การสร้างอะลูมินาพรุนโดยใช้เรโซซินอล/ฟอร์มัลดีไฮด์เจลช่วยสำหรับการประยุกต์ใช้ในการกำจัดไดยูรอนจากน้ำด้วยวิธีแอดโซลูบิไลเซชัน

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วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต

สาขาวิชาวิศวกรรมเคมี ภาควิชาวิศวกรรมเคมี

คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

ปีการศึกษา 2553

FORMATION OF POROUS ALUMINA ASSISTED BY RESORCINOL/FORMALDEHYDE GEL FOR AN APPLICATION IN THE REMOVAL OF DIURON FROM WATER VIA ADSOLUBILIZATION

Miss Sawitta Trimit

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering Program in Chemical Engineering
Department of Chemical Engineering
Faculty of Engineering
Chulalongkorn University
Academic Year 2010

Thesis Title	FORMATION OF POROUS ALUMINA ASSISTED BY RESORCINOL/FORMALDEHYDE GEL FOR AN APPLICATION IN THE REMOVAL OF DIURON FROM WATER VIA ADSOLUBILIZATION
By	Miss Sawitta Trimit
Field of study	Chemical Engineering
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
(Associate Professor Boonsom Lerdhirunwong, Dr.Ing.)

THESIS COMMITTEE

A. Sootitantawat .... Chairman
(Apinan Sootitantawat, D.Eng.)

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

.... Examiner
(Akawat Sirisuk, Ph.D.)

Kajornsak Faungnawakij .... External Examiner
(Kajornsak Faungnawakij, D.Eng.)

สวิตตา ไตรมิตร: การสร้างอะลูมินาพรุนโดยใช้เรโซซินอล/ฟอร์มัลดีไฮด์เจลช่วยสำหรับการประยุกต์ใช้ในการกำจัดไดยูรอนจากน้ำด้วยวิธีแอดโซลูบิไลเซชัน (FORMATION OF POROUS ALUMINA ASSISTED BY RESORCINOL/FORMALDEHYDE GEL FOR AN APPLICATION IN THE REMOVAL OF DIURON FROM WATER VIA ADSOLUBILIZATION) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: ผศ.ดร. วรงค์ ปวราจารย์, 63 หน้า.

อะลูมินาที่มีรูพรุนขนาดเมโซถูกสังเคราะห์ขึ้นโดยวิธีโซล-เจล ประกอบกับการสร้างเรโซซินอล/ฟอร์มัลดีไฮด์เจล ซึ่งหลังจากนำเรโซซินอล/ฟอร์มัลดีไฮด์-อะลูมิเนียมคอมโพสิตไปเผา จะได้ผงอะลูมินาพรุนที่มีพื้นที่ผิวสูงและปริมาตรรูพรุนมาก โดยอะลูมินาที่สังเคราะห์ได้มีพื้นที่ผิวจำเพาะประมาณ 194.2 ตารางเมตรต่อกรัม นอกจากนี้อะลูมินาเชิงพาณิชย์ยังถูกนำมาเปรียบเทียบกับอะลูมินาที่สังเคราะห์ได้เหล่านี้ การปรับปรุงผิวของอะลูมินาโดยสารลดแรงตึงผิวสามารถทำได้โดยใช้โซเดียมโดเดซิลซัลเฟตที่เป็นสารลดแรงตึงผิวชนิดประจุลบ โดยมีการศึกษาปัจจัยต่างๆ ที่เกี่ยวข้องในการดูดซับสารลดแรงตึงผิวนี้ ได้แก่ ไอโซเทอมของการดูดซับของโซเดียมโดเดซิลซัลเฟตบนพื้นผิวอลูมินา ผลของค่าความเป็นกรด-ด่างของสารสารละลาย และความเข้มข้นเริ่มต้นของโซเดียมโดเดซิลซัลเฟตในสารละลาย จากนั้นจึงนำอะลูมินาที่มีการปรับปรุงผิวด้วยสารลดแรงตึงผิวแล้ว ไปใช้สำหรับการกำจัดไดยูรอนออกจากน้ำ ในการศึกษานี้ แสดงให้เห็นว่า การแอดโซลูบิไลเซชัน มีประสิทธิภาพสูงในการกำจัดสารกำจัดวัชพืชออกจากน้ำ เพราะว่าเทคนิคนี้สามารถกำจัดไดยูรอนอย่างรวดเร็วและไม่ทำให้เกิดสารตัวกลางที่เป็นพิษขึ้น ในขั้นตอนของการแอดโซลูบิไลเซชันไดยูรอนออกจากน้ำ ได้มีการศึกษาถึงปัจจัยต่างๆ ที่เกี่ยวข้อง ได้แก่ ค่าความเป็นกรด-ด่างของสารละลาย ปริมาณของอะลูมินาที่มีการปรับปรุงผิวด้วยสารลดแรงตึงผิว และความเข้มข้นเริ่มต้นของไดยูรอน

ภาควิชา ....วิศวกรรมเคมี..........ลายมือชื่อนิสิต..........สวิตตา ไตรมิตร..........
สาขาวิชา..........วิศวกรรมเคมี..........ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก..............................
ปีการศึกษา..........2553..........

5270535521: MAJOR CHEMICAL ENGINEERING

KEYWORDS: POROUS ALUMINA/ ADSORPTION/ SURFACTANT/
ADSOLUBILIZATION/ DIURON

SAWITTA TRIMIT: FORMATION OF POROUS ALUMINA ASSISTED BY RESORCINOL/FORMALDEHYDE GEL FOR AN APPLICATION IN THE REMOVAL OF DIURON FROM WATER VIA ADSOLUBILIZATION. ADVISOR: ASST. PROF. VARONG PAVARAJARN, Ph.D., 63 pp.

Mesoporous alumina was synthesized by sol-gel technique assisted by resorcinol/formaldehyde (RF) gel formation. After calcination of the RF-aluminium composite, alumina powders with high surface area and pore volume were obtained. The synthesized alumina had specific surface area of about 194.2 m^2/g. Moreover, commercial alumina was also compared with the synthesized alumina. Surface modification of alumina by surfactant was done by using sodium dodecyl sulfate (SDS) as anionic surfactant. The adsorption isotherm of SDS on alumina surface, as well as effects of pH of solution during the adsorption and the initial SDS concentration was also studied. The surfactant-modified alumina (SMA) was used in the removal of diuron from water. Adsolubilization was found to have high effectiveness in herbicide removal because this technique could remove diuron rapidly and did not cause toxic intermediate. The various parameters were found to affect the adsolubilization, including pH of the solution, mass of SMA and the initial concentration of diuron.

Department : ......Chemical Engineering... Student's Signature ....Sawitta Trimit.........
Field of Study : ....Chemical Engineering.....Advisor's Signature ....
Academic Year : ....2010................

ACKNOWLEDGEMENTS

I would like to express my deeply gratitude to my advisor, Assistant Professor Dr.Varong Pavarajarn. to his extensive guidance, patience, continuous support, and encouragement throughout the entire of this research. His precious teaching the way to be good in study and research has always been greatly appreciated. Although this work had obstacles, finally it could be completed by his advises. In addition, I would also grateful to thank to Dr. Apinan Sootitantawat, as the chairman, Dr. Akawat Sirisuk and Dr. Kajornsak Faungnawakij, as the members of the thesis committee for their kind cooperation, comment, and discussions.

Moreover, I would like to thank the National Research Council of Thailand for financial support.

Sincere thanks to all my friends and all members in the Center of Excellent in Particle Technology, Department of Chemical Engineering, Chulalongkorn University, for kind suggestions and useful that always provide the encouragement and cooperate along the research study.

Finally, I would like to dedicate this thesis to my parents and my families, who generous supported and encouraged me through the year spent on this study.

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CHAPTER I

INTRODUCTION

Aluminium (III) oxide or Alumina (Al_2O_3) is one of the most materials used in many applications in industries. It has been known as catalyst supports, ceramics, ceramics, refractory, etc. Alumina is a good thermal conductivity; high strength and stiffness resist strong acid, and alkali attack at elevated temperatures. The crystal of alumina exists in many form α, χ, η, δ, κ, θ, γ, ρ. The most thermodynamically stable form is α-alumina.

Alumina is used in many shapes from various procedures of synthesis. Sol-gel process assisted by resorcinol-formaldehyde formation is one of the method can produce porous alumina with high surface area. The RF-gel formation consists of the formation of hydroxymethyl and the condensation of hydroxymethyl. The synthesized alumina has high surface area and high pore volume. RF gel is the cross-linking network which causes porosity in alumina. Alumina without RF template, after being dried and calcined, the pores can collapse and the porosity will be destroyed.

Adsorption of surfactant onto metal oxide has been extensively studied. Because adsorbed surfactant can modify solubility ability of metal solid surface for soluble the low concentration of low soluble organic pollutants from effluent. Since the point of zero charge (PZC) of alumina is about 8.5-9.1, alumina surface at low pH has positive charge that is good for SDS adsorption. In general, the adsorption of surfactant onto the surface of solid can be divided into four regions [1]. In the first region, surfactant is adsorbed into solid surface by ion exchange mechanism. In the second region, the surfactant on the solid surface forms into admicelle or hemimicelle. In the third region, further adsorption occurs through the growth of the surfactant aggregates in the second region until it reaches equilibrium concentration of the surfactant. Finally, the admicelle form becomes saturated. The transition from the third region to the fourth region occurs above the critical micelle concentration (CMC) of the surfactant.

Diuron, the phenyl urea herbicides, is a common substance that is wildly used in agriculture. Diuron is a hazardous compound for human. It can contaminate soil and water, which causes the environmental problems. The convention methods for diuron removal from the water environment involve processes such as thermal degradation [2], chemical degradation [3], biodegradation [4-6], photocatalytic degradation [7-9], solid-phase extraction (SPE) [10], and adsorption [11, 12].

–Adsolubilization” or –surface solubilization” is the process that surfactant adsorbed onto solid oxide surface. Because of the surfactant properties that can solute the organic compound having low water solubility, the use of surfactant adsorbed on surface of solid can remove organic solute from water into surfactant layer [1, 11, 13-15].

In this study, diuron was the example of herbicide in this group and it was selected as representative for an investigation of phenylurea adsolubilization on surfactant-modified alumina.

