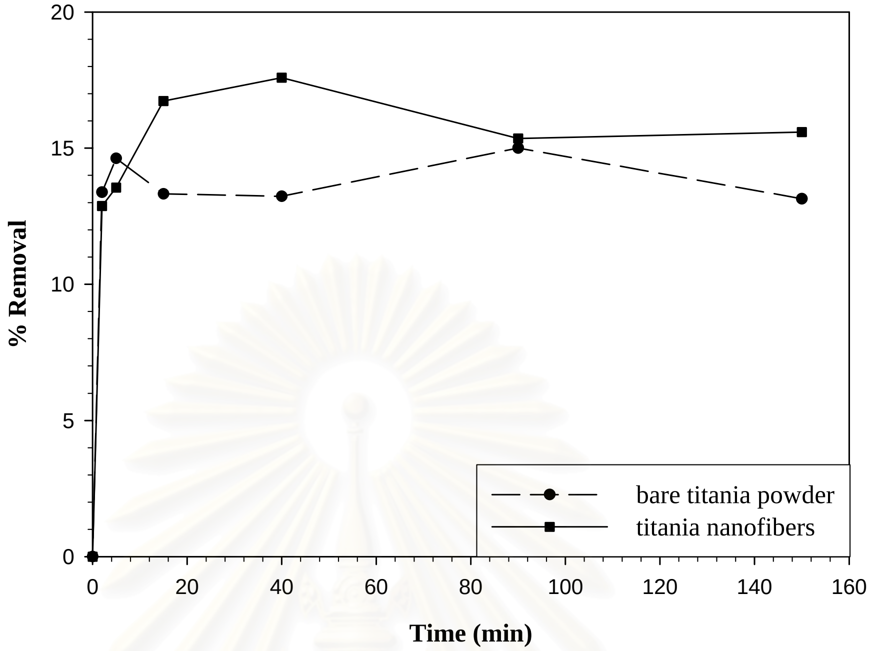


Figure 4.22 Removal of diuron by adsorption on bare titania, with respect to time.

4.3.2 Effect of Surfactant Content

Many researches have suggested that SDS, which has been adsorbed on the surface oxide, has ability to adsolubilize hydrophobic organic compounds. In this section, SDS-modified titania is used in the adsolubilization process for the removal of diuron, isoproturon and linuron. Figure 4.23 shows efficiency of diuron removal by titania powder modified with SDS in various concentrations. As previously described in section 4.2.3, adsorption of SDS depends upon the concentration of SDS in the solution during titania-surface modification process. The higher the concentration, the more SDS adsorbed, especially when the concentration exceeds CMC. According to Figure 4.23, it can be seen that the adsorbed surfactant can enhance the adsolubilization of herbicide, especially in the case of isoproturon and linuron. The present of surfactant attracts hydrophobic molecules to be adsolubilized on the surface of titania. The higher content of SDS on the surface generally results in the better adsolubilization of herbicides. This behavior is observed in case of diuron and linuron, which have relatively similar molecular structure. However, the reverse trend is found on isoproturon. The reason for this reverse behavior can not be clearly explained in this research, but it should associate with molecular structure of isoproturon, which is slightly more complex than diuron and linuron. The presence of branched alkyl groups at both ends of the molecule may cause steric effect, which inhibits effective adsolubilization, especially when SDS is densely adsorbed on the surface of titania.

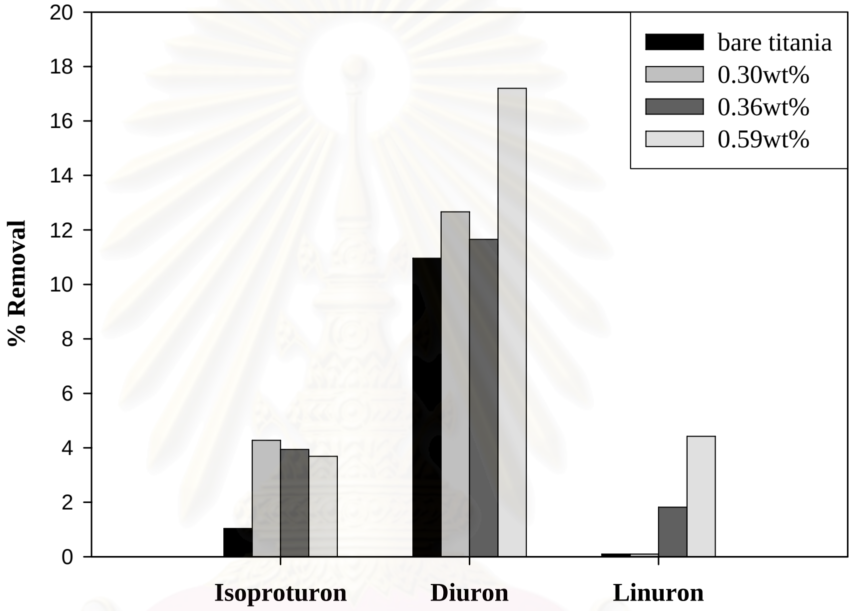


Figure 4.23 Herbicide removal efficiency of titania powder modified with SDS in various contents.

Since titania modified with the highest content of surfactant given the best adsolubilization capability, in the next step, titania modified with various types of surfactant, i.e. DTAC, AOT and Tween40, at this concentration will be investigated for the removal of herbicides.