The objectives of this research are listed following:

1. To study the adsorption of surfactant on surface of porous alumina for modification of alumina surface.
2. To investigate the adsolubolization behavior of diuron on SDS-modified porous alumina for the removal of diuron from water.

The expected benefits of this research:

The expected benefit to be obtained from this research will remove diuron from water by using surfactant-modified on synthesized alumina via adsolubilization process. The knowledge of this research should be the alternative for water treatment of environmental problems from agriculture.

This thesis is divided into five chapters. Chapter I is introduce the overall of the study, including the scope and objective of thesis. Chapter II describes the basic theory about resorcinol-formaldehyde gel formation, surfactant adsorption onto metal surface and adsolubilization of diuron. The literature reviews about the adsolubilization process in organic compounds removal are also studied. Chapter III shows the necessary materials and the experimental apparatus of this work including the preparation of alumina, adsorption process of surfactant onto alumina and adsolubilization process of diuron from the solution. Chapter IV is the part about the results and discussion. In the last chapter, the overall conclusion from the results and recommendation for future work are presented.

CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Physical and Chemical Properties of Alumina

Aluminum oxide or alumina (Al_2O_3) has been used in many applications such as ceramics, catalyst support, refractory, etc. The important properties of alumina include high strength and stiffness as well as resistivity to strong acid and alkali attack at elevated temperature. Aluminium oxide exists naturally in many forms, e.g., α, χ, η, δ, κ, θ, γ, ρ. These phase arise during the heat treatment of aluminium hydroxide or aluminium oxy hydroxide. The most thermodynamically stable form is α-aluminium oxide.

The γ -alumina can be formed by calcination of boehmite at temperature between 500 - 800 ^{o}C. Formation of γ – alumina in the structure occurs at the calcinations temperature greater than 1000 $^{\circ}$C [16]. The structural and compositional differences among various forms of alumina are associated with differing particulate size, particulate surface area, surface reactivity and catalytic activity.

The structure of γ- alumina is cubic with space group Fd-3m and is based on an fcc . . .ABCABC. . . stacking of oxygen. The structure is often described as a defect cubic spinel structure with vacancies on part of the cation positions. Each unit cell contains 32 oxygen and 64/3 aluminium ions to fulfill stoichiometry. The aluminium ions occupy both octahedral and tetrahedral positions, but the relative partial occupancy in each position is still a matter of dispute. The structure of γ - alumina is shown in Figure 2.1.

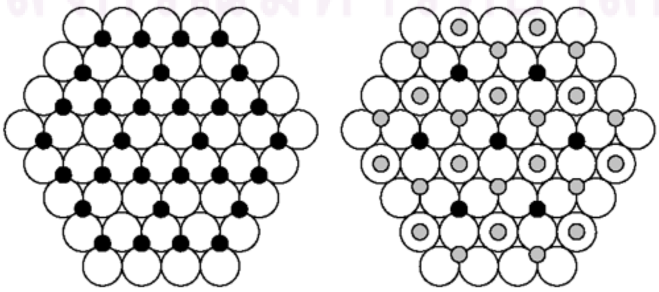


Figure 2.1 Schematic drawing of the first two layers in the gamma-alumina structure.

Porous alumina in gamma phase has higher surface area than alpha phase. Gamma alumina has been regarded as consisting of molecular water strongly adsorbed on the surface of the alumina. Therefore, gamma alumina is suitable for various applications such as adsorbents in adsorption process, catalyst, membranes and template for nano particles synthesis. Moreover, in the adsorption process, the use of alumina as the adsorbent has lower operation cost than activated carbon [17].

2.2 Resorcinol-Formaldehyde Gel Formation

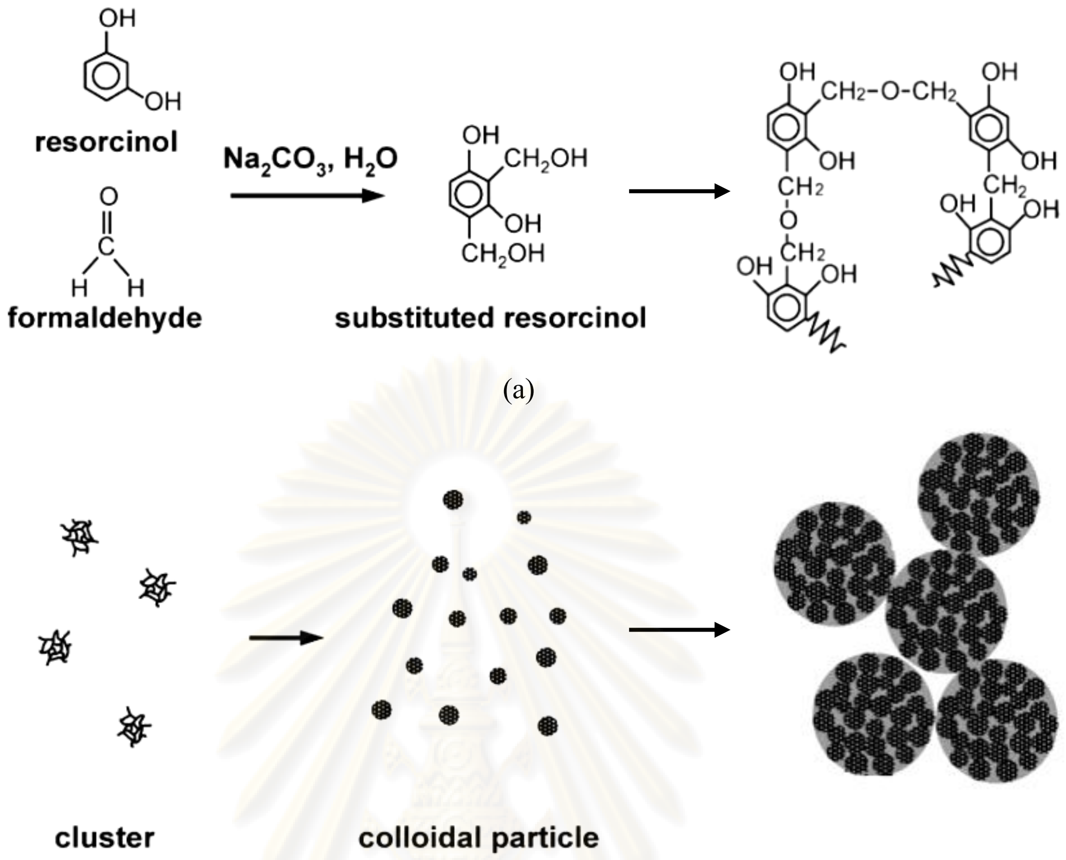
Sol-gel process involves the formation of sol following by that of gel. Sol, which is suspension solid in liquid with particle size ranging from 1 nm to 1 μm, can be obtained by the hydrolysis and partial condensation of a precursor such as an inorganic salt or metal alkoxides. Further condensation of 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 other cases, the materials are called aquasol (or aquagel) if water is used as solvent and called alcosol (or alchogel) if alcohol is used. The water in the sol-gel structure can be removed by evaporation or drying with supercritical extraction.

The first resorcinol-formaldehyde (RF) gel was produced by Pekala via the sol-gel polycondensation of resorcinol (R) and formaldehyde (F) with sodium carbonate (C) as basic catalyst [18]. The intermediates formed during the reactions further react to form a cross-linked polymer network (a three-dimentional network).

The two major reactions include:

(i) the formation of hydroxymethyl ($-CH_2OH$) derivatives of resorcinol.
(ii) the condensation of hydroxymethyl derivatives to form methylene ($-CH_2-$) and methylene ether ($-CH_2OCH_2-$) bridged compounds [18].

Porosity of the final products depends on the structure of their parent hydrogel, which is mostly formed during the RF-gel transition. The catalyst initially promotes the generation of resorcinol anions. These anions are subsequently transformed into substituted resorcinols, which form RF clusters through polycondensation. Then RF clusters react with each other and grow into colloidal particles, which finally form a RF hydrogel as shown in Figure 2.2 [19].



(a)

(b)

Figure 2.2 Schematic diagram of the sol-gel polycondensation of a RF solution (a) Addition Reaction, (b) Condensation Reaction [19].

The parameters that affect RF-gel formation are the ratio of R, F and C. The effect of R/C ratio is the factor that controls the surface area, total pore volume, and mechanical properties of RF aerogels [20]. The effect of R/F ratio is the factor that control particle sizes and pore sizes [21].

2.3 Point of zero Charge and Zeta Potential

Zeta potential refers to the electrostatic 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 charge surface. These ions are temporality bound to the surface and shield the charge of the original surface. The graphical presentation of the electrical double layer is shown in Figure 2.3.

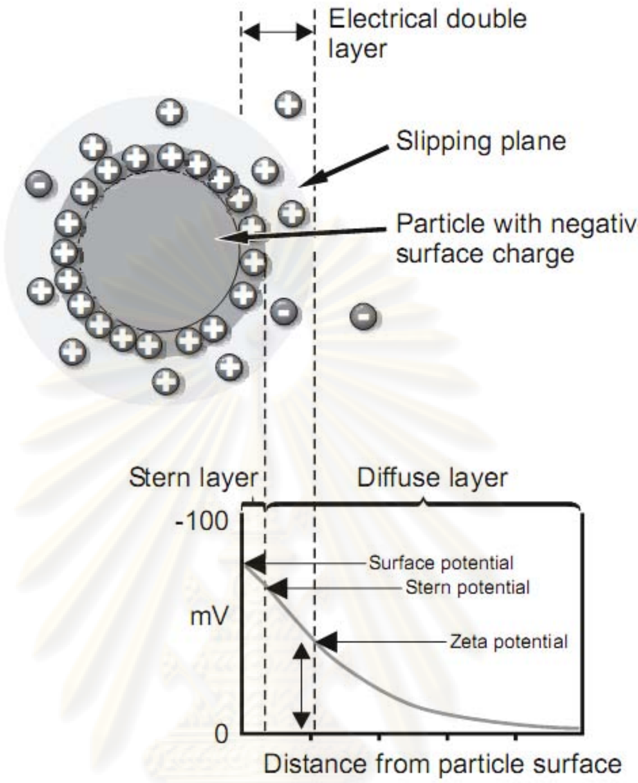


Figure 2.3 Basic description of the zeta potential.

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

i) Preferential adsorption ions
ii) Dissociation of surface charged species
iii) Isomorphic substation of ions
iv) Accumulation or depletion of electrons at surface
v) Physical adsorption of charged species onto the surface

The surface potential of solid varies with the concentration of the ions in the surrounding solution, and can be classified into two parts; an inner region called the *Stern layer*, where the ions are strongly bound and outer region called *Diffuse layer*, where they are less firmly attached. Within the Diffuse layer there is notional boundary, inside which the ions and particles form a stable entity. When a particle moves, 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 hydrodynamic shear or slipping plane. The potential that exist at this boundary is known as 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 add 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 buildup of positive charge. Therefore, zeta potential will be positive at low pH and becomes negative at high pH.

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

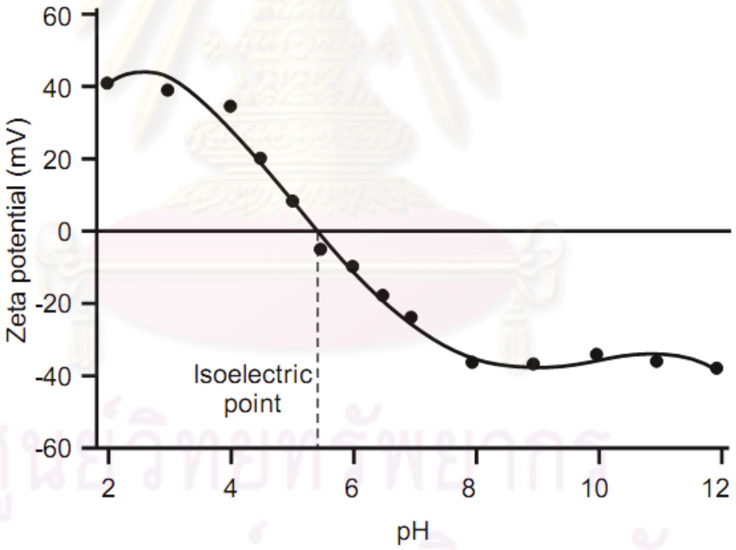


Figure 2.4 Basic definition of the isoelectric point.

The adsorption on metal oxide is pH sensitive. Below a particular pH, a metal oxide possesses a positive surface charge, whereas above that pH the surface becomes negatively charged. The pH at which the surface charge is zero is called “the point of zero charge”, pH_{PZC}. The surface charge on the oxides is mainly derived from preferential dissolution or deposition of ions. Ions adsorbed on the surface determine the surface charge, and thus are referred to as charge determining ion, also known as co-ions or coions. In the oxide system, typical charge determining ions are protons and hydroxyl groups, of which the concentration are described by pH (pH = -log [H^+]). As the concentration of the charge determining ions varies, the surface charge density changes from positive to negative or vice versa.

2.4 Surfactant

The term surfactant comes from ―Surface-active agent”. Surfactant refers to the substances that lower the surface tension of a liquid and can dissolve in two insoluble liquid. The surfactants are usually organic compounds that are amphiphilic, meaning that they contain both hydrophobic groups (their tails) and hydrophilic groups (their heads). The hydrophobic group is usually a hydrocarbon long chain of 10-20 carbon atoms. The hydrophilic portion may or may not be ionized depending on the type of surfactant [22].

The surfactants are classified into four primary groups; anionic, cationic, non-ionic, and zwitterionic (dual charge). Anionic and cationic surfactants are called ionic surfactant. Approximately two-third of the surfactants are ionic surfactants and more than 90% of the ionic surfactants are anionic surfactants. Therefore anionic surfactants (AS) are the major class of surfactant used in detergent formulations. The type of anionic surfactants is branched alkylbenzene sulfonate (ABS), linear alkylbenzene sulfonate (LAS) and linear alkyl sulfate. An example of linear alkyl sulfate is sodium dodecyl sulfate (SDS), which is a representative of AS [23]. The properties of SDS are shown in Table 2.1.

Table 2.1 Properties of SDS.

Chemical Structure	
Surfactant	Sodium dodecyl sulfate (SDS)
Molecular formula	$CH_3(CH_2)_{11}OSO_3Na$
Molecular weight	288.8 g/mol
CMC	2310.4 mg/ l [24]
Type	Anionic (-)

A micelle is an aggregate of surfactant molecules dispersed in liquid. A typical micelle in aqueous solution forms roughly spherical or globular aggregate with the hydrophobic “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 bilayer 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 micelle is known as micellization and the surfactant concentration which at micelle is spontaneously formed is called “*critical micelle concentration (CMC)* ” [25].

The surfactant is wildly used in textiles, fibers, foods, paints, polymers, cosmetics, pharmaceuticals, mining, oil recovery, pulp-paper industries, etc [26, 27]. Various surfactants have been tested for their sortive behavior onto different sorbents such as alumina, silica, titania, zeolite clay and activated carbon [24, 28]. Gawade et al [28] modified alumina surfaced by adsorption of an anionic surfactant, i.e. sodium dodecyl sulfate (SDS), for removal herbicide from water. It was found that surfactant-treated alumina have greater adsorption capacity for herbicide (isoproturon) than untreated alumina. In this work, Sodium dodecyl sulfate (SDS) is selected to be adsorbed surfactant on alumina surface.

2.5 Adsorption Process

Adsorption is a phenomenon at a surface or interface by the result of binding force between atoms, molecules, and ions of the adsorbate on the surface of adsorbent [29]. The adsorption occurs when liquid or gas (called *adsorbate*) accumulates in molecular or atomic form on the surface of solid or liquid (called *adsorbent*). It is different from absorption, where a substance diffuses into a liquid or solid to form a “solution.” The adsorption is wildly used in industrial applications such as activated carbon, synthetic resins, and water purification.

The adsorption occurs when ions, atoms, or molecules are selectively transferred from fluid phase to the surface of the adsorbent by surface energy similar to surface tension. However, atoms on the surface of the adsorbent are not wholly surrounded by other adsorbent atoms and therefore can attract adsorbates. The adsorption process is generally classified as physisorption (characteristic of weak van der Waals forces) or chemisorptions (characteristic of covalent bonding).

There are number mechanisms by which surface-active molecules may adsorb onto the solid substrates from aqueous solution [30]. In general, the adsorption of surfactants involves single ions rather than micelles [30].

(i.) Ion exchange: Replacement of counter ions adsorbed onto the substrate from the solution by similarly charged surfactant ions.

(ii.) Ion pairing: Adsorption of surfactant ions from solution onto oppositely charged sites unoccupied by counter ions.

(iii.) Hydrophobic bonding: Adsorption occurs by this mechanism when there is an attraction between a hydrophobic group of adsorbed molecule and a molecule present in the solution.

(iv.) Adsorption by polarization of p electrons: When the surfactant contains electron-rich aromatic nuclei; the solid adsorbent has strongly positive sites, attraction between electron rich aromatic nuclei of the adsorbate and positive sites on the adsorbent results in adsorption.

(v.) Adsorption by dispersion forces: Adsorption by London–van der Waals force between adsorbate and adsorbent increases with the increasing molecular weight of the adsorbate [31].

The interaction between the surface of the adsorbent and the adsorbate in adsorption from solution to solid 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 [32].

The formation of surfactant on metal oxide surface at low pH was shown in Figure 2.5. In the first region, the surfactant is adsorbed onto the solid surface by coulombic attraction between charged alumina surface and the oppositely charged surfactant head group. In the second region, the surfactant on the solid surface forms into admicelle or hemimicelle by van der Waals forces between the long chains of surfactants. In the third region, further adsorption occurs through the growth of the surfactant aggregates in the second region until it reaches equilibrium concentration of the surfactant. Finally, the admicelle form becomes saturated. The transition from the third region to the fourth region occurs above the critical micelle concentration (CMC) of the surfactant.

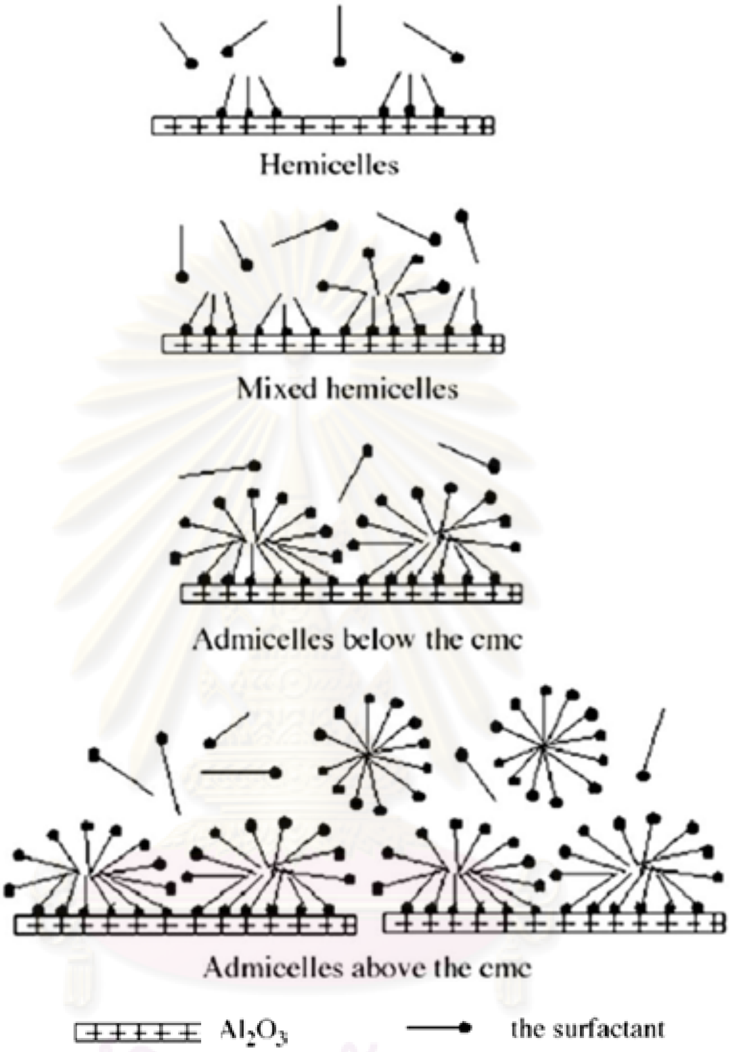


Figure 2.5 Structure of surfactant aggregates on the alumina surface [33].