4.3.3 Effect of Type of Surfactant

Figure 4.24 shows different capability in the adsolubilization of herbicides from titania powder modified with various surfactants. It also shows the effect of the pH adjustment during the process of titania surface modification by surfactant. Type of surfactant is found to be crucial factor for the adsolubilization of specific herbicide. For instance, DTAC is the most effective surfactant for the removal of isoproturon, but it does not show any sign of adsolubilization for linuron. The influence of surfactant type dominates the amount of surfactant adsorbed on the surface of titania. As previously discussed, AOT can adsorb onto titania much better than SDS, although both surfactants are anionic surfactant. However, the adsolubilization results for both AOT and SDS are similar.

The results in Figure 4.24 also suggests that pH adjustment during surfactant adsorption process may alter properties of the surfactant. Dramatic increase in adsolubilization capacity is observed in case of DTAC, when the pH of the surfactant solution was adjusted to 10.06. This enhancement is not related to the amount of DTAC adsorbed on the surface of titania, since the TG analysis confirms that titania powders modified with DTAC with and without pH adjustment have approximately the same organic content. On the contrary, the pH adjustment during the adsorption of the surfactant seems to have insignificant effect in case of SDS, although the surface modification by SDS with pH adjustment results in increased amount of adsorbed SDS.

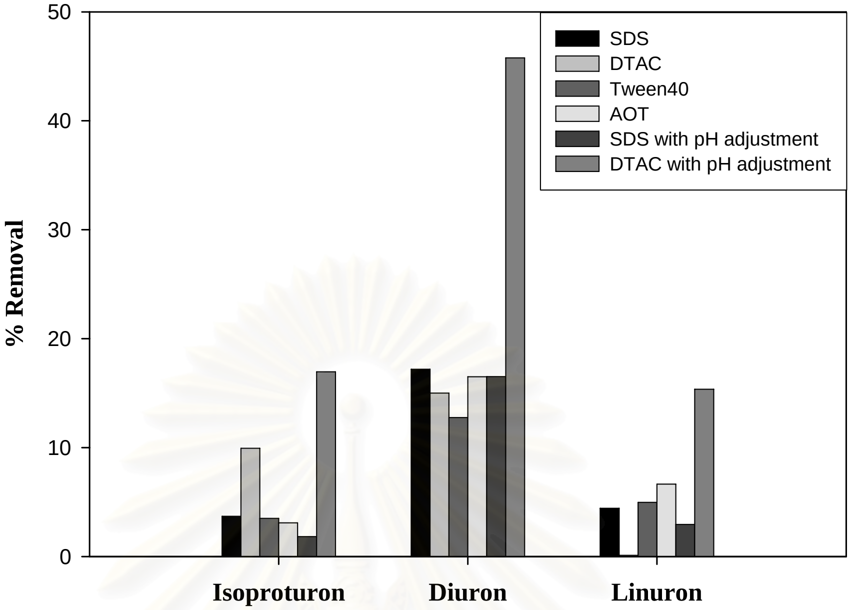


Figure 4.24 Herbicide removal efficiency of titania powder modified with various surfactant.

Figure 4.25 shows the progress of the adsolubilization for the removal of herbicides from water, using DTAC-modified titania (with pH adjustment). It is found that diuron molecule can be adsolubilized more effectively than linuron and isoproturon. Removal for diuron is 25% whereas that for linuron and isoproturon is 20% and 12%, respectively. It should be noted that the results in Figure 4.25 are quite different than those presented in Figure 4.24, although the same adsorbent was employed. This is the result from the fact that the experiments for kinetic data (Figure 4.25) were conducted in large scale, since large amount of the herbicide solution had to be periodically drawn out of the system for HPLC analysis. Such enlargement may cause mass transfer problem in the system is the mixing pattern may not be the same as what have been done in a small system.

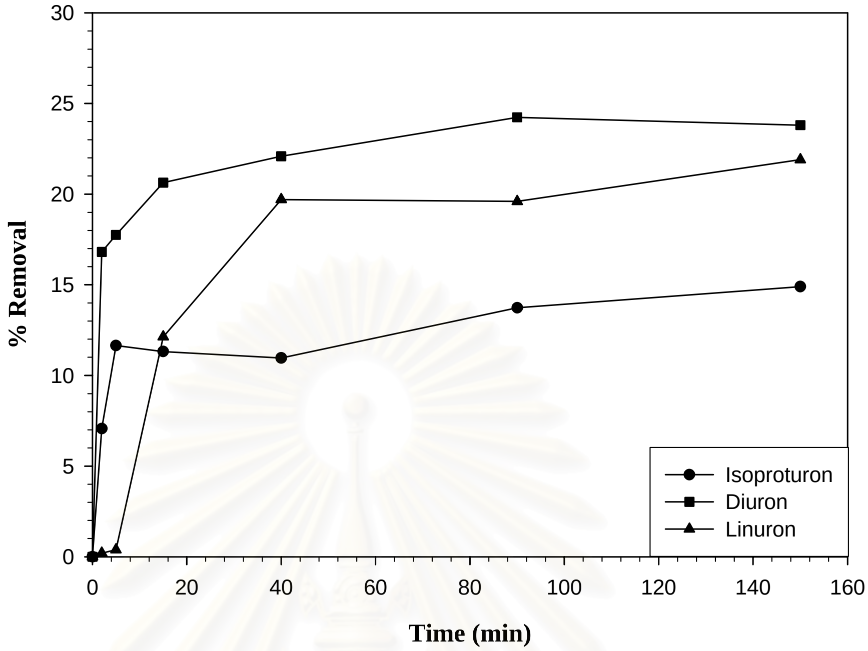


Figure 4.25 Removal of herbicides by adsolubilization on DTAC- modified titania powder (with pH adjustment), with respect to time