Adsorption isotherm: The adsorption is usually described through isotherms, that is, the amount of adsorbate on the adsorbent as a function of its pressure (if gas) or concentration (if liquid) at constant temperature. The quantity adsorbed is always normalized by the mass of the adsorbent to allow comparison of different materials. The adsorption isotherm defines the equilibrium state of the process. Several models have been developed to define the adsorption isotherm [34]. Among the isotherm models, the model proposed by Langmuir and Freundlich have been generally considered for the liquid–solid system.

Langmuir isotherm: The Langmuir isotherm described adsorbate-adsorbent systems in which the extent of adsorbate coverage is limited to one molecular layer at or before a relative pressure (in gas) or concentration (if liquid) of unity is reached. Although the isotherm is more usually appropriate for the description of chemisorption, the equation is nevertheless obeyed at moderately low coverage by a number of systems, and can be readily extended to describe the behaviour of binary adsorbate systems. The Langmuir isotherm is based on four assumptions:

(i) The surface of the adsorbent is uniform, that is, all the adsorption sites are equivalent.
(ii) Adsorbed molecules do not interact.
(iii) All adsorption occurs through the same mechanism.
(iv) At the maximum adsorption, only a monolayer is formed: molecules of adsorbate do not deposit on other, already adsorbed, molecules of adsorbate, only on the free surface of the adsorbent.

The Langmuir adsorption isotherm is limited application since for real surfaces the surfactan is not the same for all sites in real surfaces and interactions between adsorbed molecules cannot be ignored.

According to the linearized form of the Langmuir isotherm model:

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{bq_{max}}\frac{1}{C_e} \tag{2.1}$$

where,

q_e = amount of adsorbate on adsorbent at equilibrium (mg/g)
q_{max} = maximum adsorption capacity (mg/g)
C_e = equilibrium concentration (mg/l)
b = constant related to energy of the sorption system

Freundlich isotherm: The Freundlich equation or Freundlich adsorption isotherm is an adsorption isotherm, which is a curve relating the concentration of a solute on the surface of an adsorbent, to the concentration of the solute in the liquid with which it is in contact. The Freundlich isotherm may be used to describe heterogeneous systems. Theoretically, using this expression, an infinite amount of adsorption can occur.

The Freundlich equation agrees well with the Langmuir equation over moderate concentration ranges but, unlike the Langmuir expression, it does not reduce to the linear isotherm (Henry’s law) at low surface coverage. Both these theories suffer from the disadvantage that equilibrium data over a wide concentration range cannot be fitted with a single set of constants [35].

According to the linearized form of Freundlich isotherm model:

$$ln\, q_e = \ ln\, k_f + \frac{1}{n} ln\, C_e \tag{2.2}$$

where,

k_f = Freundlich constant related to adsorption capacity

$\frac{1}{n}$ = adsorption intensity.

These adsorption isotherms can be used to describe the mechanism of the adsorption process at the surface of alumina by fitting curve with the equations.

2.6 Adsolubilization Process

―Adsolubilization” or ―surface solubilization” is the process that surfactant adsorbed onto solid oxide surface. Because of the surfactant properties that can solubilize the organic compound having low water solubility, the use of surfactant adsorbed on the surface of solid can remove organic solute from water into the surfactant layer [1, 11, 13-15]. For the last two decades, this process has been extensively study. There are many research groups that use this process for various purposes such as waste water treatment, polymerization, pharmaceutical, and oil recovery [13].

The adsorbed surfactant aggregates, called as 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, sphere, and cylinders [36-38]. 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 solute with different polarities and structure 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 mechanism of adsolubilization process as shown in Figure 2.6 starts when the surfactant adsorbs at the solid-liquid interface. The surfactant aggregates are formed on the solid surface and the behavior is very similar to that of micelles. If the surfactants are adsorbed in monolayer, then the aggregates are called –hemimicelle” and if they form bilayer structure, then it is called –admicelle.” [34]. The adsorption of the surfactant on the solid surface occurs due to electrical attraction. At this state, monolayer formation takes place. After that, the interaction between the long hydrocarbon chains of the surfactant molecules of the already formed monolayer and incoming surfactant molecules takes place to form bilayer structure [39]. These bilayers can be used for removal of organic pollutant from water.

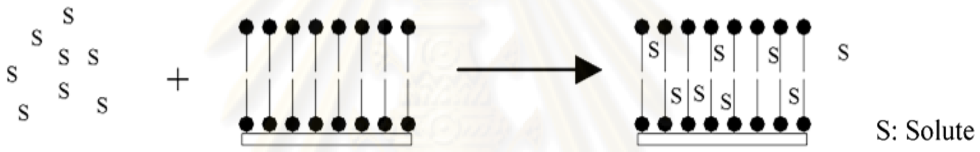


Figure 2.6 Schematic diagram showing adsolubilization on surfactant-modified alumina (SMA).

The adsolubilization process is one of the effective ways to remove the low concentration of low soluble organic pollutants from effluent. Several studies have shown that the adsolubilization has great efficiency (about 90%) in removal various kinds of pollutants from water [11, 14, 15, 28, 29, 33, 40, 41]. Adsolubilization can remove organic compound at low concentration but can not degrade organic compound. It is only collect diuron molecules in order to increase their concentration. This collected diuron has to be degraded by other methods such as photocatalysis (photodegradation). Adsolubilization is a good technique for the solution having low concentration that is a limit for some methods.

The important factors affect on adsolubilization process are pH of solution, initial concentration, agitation speed, mass of adsorbent and temperature. Gawade et al modified alumina surfaced by adsorption of an anionic surfactant, i.e. sodium dodecyl sulfate (SDS), for removal herbicide from water [28]. The effect of pH on adsorption and other factors such as initial concentration, agitation speed, mass of adsorbent and temperature have been studied.

It was shown that 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.

The effect of pH of solution is the most important factor in the adsolubilization process. The studies confirmed that pH of the solution has an effect on the removal of organic compounds from water. At pH less than pH $_{PZC}$ of the adsorbent (alumina), the adsorption amount is much greater than at pH higher than pH $_{PZC}$. The results have shown that when pH is increased, the amount of adsorption decreases. It can be shown that the density of positive charges alumina surface was lowered, so that the electrostatic attraction between negative charges of the surfactant (SDS) and positive charges of alumina surface was not strong enough to immobilize organic compound on its surface.

2.7 Diuron

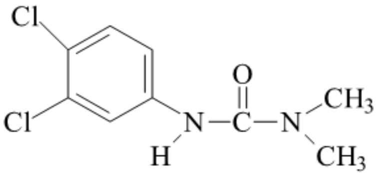
In agricultural countries, using herbicide was presented wild spread. These chemicals from agriculture can cause the toxic contaminant in environmental problem. Phenylurea herbicide is one of the most wildly used in order to inhibit photosynthesis of weeds and grass [42]. The water contaminated by herbicide affects human health. The herbicides not only contaminate soil but water as well. The toxic in soil and water can degradation by itself but it has long times.

Diuron or DCMU (3-(3,4-dichlorophenyl)-1, 1-dimethylurea) is a herbicide which is widely used in agriculture in order to inhibit photosynthesis in crops and grass. It blocks the light reaction to chemical energy by preventing oxygen production in plants. Therefore, diuron is used on non-crop area such as road, garden path, or railway line [6]. However, the widespread use of diuron leads to environment impact not only in soil but also in water [2].

The convention methods for diuron removal from the water environment involve processes such as thermal degradation [2], chemical degradation [3], biodegradation [4-6], photocatalytic degradation [7-9], solid-phase extraction (SPE) [10], and adsorption [11, 12].

Diuron (CAS number: 330-54-1) is a solid colorless crystalline compound in its pure form at ambient temperature. The physical properties of diuron are shown in Table 2.3.

Table 2.2 Physical properties of diuron.

Structure formula	
Molecular formula	$C_6H_{10}C_{l2}N_2O$
Molecular weight	233.10 g/mol
Melting point	158 – 159 °C
Vapor pressure	0.0041 Pa at 30 °C
Appearance	White crystalline solid
Solubility	42 ppm in water at 25 °C
Synonyms	Cekiuron; Crisuron; Dailon; Di-on; Krovar; Unidron; Vonduron; Xarmex; etc.
Toxicity	The concentrated material may cause irritation to 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

CHAPTER III

EXPERIMENTAL

This chapter describes experimental system and procedures for adsolubilization process. It is divided into four different parts. The first described the synthesis of porous alumina. The second part describes the preparation of SMA. The third was to investigate the removal of diuron from water environment using the prepared SMA, and the characterizations of the obtained products are described in the last part.

3.1 Preparation of Porous Alumina Powder

3.1.1 Materials

1. Aluminum acetylacetonate ($C_{15}H_{21}AlO_6$, 95%, Fluka)
2. Resorcinol ($C_6H_4(OH)_2$, 99%, Fluka)
3. Formaldehyde (HCOH, 37% w/v; stabilized by 11-14 wt% methanol, Ajax Fine Chemical)
4. Sodium carbonate (Na_2CO_3, 99%, Ajax Fine Chemical)

3.1.2 Preparation procedure

The experiment started with the alumina synthesis. Alumina was produced by sol-gel process assisted by resorcinol-formaldehyde formation.

Resorcinol (denoted by R), deionized water (denoted by W), and sodium carbonate (denoted by C) were added together with R:W and C:W molar ratio of 0.15 and $1.8x10^{-5}$, respectively. Then, formaldehyde (denoted by F) was added to the mixture with R:F molar ratio of 0.5. The RF solution was kept at room temperature for aging time of 21 h. at the mean time, aluminum acetylacetonate (denoted by A) was stirred with ratio 1 g of aluminium acetylacetonate 4.35 ml of formaldehyde that aluminum acetylacetonate can be dissolved. Then the aluminium acytylacetonate mixture was added to the RF solution with A:R molar ratio of 0.05. The mixture was stirred for 30 minutes and aged under low-humidity atmosphere, controlled by the presence of silica gel in the aging container, for 51 h (total aging time 72 h).