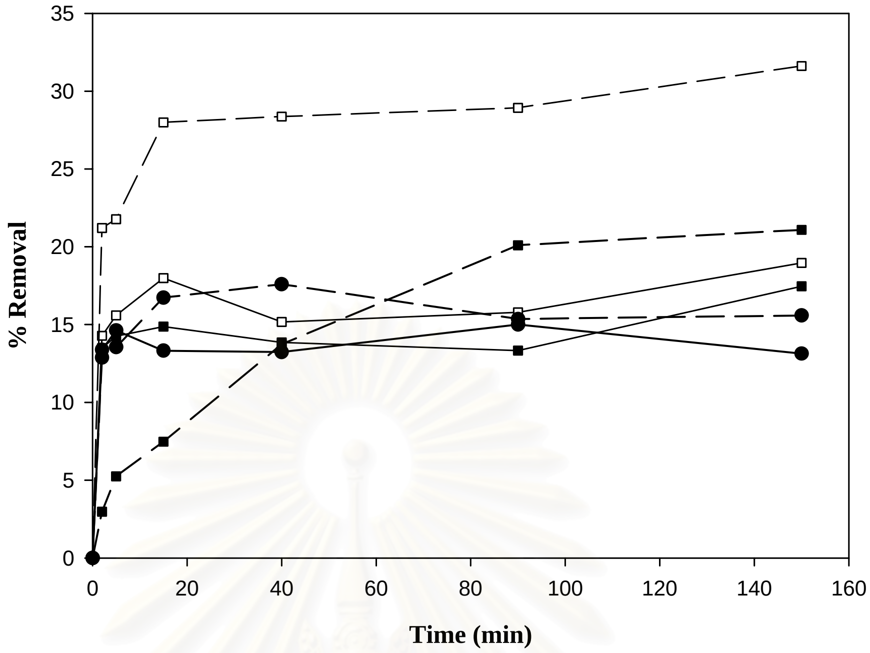


Figure 4.26 Removal of diuron by adsolubilization on SDS-modified titania powder and nanofibers, with respect to time:
(——) titania powder, (−−−−) titania nanofibers;
(●) bare titania, (■) titania modified without pH adjustment, (□) titania modified with pH adjustment.

Finally, the results for diuron adsolubilization on titania nanofibers are compared with those from commercial powder, as shown in Figure 4.26. It is found that the synthesize nanofibers have higher adsolubilization capacity than that of the titania powder, in all cases. This enhanment is the result from larger pore size of the fibers, which is more accessible for the large herbicide molecule, than that of the commercial powder,as evidenced earlier. The result from the best titania fibers, i.e. modified with pH adjustment, is almost twice as good, in term of diuron removal, as the bare titania powder.

4.3.4 Effect of Amount of Adsorbent on the Adsolubilization

Since amount of the adsorbent is expected to have significant effect on the removal of herbicide, the effect of this parameter was studied. Batch experiments were conducted using 10 ppm of herbicide solution and different amount of adsorbent in the range of 2 to 20 mg of adsorbent in the 10 ml of the herbicide solution. The adsorbent used in this study was DTAC-modified titania, which was prepared with pH adjusted to around 10. An expected trend, i.e. the increased amount of adsorbent results in the increased amount of adsolubilized herbicide, is observed in case of linuron. However, the unusual trend is observed for diuron and isoproturon. The optimum adsorbent dose is found for diuron and isoproturon adsolubilization. At the adsorbent dose higher than 10mg/10ml, % removal of diuron and isoproturon decrease. The decrease in the adsolubilization capacity at high adsorbent dose may be the result from the change of pH of the solution after large amount of adsorbent was put into the solution. The effect of pH on the adsolubilization will be discussed in the next section.