The RF-aluminium composite was dried at 110 °C in an oven for 24 h and subsequently calcined at 700 °C for 2 h in air, using the heating rate of 5 °C/min. The obtained alumina powder was characterized by SEM, XRD, and surface area measurement via BET method.

3.2 Preparation of Surfactant-Modified Alumina (SMA)

3.2.1 Surfactant

- Sodium dodecyl sulfate (SDS, ≥ 99%, Fluka)

3.2.2 Adsorption process

The adsorption of SDS onto alumina was conducted in batch by adding 0.5 g of alumina to 20 ml SDS solution with various concentrations (1-150% CMC of SDS), which the critical micelle concentration of SDS is 8.1x10^{-3} mol/L. The mixture was stirred for 24 h at controlled temperature (at room temperature ~23-25 ^{o}C). The pH of the mixture was adjusted by using 1 N HCl or 1 N NaOH solution. Then, powder was separated from the solution using centrifuge and dried at 60°C for 24 h. The obtained powder was called ~~–s~~urfactant-modified alumina" or SMA.

The content of SDS adsorbed on the surface of alumina was determined by solvent extraction spectrophotometric method, using acridine orange (ACO) as anion-pairing agent. The sample solution (10 mL) containing SDS was transferred into a 25 mL separating funnel. ACO (5×10^{-3} M) and 100 µL of glacial acetic acid was then added into the solution. Then, 5 mL of toluene was added to it and shaken for 1 min. The aqueous layer was then discarded and the content of SDS in toluene layer was measured by UV/Visible spectroscopy at wavelength of 499 nm [11, 23, 34, 40, 43, 44].

3.3 Adsolubilization of Diuron on SMA

3.3.1 Herbicide

- Diuron (3-(3,4-dichlorophynyl)-1,1-dimethylurea, 98%, Sigma-Aldrich)

3.3.2 Adsolubilization Process

For the adsolubilization experiments, 0.5 g of the surfactant-modified alumina was mixed into 100 ml of diuron aqueous solution at the concentration between 1 to 10 ppm at room temperature (25 ºC). The pH of diuron solution was adjusted to the value in range of 3 to 11 by using 1 N of HCl or 1 N of NaOH solution. The mixture was stirred for 3 h and the solution was periodically taken for the measurement of diuron concentration via HPLC.

3.4 Characterizations

3.4.1 Characterizations of porous alumina

3.4.1.1 Scanning electron microscopy (SEM)

Surface morphology and size of the synthesized alumina powders were obtained by using scanning electron microscopy (SEM) model JSM-6400 at Scientific and Technological Research Equipment Centre, Chulalongkorn University. Size of the products was then measured from the micrographs, using image processing software (JEOL Semafore 5.0).

3.4.1.2 X-ray Diffraction (XRD)

The phase composition of synthesized alumina powders were identified by using X-ray diffractometer. The crystalline phases of Al_2O_3 were identified by using a Bruker D8 Advance equipped with a Cu Kα radiation source ($\lambda = 0.15406$ nm) and operated at 40 kV and 40 mA.

3.4.1.3 Surface area measurement

The surface area and pore size distribution were calculated from nitrogen adsorption isotherms using the Brunauer, Emmett, and Teller (BET), and Barrett, Joynerand Halenda (BJH) methods, by an BELSORP-mini adsorption analyzer at the center of excellence on particle technology, Chulalongkorn University. Use nitrogen as the adsorbate. The operating conditions are as follows:

Sample weight	~ 0.1-0.2 g
Degas temperature	150 °C
Vacuum pressure	< 10 mmHg

3.4.2 Characterization of SMA

3.4.2.1 Fourier Transform Infrared Spectroscopy (FT-IR)

Functional groups of the SDS and diuron on alumina surface were obtained by using Fourier Transform Infrared Spectroscopy (FT-IR) Model Spectrum One (Perkin Elmer). Infrared spectra were recorded between wavenumber of 400 and 4000 cm^{-1}.

3.4.2.2 Ultra-Violet/Visible (UV-Vis) Spectrophotometer

The concentrations of SDS in the supernatant after adsorption surfactant onto alumina surface were investigated by using UV-Vis spectrophotometer at wavelength of 499 nm.

3.4.3 Characterization of adsolubilization process

The amount of diuron adsorbed on alumina surface was calculated from amounts of diuron disappearing from initial diuron solution. The solution was characterized by using High-performance liquid chromatography (HPLC). The concentration of diuron in the solution was monitored by a reverse-phase liquid chromatography (HPLC, Shimadzu) and C18 column (Phenomenex Luna 5 μm particle size, 250×4.6 mm). The mobile phase was consisted of 70% acetronitrile and 30% deionization water with flow rate of 1.5 ml/min.

CHAPTER IV

RESULTS AND DISCUSSION

Adsolubilization on surfactant-modified alumina powders can be applied to remove many organic compounds from water. Porous alumina powders were prepared by sol-gel process assisted by RF gel. The surface of alumina was modified by surfactant via adsorption. Then, the modified solid was used as adsorbent for the adsolubilization of diuron. Effects of many factors involving in the process were investigated and described in this chapter. The chapter can be divided into 3 parts, i.e., properties of the synthesized alumina, properties of surfactant-modified alumina and adsolubilization of diuron on the surfactant-modified alumina.

4.1 Properties of Synthesized Alumina

Porous alumina powders were synthesized assisted by RF gel, which was prepared from resorcinol, formaldehyde, water and sodium carbonate via sol-gel process. Aluminium acetylacetonate was used as aluminium precursor. After 3 days of aging, RF/alumina composite was dried and calcined at 700 ºC for 2 hours with heating rate of 5 ºC/min.

4.1.2 X-ray Diffraction Analysis

The product obtained after the calcination of RF/alumina composite at 700 ºC for 2 hours was characterized for phase transformation by using X-ray diffraction analysis. It can be seen from Figure 4.1 that the XRD patterns of both commercial alumina and synthesized alumina from amorphous were found to be alumina in γ-phase. The powders are transformed to crystalline γ-Al_2O_3 during calcination.

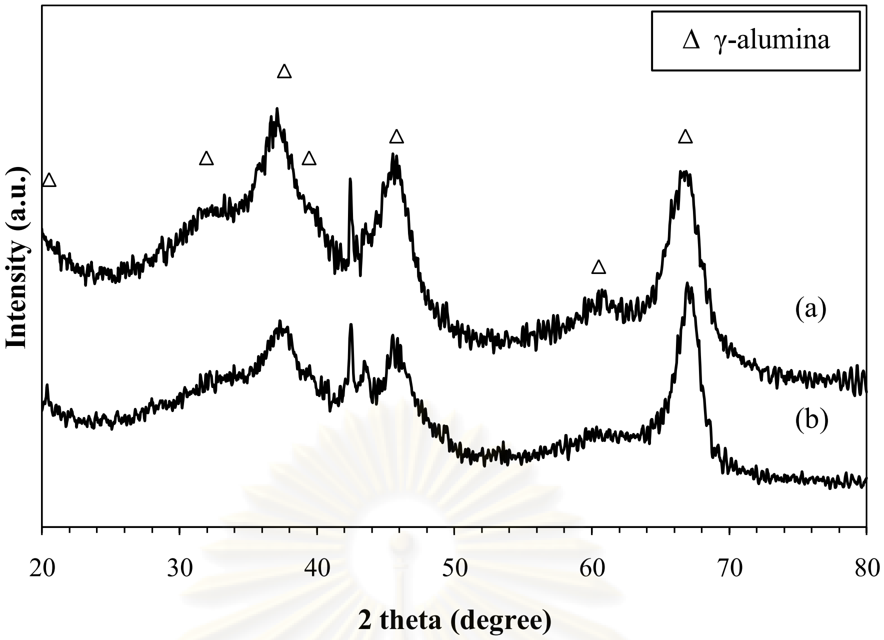


Figure 4.1 XRD patterns of synthesized alumina (a) and commercial alumina (b) after calcination.

4.1.2 Morphology of porous alumina

For alumina powders after the calcination, the synthesized alumina was characterized by SEM. The results are shown in Figure 4.2.

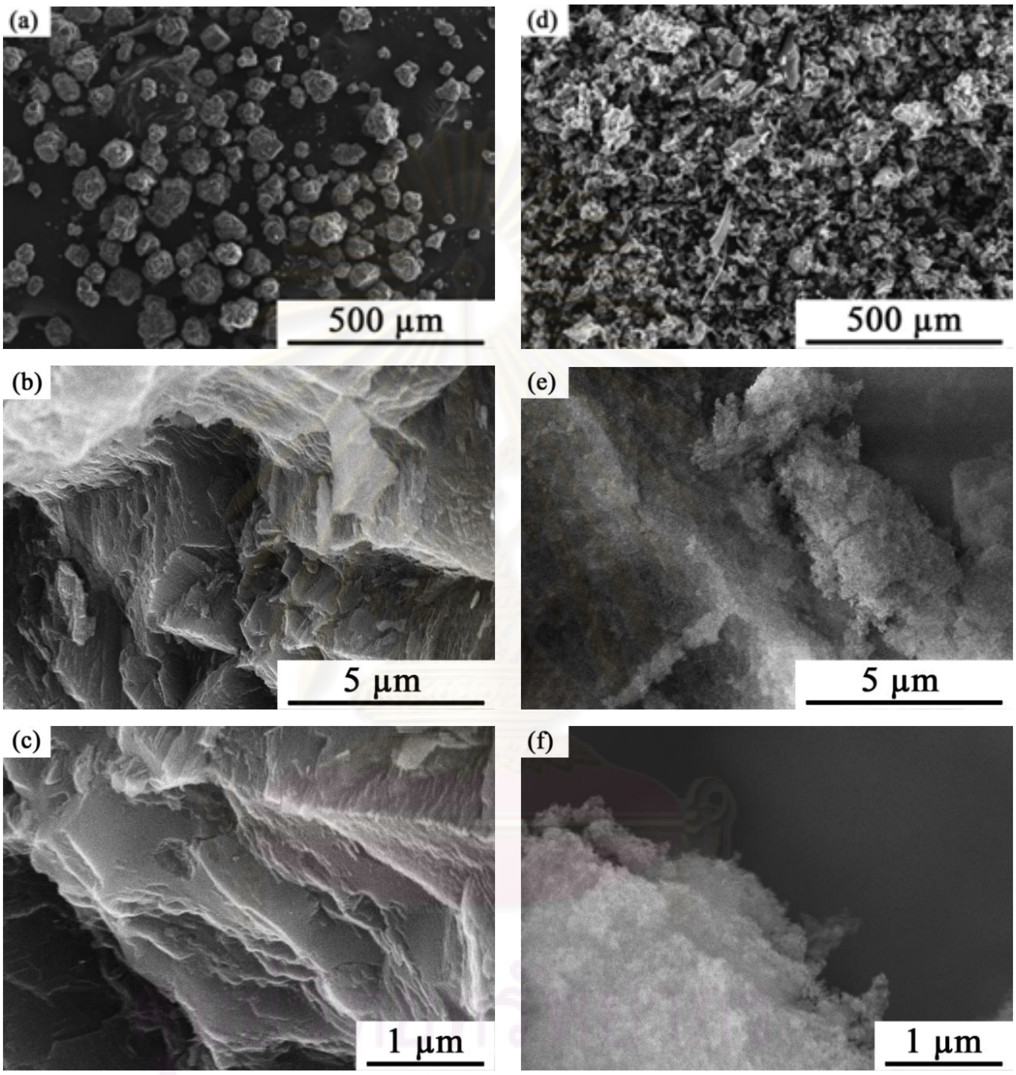


Figure 4.2 SEM micrographs of commercial alumina (a), (b) and (c) as well as synthesized alumina (d), (e) and (f).

It is found that the particle size of commercial alumina is larger than that of the synthesized alumina. The commercial alumina is less porous than the synthesized alumina but the shape of the particle is more spherical than the synthesized alumina. The high magnification image shows that synthesized alumina is formed from aggregation of small grains. The picture also shows that synthesized alumina is in fact consisted of many nanoparticles and has higher porosity than the commercial alumina. It is suggested that the aluminium precursor disperses uniformly within the porous structure of RF gel and forms into nanosized alumina via sol-gel process during aging. The nanosized pores are caused by the removal of the RF network via the calcination.

Table 4.1 shows the BET data of both types of alumina. The specific surface area (SSA) and pore volume of the synthesized γ-alumina is about 200 m^2/g and 0.5526 cm^3/g respectively. The BET specific surface area and pore volume of the commercial alumina is about 137.6 m^2/g and 0.1742 cm^3/g respectively. In some experiments, the used synthesized alumina was prepared in different batch such that it results in quite different in some properties of the synthesized alumina. Comparison of the properties of alumina in both batch are shown in the table 4.1. The adsorption/desorption isotherm as shown in Figure 4.3 could be identified as Type IV (IUPAC classification), which suggested the presence of mesopores within both of the commercial alumina powder and the synthesized alumina powder. From BJH pore size distribution in Figure 4.4, it is shown that the average pore diameter of the synthesized alumina and the commercial alumina are 2.71 and 2.1 nm, which are consistent with both shape of the adsorption/desorption isotherm and the observation of SEM image in Figure 4.2. It shows that the aerogel from resorcinol and formaldehyde polymerization can synthesize mesoporous alumina with high surface area and high pore volume. However, the BJH pore size distribution peak of the commercial alumina is narrower than that of the synthesized alumina.

Table 4.1 The properties of commercial alumina and synthesized alumina.

Alumina particle	**SSA (m^2 g^{-1})**	**Pore Diameter (nm)**	**Pore Volume (cm^3 g^{-1})**
Commercial alumina	137.6	2.71	0.1742
Synthesized alumina (A)	194.2	2.1	0.5526
Synthesized alumina (B)	195.0	2.38	0.2765

*SSA is Specific surface area.

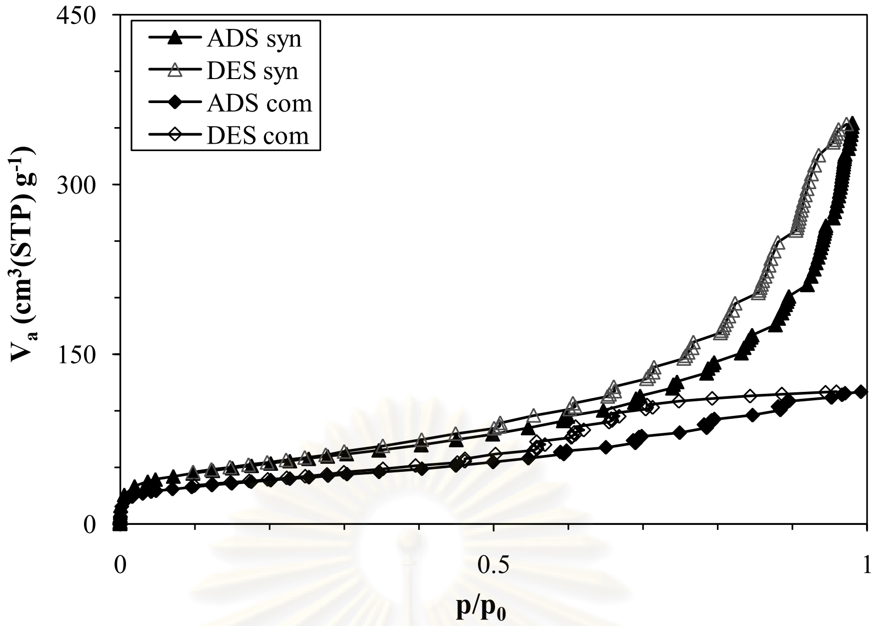


Figure 4.3 Nitrogen adsorption/desorption isotherm of alumina powder: (▲) the nitrogen adsorption of synthesize γ-alumina; (△) the nitrogen desorption of synthesize γ-alumina; (◆) the nitrogen adsorption of commercial alumina; (◇) the nitrogen desorption of commercial alumina.

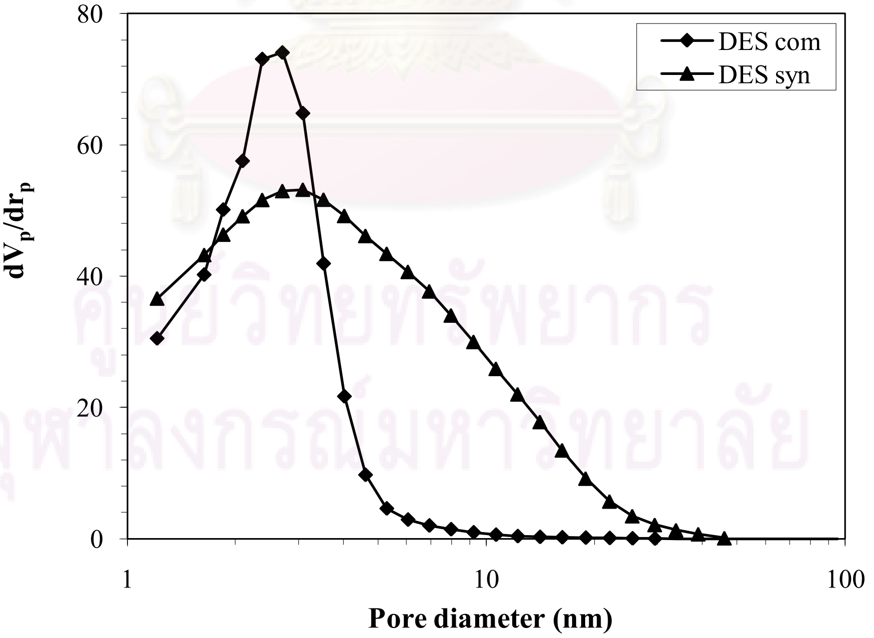


Figure 4.4 Pore size distribution of alumina powder: (▲) the synthesize γ-alumina; (◆) commercial alumina.

4.2 Surfactant-Modified Alumina

4.2.1 Adsorption of surfactant on porous alumina

To confirm that SDS was successfully coated on the surface of alumina particles after adsorption, the powder was characterized by FTIR. The result is shown in Figure 4.5. Indeed, the analysis of these FTIR spectra shows that

- The band around 3457 cm^{-1} is assigned to OH-stretching
- The small bands appearing at 2919 and 2852 cm^{-1} are characteristic of the stretching of asymmetrical and symmetrical of alkyl CH (-CH$_2$-) group, respectively. The band at 2959 cm^{-1} is assigned to the asymmetrical stretching of –CH$_3$, as well as at 1471 and 1221 cm^{-1} from the deformation of alkyl CH groups of SDS [45, 46].
- Moreover, the stretching vibration of sulfate group is also observed at wavenumber around 1050-1120 and 1220-1300 cm^{-1} [47].

It is therefore confirmed that the surfactant could be adsorbed onto alumina via this technique.

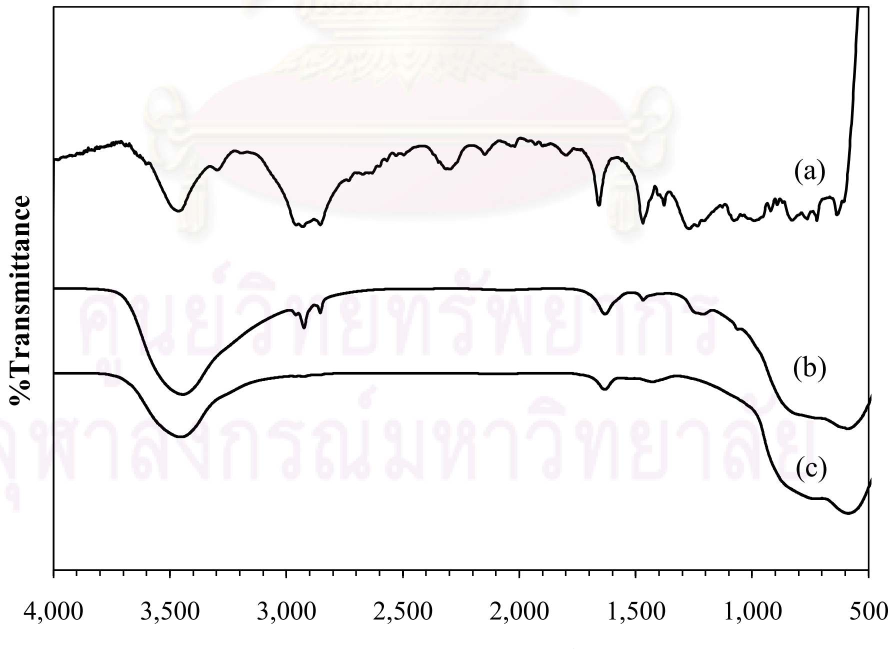


Figure 4.5 FTIR spectra of pure SDS (a), synthesized alumina powder modified with SDS at 100%CMC (b) and bare synthesized alumina powder (c).