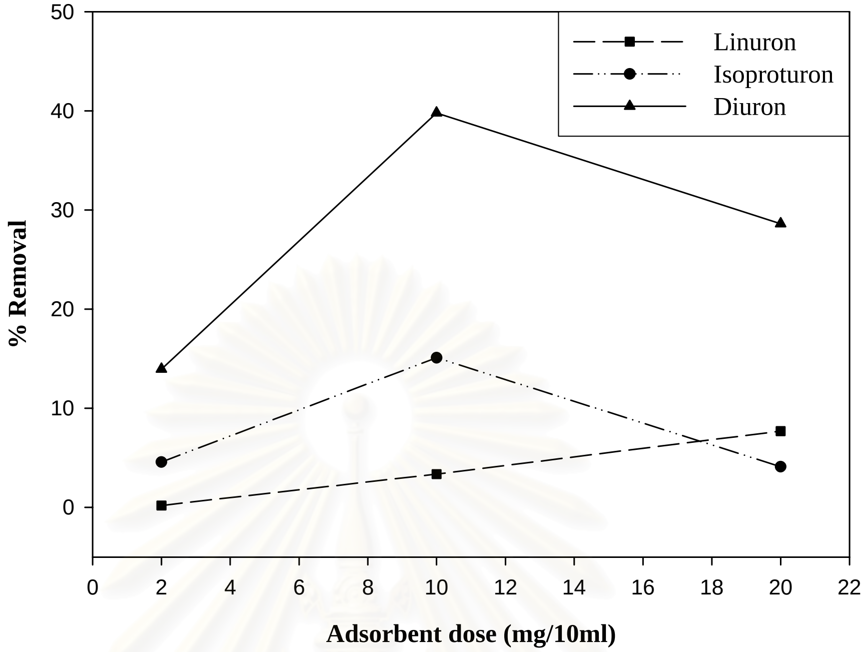


Figure 4.27 Removal of herbicide at different adsorbent doses: linuron and isoproturon uptake by DTAC-modified titania nanofibers (adjusted pH=10.5), diuron uptake by DTAC-modified reference titania (adjusted pH=10.06).

4.3.5 Effect of Temperature on Herbicide Adsolubilization

Adsolubilization of phenylurea herbicides by DTAC-modified reference titania (adjusted pH=10.06) was studied at three different temperature: 30, 40 and 60^{o}C. In the Figure 4.28, it is found that behaviors of both linuron and isoproturon are the same. Maximum removal efficiency can be obtained at 40^{o}C. For diuron, its adsorption is high at low temperature (30^{o}C), at which 45.77% of diuron can be removed by adsolubilization. This result implies that the adsorption of diuron is the exothermic adsorption. This observation contrasts the finding reported in the literature. In the investigation of diuron adsorption on activated carbon, it was found that the adsorption capacity increased as the temperature increased (Fontecha-Camara et al. 2006). However, that study was conducted at low temperature range (15-35^{o}C) whereas diffusion of diuron may be the limiting step in the adsorption process.

Nevertheless, despite the difference in the observed trend, the importance of temperature in the adsorption of organic compounds from aqueous solutions onto titania surface is evident.

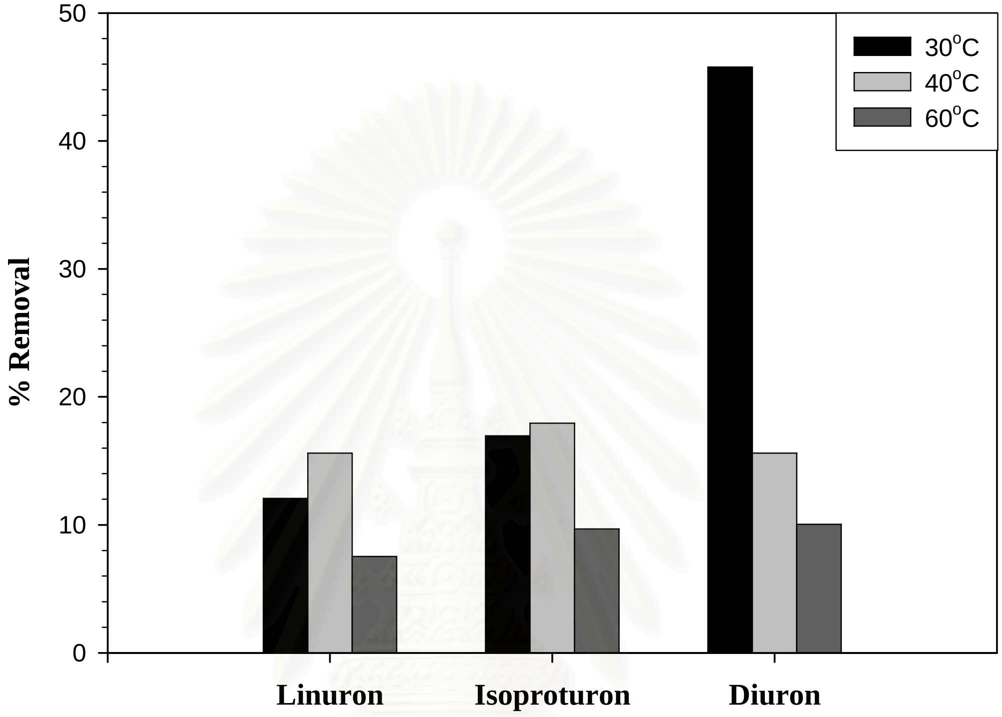


Figure 4.28 Effect of temperature on herbicide adsolubilization by DTAC- modified reference titania (adjusted pH=10.06).

4.3.6 Effect of pH for the Adsolubilization of Herbicide

The adsolubilization of herbicides was carried out to see the effect of pH of the herbicide solution, in the range of 2.7-9. The pH of the solution was maintained by adding either H_2SO_4 or NaOH. The results are shown in Figure 4.29. For diuron adsolubilization, the removal of diuron decreases with the increase in pH. No such trend is found for linuron and isoproturon. The optimum pH for linuron adsolubilization is found to be 5.5. However, according to the result, isoproturon can be adsolubilized only in acid and basic aqueous solution. These results infer that pH in the adsolubilization of organic compounds from aqueous solutions is largely important factor for the removal efficiency.

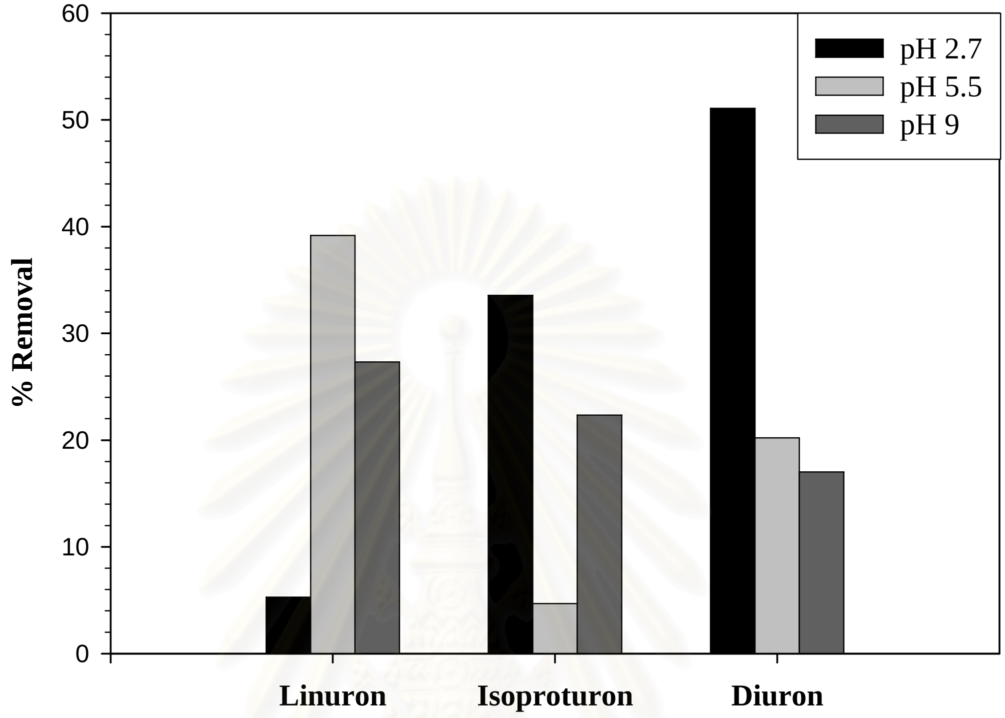


Figure 4.29 Effect of pH of herbicide solution on the removal of herbicide by SDS-modified titania nanofibers.

4.4 Photocatalytic Regeneration of Titania Nanofibers

There are numerous reports that pertain to the photocatalysis degradation of hydrocarbon surfactants on titania. Yuan et al. (2001) investigated the degradation of SDS and PFOS (potassium perfluoro octylsulfonate) in the presence of titania. It was reported that 93% of SDS was degraded within 40 min of irradiation, whereas PFOS was not degraded even after 30 hours of irradiation. This is in agreement with other reports an SDS degradation on TiO_2 under UV irradiation. In this research, it is intended to use photooxidation of an organic compound on the titania surface as a mean to regenerate the adsorbent. The experiment took place after adsolubilization of diuron on DTAC-modified titania powder, of which the pH of the modification step was adjusted to be 10.06. As the result, adsolubilization of diuron was found to be about 25% of diuron in the solution. In the other word, about 0.14 mg of diuron adsorbed on 50 mg of titania. For the regeneration experiment, 50 mg of the titania powder after the adsolubilization was suspended in 500 ml of distilled water and subjected to UV irradiation for 6 hours. The liquid was periodically taken out of the system to be analyzed for any trace of organic matter by HPLC. However, nothing was detected. The reason attributed is that the initial concentration of diuron in the system was too low to be detected by HPLC. Assuming that all diuron originally resided on titania powder was released to the 500 ml of distilled water used in the photooxidation experiment, the concentration of diuron is approximately 0.29 ppm, which is too dilute to be detected by HPLC. In reality, diuron is not simultaneously oxidized. The oxidation rate has been reported to be slow (Klongdee et al. 2005). Therefore, the actual concentration of any organic matter in the system would be extremely low.

Another technique was used to verify the photocatalytic regeneration process. XPS analysis was performed on the titania powder after 6 hours UV irradiation in water. The results are compared with those of bare titania powder (P-25). XPS characterization results show that no chlorine is present on the surface of both titania powders, but nitrogen is detected only on the powder after photooxidation process (Figure4.30). It should be noted that the peak located at around 277 eV in the XPS spectra is corresponding to C 1s in the sample. The peak for chlorine (if any) should be located at the binding energy of 270 eV. Since the molecule of diuron contains Cl amd N atoms, while DTAC contains only N atoms (besides C, O and H), the XPS results suggest that there is no diuron adsorbed on the surface of titania, after 6 hours of photooxidation treatment. Only DTAC (or its chemical fragments) is left on the surface.