4.2.2 Effect of surfactant concentration

The adsorption isotherm was drawn to understand the nature of the equilibrium distribution of SDS on the surface of alumina. The isotherm for the adsorption of SDS onto the surface of alumina was investigated by analysis of the concentration of the surfactant in the supernatant solution after stirring with 0.5 g of alumina for 3 h at room temperature (25 ± 2 ºC). The initial concentration of SDS was varied from 8.1×10^{-6} to 2.02×10^{-1} mol/l. The pH of solution was adjusted to 3 by adding HCl so that alumina surface became positively charged. After 3 h, the solution reached the equilibrium, then, the equilibrium concentration was determined to find out the SDS adsorption capacity on alumina surface. In general, a typical isotherm can be subdivided in to four regions when plotted on a log-log scale [31, 39, 48-52]. Figure 4.6 presents the adsorption isotherm of surfactant on the solid-liquid interface in a wide range of concentrations of the CMC. It is a plot between the amounts of surfactant adsorbed on alumina versus the equilibrium surfactant concentration in the supernatant.

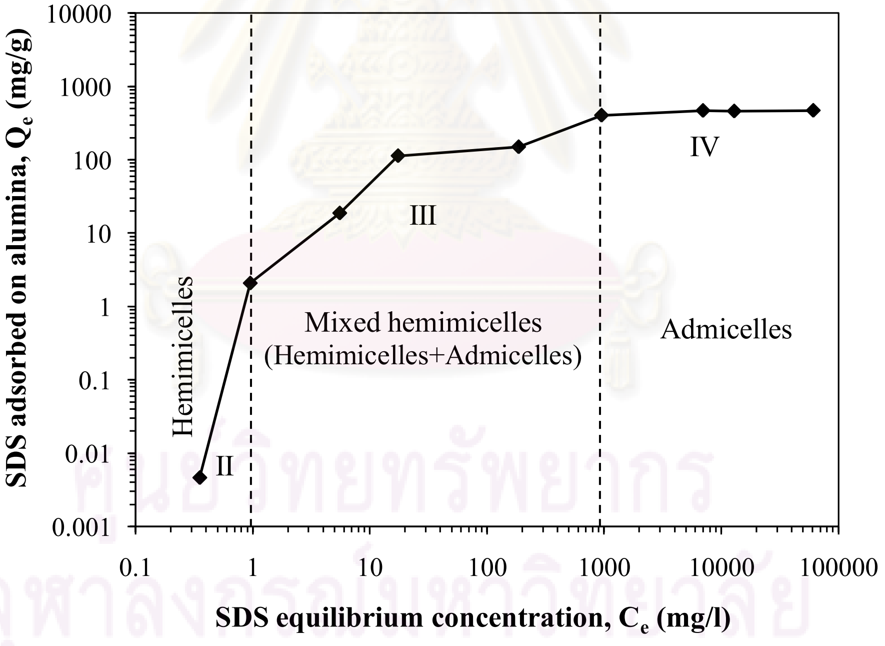


Figure 4.6 Adsorption isotherm of SDS on alumina at pH 3.

At the adsorption of SDS using the initial concentration below the CMC, the amount of SDS adsorbed onto the surface of alumina increases sharply as the SDS concentration is increased. This is the result from positive charges on the surface of alumina attracting anionic head group of SDS, which consequently forms into hemimicelle and mixed hemimicelle on alumina. At the concentration of SDS higher than its CMC, however, SDS on the surface forms admicelle structure such that SDS in the solution, which had already formed micelle, could no longer adsorb on the surface.

In the first region (the Henry's law region) in Figure 4.7, surfactant molecules are electrostatically adsorbed to the charge surface sites. At this point, the adsorption is sparse so that interactions between adsorbed surfactant molecules are negligible. From the results in Figure 4.6 and 4.7, it is observed that the isotherm for the adsorption of SDS on alumina does not have adsorption in first region. It might suggest that from the charge sites on alumina surface are populated in the some area, so SDS adsorbed on alumina surface in that area are enough to form layer of surfactant and become hemimicelles structure. Because of the absence of region I, it is therefore suggested that the hydrophobic interactions in the low SDS contents has dramatic effect. The region II involves strong lateral interaction between adsorbed monomers, resulting in the formation of primary aggregates, known as hemimicelles. The adsorption is thus driven both by hydrophobic interactions and electrostatic attraction [52]. Hemimicelles structure has been occurred at the equilibrium concentration below 0.95 mg/l (0.015 % CMC). The transition from region II to III at equilibrium concentration of 0.95 mg/l represents the formation of admicelles form on the alumina surface, so the structures of hemimicelles and admicelles are called mixed hemimicelles. The equilibrium SDS concentration corresponding to the transition from region III to IV displays only admicelles forming on alumina surface. This structure occurs at the equilibrium SDS concentration above 950.12 mg/l. From this isotherm study, the maximum adsorption capacity is found to be 186.2 mg/g at the initial SDS concentration of 11664 mg/l (500 % CMC). According to the previous report, the CMC value of SDS is 2332.8 mg/l (8.1×10^{-3} mol/l).

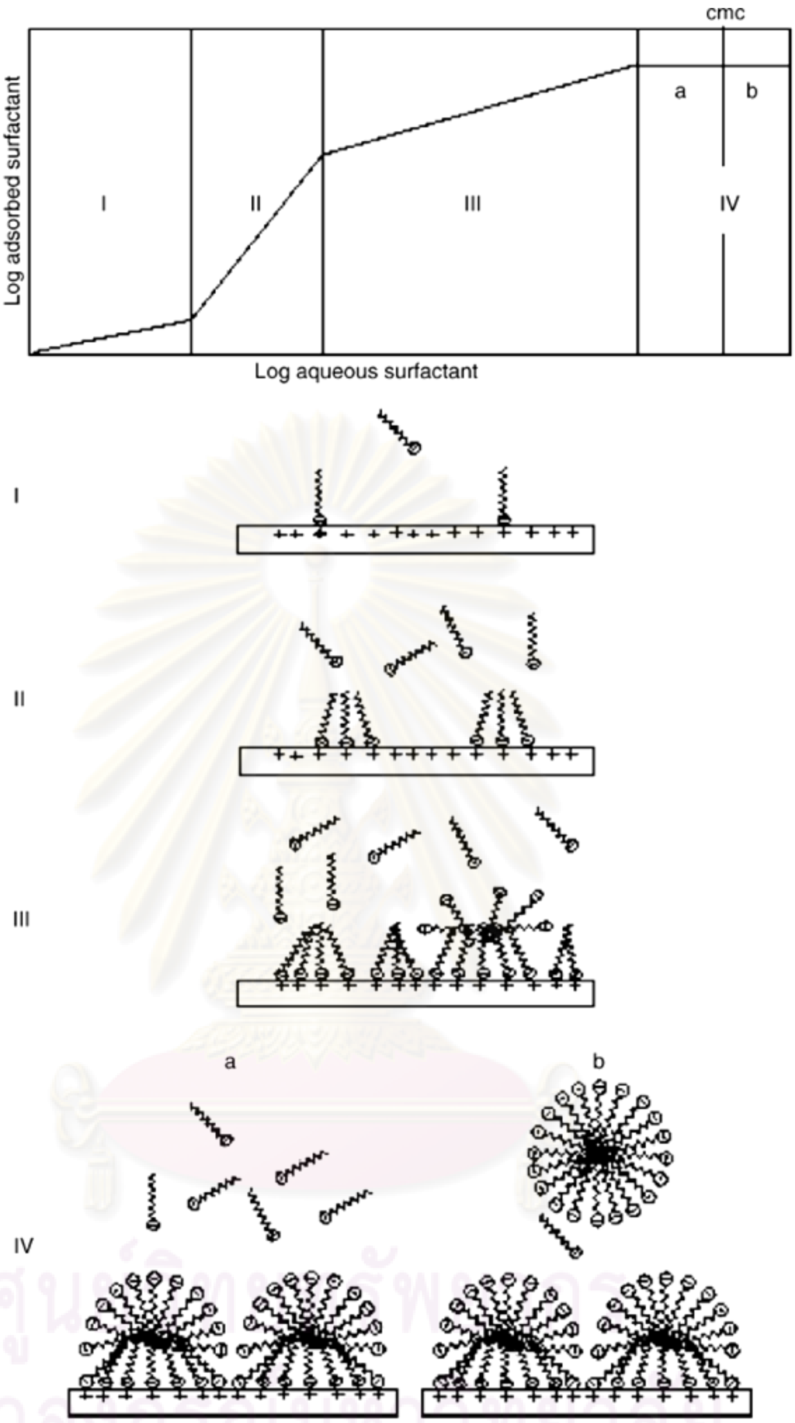


Figure 4.7 Typical adsorption isotherm for surfactants on mineral oxide surfaces and proposed surfactant aggregates in each isotherm span [52].

4.2.3 Effect of pH for the modification of alumina

One of the most important factors in adsorption process is effect of pH. The effect of pH on the adsorption of SDS on alumina was studied by changing the pH of solution at pH 3 and 11. The results are shown in Figure 4.8. It is shown that at lower pH (pH 3), amount of SDS adsorbed is much greater than at very high pH (pH 11). At pH 3 which is below the point of zero charge (PZC) of alumina (i.e. 8.5), the alumina surface is positively charged. So, the adsorption of anionic surfactant such as SDS onto alumina surface is enchanced. On the other hand, alumina surface is negatively charged at pH 11. The characters of adsorption of SDS on alumina at pH 3 and 11 are different as shown in Figure 4.8 and Table 4.2. It is observed that the amount of SDS adsorbed on alumina at pH 3 increases when the amount of SDS in the solution is increased. At low pH whereas alumina is positively charged, head group of SDS is adsorbed on the surface by coulombic attraction. As the SDS concentration is increased, SDS can further adsorb between long chains of the already adsorbed surfactants by van der Waals force. However, at pH 11, the SDS adsorption capacity increases slower than at pH 3. Negatively charged surface of alumina repels the SDS head group, so that these ions can not effectively adsorb onto alumina surface. Even though SDS is repelled by negatively charged, some SDS can still be adsorbed by dispersion force. The adsorption occurs not only by electrostatic attraction but also by van der Waals force, so the surfactants are physically adsorbed rather than electrostratically or chemisorbed. So, some surfactants can aggregate on the alumina surface.