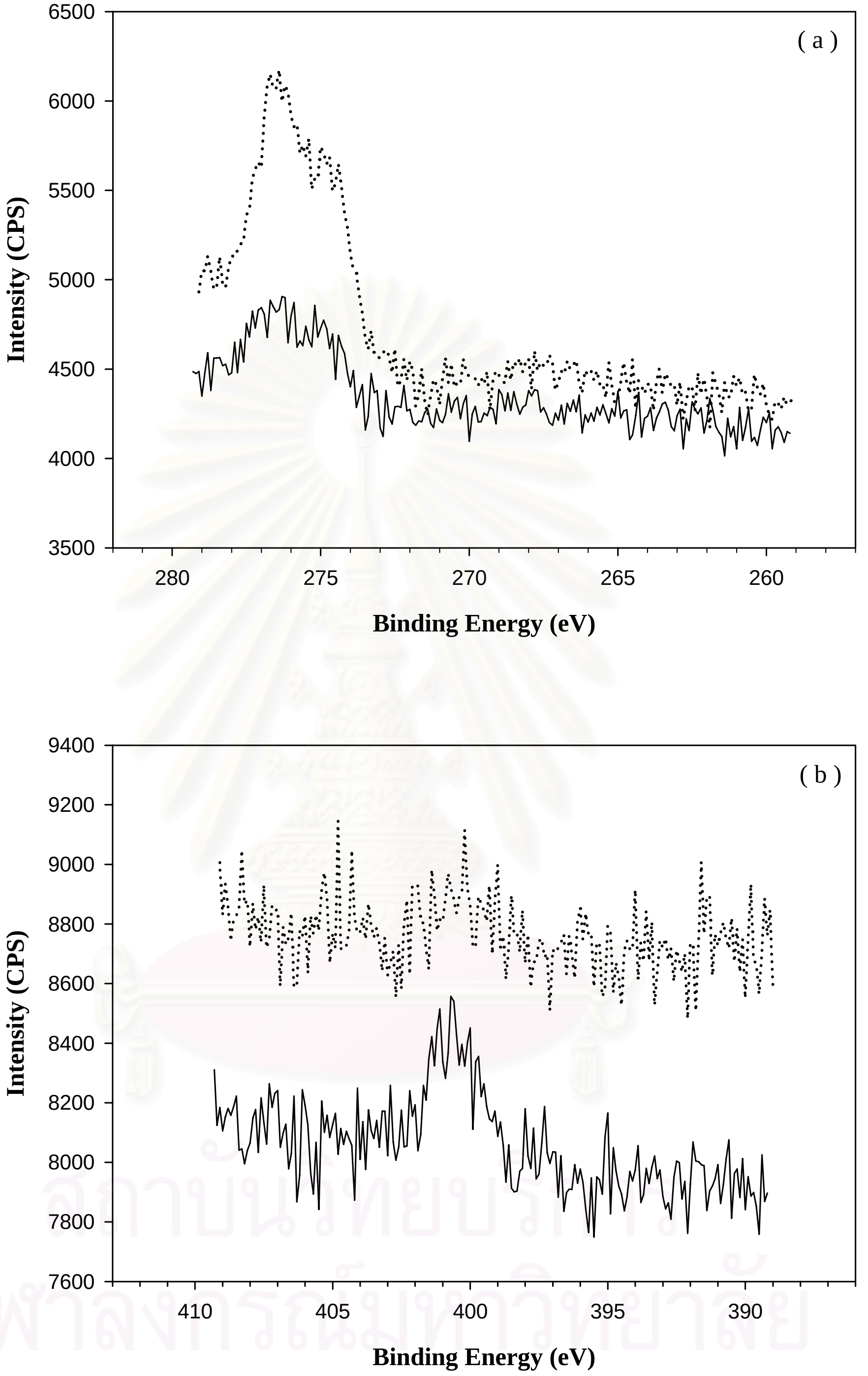


Figure 4.30 XPS analysis of DTAC-modified titania, after photooxidation process; Cl 2s (a) and N 1s (b): (········) P25 titania powder, (———) titania powder after photooxidation.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The conclusions of the present research are the following:

1. Titania nanofibers can be prepared from combination of sol-gel and electrospinning techniques. Average diameter of the fibers obtained is 165 nm and average pore size diameter is 50 Å.

2. Surfactants can be successfully adsorbed onto the surface of titania, whereas the adsorption is controlled by pH and initial concentration of the surfactant.

3. Surface modification by surfactant can increase herbicide removal capability of titania via adsolubilization process. Adsolubilization of herbicides is controlled by temperature, mass of adsorbent and pH of the solution.

4. DTAC is more suitable for adsolubilization of phenylurea herbicides than SDS, AOT and Tween40.

5. Photooxidation can not completely degrade organic compounds on the surface of titania.

5.2 Recommendations for the Future Studies

Regarding the previous conclusions, the following recommendations for the future studies are proposed.

1. Effect of the other types of surfactant in adsorption on the surface of titania should be investigated and should be tested for herbicide adsolubilization capability.

2. Other metal oxide fibers should be investigated for adsorbent.

3. The other applications for surfactant-modified titania nanofibers should be also investigated.

4. Other regeneration techniques for the used titania should be investigated.

5. Adsolubilization of phenylurea herbicides in solution containing organic solvent should be investigated.

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APPENDICES

APPENDIX A

POINT OF ZERO CHARGE DETERMINATION

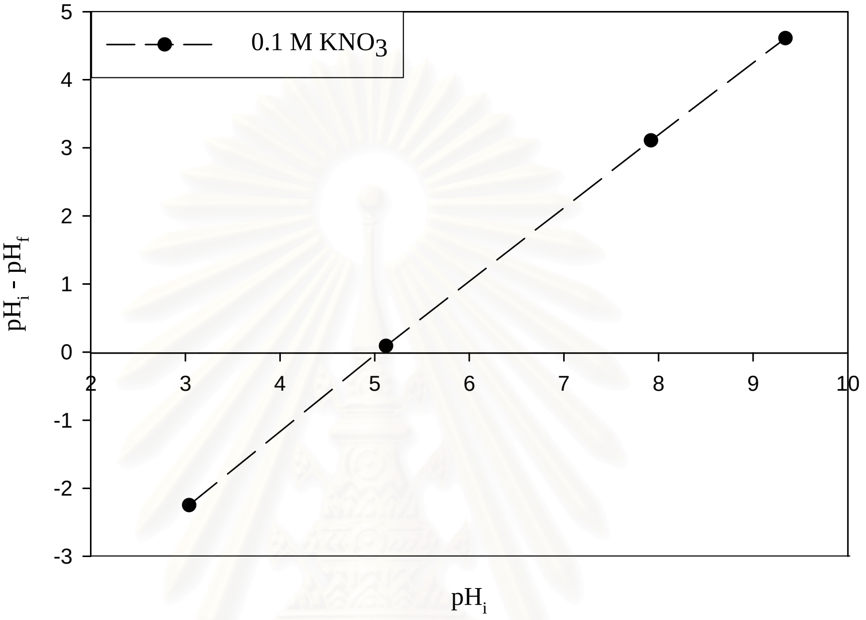

Figure A.1 Determination of the point of zero charge of titania powder (Degussa P25)

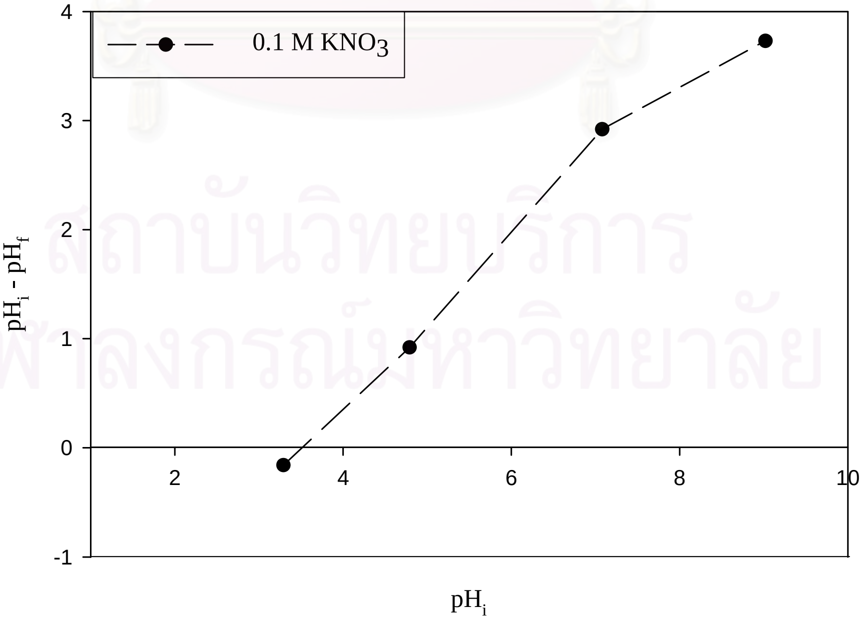

Figure A.2 Determination of the point of zero charge of titania nanofibers

APPENDIX B

LIST OF PUBLICATIONS

1. Pamornrat Chantam, Alisa S. Vangnai and Varong Pavarajarn. “Removal of phenylurea herbicide from water by surfactant-modified titania”, Regional Symposium on Chemical Engineering, Singapore, December 3-5, 2006.

Removal of Phenyl Urea Herbicide from Water by Adsolubilization on Surfactant Modified Titania

Pamornrat Chantam [a], Alisa S. Vangnai [b] and Varong Pavarajarn [a,*]
[a)] Center of Excellence on Catalysis and Catalytic Reaction Engineering, Department of Chemical Engineering, Chulalongkorn University, Bangkok 10330, Thailand
[b)] Department of Biochemistry, Chulalongkorn University, Bangkok 10330, Thailand
[*] Corresponding author: Tel. +66-2-218-6890, Email: fchvpv@eng.chula.ac.th

ABSTRACT

Adsolubilization is the solubilization of organic compounds into adsorbed surfactant aggregates, and has been introduced to variety of new commercial applications. This work studied adsolubilization of diuron [3-(3,4-dichlorophynyl)-1,1-dimethylurea], which is an herbicide belonging to the phenyl urea family and has been considered as a biologically active pollutant in soil and water, on surfactant-modified titania. Effect of type of surfactant, i.e. anionic, cationic and nonionic, on the effectiveness of diuron removal from water was investigated. Physical and chemical properties of the modified titania were characterized by various techniques including X-ray diffraction (XRD), Scanning electron microscopy (SEM), Thermogravimetric analysis (TGA) and X-ray photoelectron spectroscopy (XPS), while residual diuron in water was measured by high performance liquid chromatography (HPLC). It was found that an anionic surfactant, e.g. sodium dodecyl sulfate (SDS) could enhance the adsolubilization of diuron on titania. Effect of pH, diuron concentration, surfactant content and temperature on diuron adsolubilization was also investigated.

INTRODUCTION

Phenyl urea herbicides are common substances that have been widely used through out the world to control unwanted weeds in agriculture. However, it is the major cause of many contaminating problems of an environment, especially in soil and surface water. Separation of these herbicides, which often appear in dilute concentration, from aqueous stream is a challenging problem for chemical, pharmaceutical industries, as well as for the environmental remediation operation. One of a few technologies currently available for such dilute solution is adsorption technology. In this work, further development of the adsorption, namely adsolubilization on surface modified titania, is proposed to be used as an alternative tool for residual herbicide removal.

Nanocrystalline titania (TiO_2) was chosen in this work because of its good physical and chemical properties, relatively high surface area and distinct adsorption behavior[1]. More importantly, photocatalytic capability of titania offers good solution for further decomposition of the adsorbed herbicides.

MATERIALS AND METHODS

For the process of titania modification, 5 g of reference anatase titania (JRC-TIO-1 from the Catalyst Society of Japan) was mixed with 50 ml of aqueous solution of surfactant, i.e. sodium dodecyl sulfate (SDS), dodecyl trimethyl ammonium chloride (DTAC) and polyoxyethylenesorbitan trioleate tween (Tween 40), in the predetermined concentration. The mixture was stirred for 24 h at room temperature, during which pH was adjusted, using either 1 N of H_2SO_4 or 1 N of NaOH solution to get the desired value, in the range of 3 to 7. Then, the surfactant-modified titania was separated from the solution by centrifugation. The dried power was characterized by various techniques, such as XRD, SEM, TGA, XPS and surface area measurement via BET method.

Diuron [3-(3,4-dichlorophynyl)-1,1-dimethylurea], which is one of the most common phenyl urea herbicides was used as the model substance. For the adsolubilization experiments, 0.5 g of the surfactant-modified titania was mixed with 500 ml of diuron aqueous solution (concentration of 10 and 1 ppm, respectively), at temperature in the range of 30 to 60°C. Amount of diuron in the solution was periodically monitored by using HPLC.

RESULTS AND DISCUSSION

For the preliminary investigation of titania used in this work, it was confirmed by XRD and BET analysis that titania was in pure anatase phase with surface area of 53 m^2/g. In the process of titania modification, when surfactant solution was mixed with titania (surfactant concentration of 2% by weight of solution) without adjusting pH of the solution, it was found that anionic surfactant, i.e. SDS, could adsorb onto surface of titania more effectively than other surfactants. Amount of the surfactant adsorbed on titania was in the following order: SDS > Tween 40 > DTAC. Since a point of zero charge (p.z.c.) of titania is 6.0, surface of titania in SDS solution, which had pH of 5.47, was positively charged. Consequently, electrostatic interaction between anionic functional group of SDS and titania was responsible for good SDS adsorption, as high as 1.61% by weight of titania..

This mechanism was confirmed by the results when pH of the SDS solution was adjusted to 3.28 and 6.83, respectively. It was found that the amount of SDS adsorbed was increased to 1.72% by weight of titania when pH was decreased to 3.28. On the contrary, the adsorbed SDS was sharply decreased to 0.53% wt. for the pH of 6.83.

Next, the SDS-modified titania was used for the adsolubilization of diuron. According to Figure 1, about 38% of diuron could be removed from 10 ppm diuron aqueous solution within less than 5 minutes. For the purpose of removing the contaminated diuron from water, this result was more than 10-fold faster than the removal via photocatalytic degradation, in which it would take about 60 minutes to remove equivalent amount of diuron by using same amount of titania[2]. Another important advantage of this technique is that no reaction intermediate, which has been reported to be equivalently toxic as diuron, was detected. It should be noted that only about 5% of diuron was removed when the untreated titania was used. Furthermore, no adsolubilization was observed on DTAC-modified titania.

When the initial concentration of diuron solution was reduced to 1 ppm, the absolute amount of diuron removed from the solution was lower than that removed from 10 ppm solution. Only around 50% removal was achieved. This result indicated that the adsolubilization process was controlled by mass transfer of diuron from bulk fluid to the surface of titania.

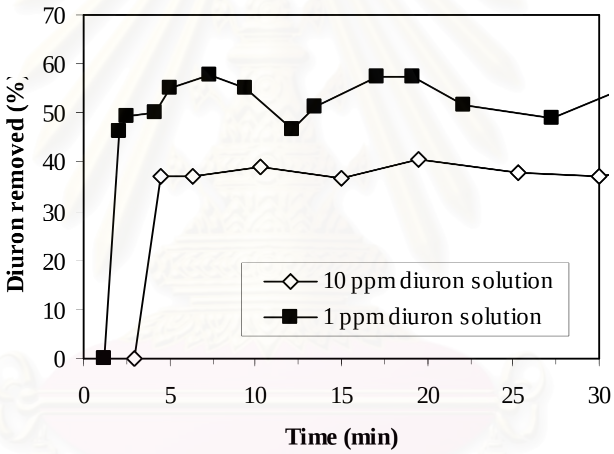

Figure 1. Diuron removal via adsolubilization on SDS-modified titania.

CONCLUSION

Adsolubilization is an alternative approach to remove toxic phenyl urea herbicide from water. In this work, SDS-modified titania has shown to be an effective sorbent for diuron removal. Significant amount of diuron can be removed within relatively short time. The adsolubilization was found to be mass transfer limited process. Effectiveness of diuron removal also depended upon amount of SDS adsorbed on titania. It was found that type of surfactant, pH as well as the concentration of surfactant used during titania surface modification influenced amount of the surfactant adsorbed on the surface of titania.

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VITA

Miss Pamornrat Chantam was born on December 9, 1981 in Nakornratchasima, Thailand. She received the Bachelor's Degree in Chemical Engineering from Suranaree University of Technology in December 2004, She entered the Master of Engineering in Chemical Engineering at Chulalongkorn University in June, 2005.