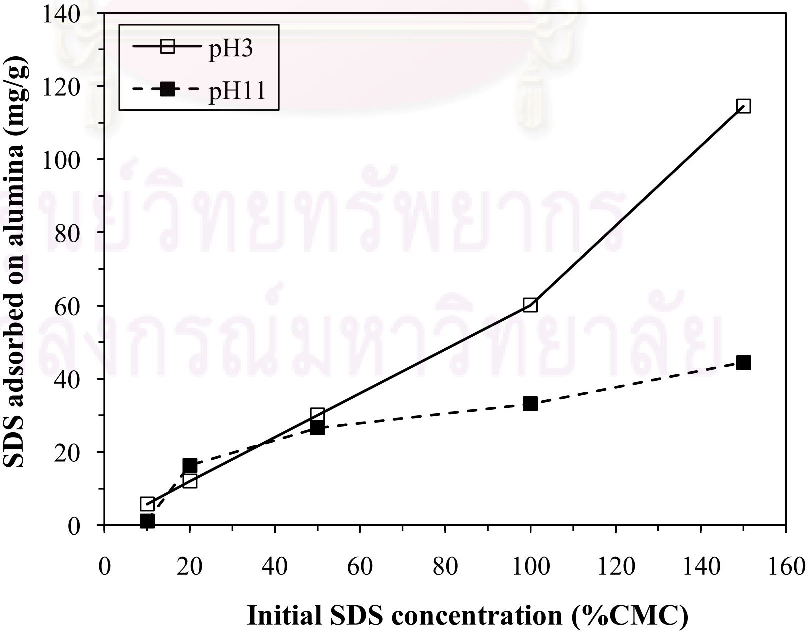


Figure 4.8 Effect of pH on adsorption of SDS on alumina.

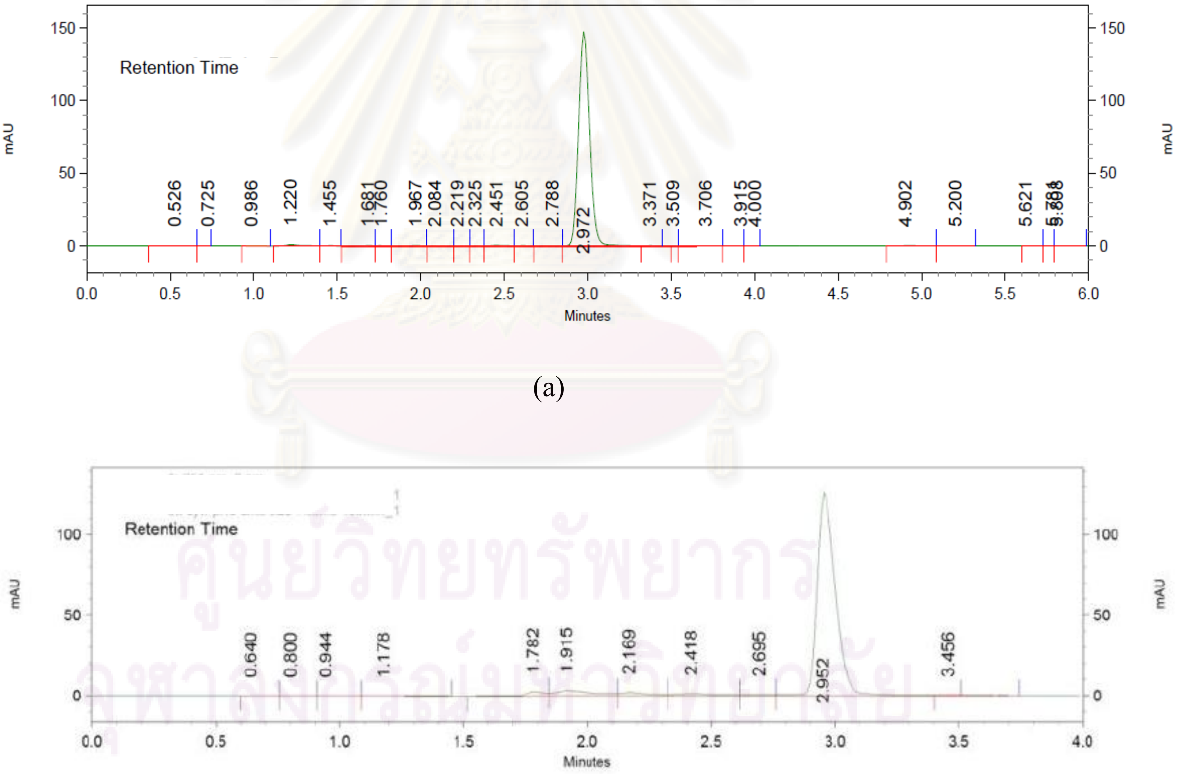
Table 4.2 Content of SDS adsorbed onto alumina at different pH and SDS concentration.

Alumina	Adsorption pH	Initial SDS concentration (%CMC)	%wt. of adsorbed
Synthesized alumina	3.0	1	54.4
		10	61.2
		20	64.5
		50	64.5
		100	64.5
		150	81.8
	11.0	1	3.0
		10	12.4
		20	87.3
		50	57.0
		100	35.5
		150	31.8
Commercial alumina	3.0	1	95.6
		10	97.1
		50	98.5
		100	88.9

4.3 Adsolubilization of Diuron on Surfactant-Modified Alumina

4.3.1 Preliminary experiments: Intermediate study

After modification of SDS onto alumina surface, the obtained SMA was used in adsolubilization of diuron from water. The result from the preliminary experiment shows that diuron can be removed from water. The most important advantages of the removal of diuron via adsolubilization when compared with other methods is not only that diuron can be removed rapidly but also about the toxic intermediate is not found in this method. It can be confirmed by Figure 4.9 and Table 4.2 and 4.4 that only peak of diuron at the retention time about 2.952 minutes can be observed. Because adsolubilization process is the physical technique in removal diuron, so it does not react with diuron molecules and does not cause the intermediate.



(a)

(b)

Figure 4.9 The chromatogram analyzed by HPLC of diuron solution at 10 ppm (a) and diuron solution after adsolubilization by SMA with 1% CMC of SDS concentration in adsorption and adsolubilization at pH 3 (b).

Table 4.3 Data of chromatogram of diuron solution at 10 ppm analyzed by HPLC.

Pk# Name	Retention time	Height
1	0.526	39
2	0.725	9
3	0.986	56
4	1.220	965
5	1.455	355
6	1.681	287
7	1.76	258
8	1.967	254
9	2.084	222
10	2.219	176
11	2.325	166
12	2.451	423
13	2.605	202
14	2.788	152
15	2.972	147452
16	3.371	42
17	3.509	3
18	3.7006	43
19	3.915	12
20	4.000	13
21	4.902	118
22	5.200	44
23	5.621	10
24	5.781	11
25	5.808	16

Table 4.4 Data of chromatogram of diuron 10 ppm analyzed by HPLC.

Pk# Name	Retention time	Height
1	0.640	29
2	0.800	69
3	0.944	124
4	1.178	158
5	1.782	2714
6	1.915	3152
7	2.169	2105
8	2.418	1455
9	2.695	743
10	2.952	126169
11	3.456	22

The SMA after the adsolubilization was analyzed for the functional group of diuron and SDS on alumina surface by FTIR study. Figure 4.10 shows the result that the SMA after adsolubilization does not show the peak corresponding to diuron. It might be resulted from the fact that the diuron concentration is too small that the instrument can not detect the signal of diuron.

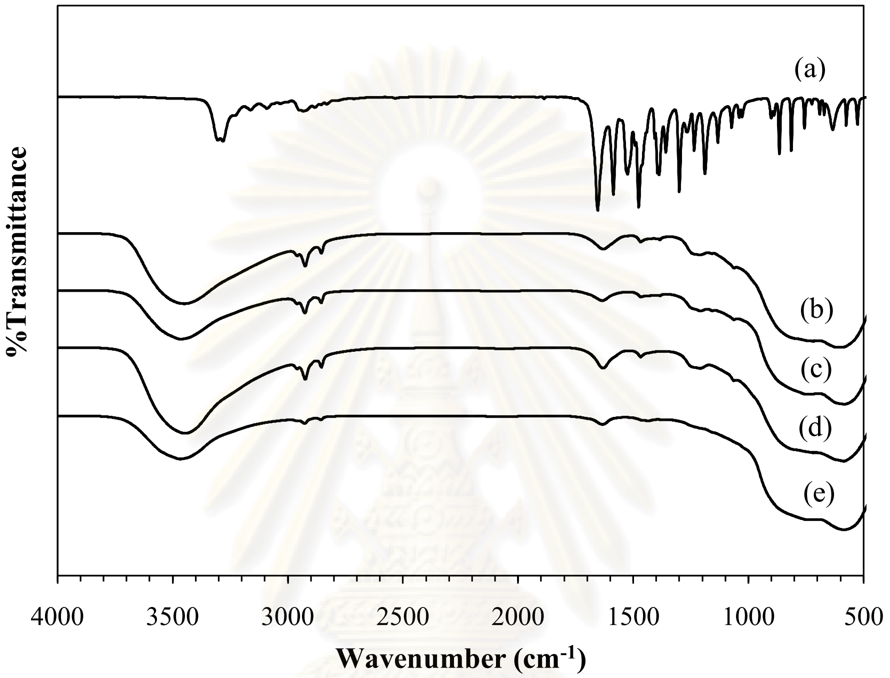


Figure 4.10 FTIR spectra of pure diuron (a), synthesized SMA after adsolubilization at pH 3-3 (b), synthesized SMA after adsolubilization (c), synthesized SMA with 100 %CMC (d) and bare synthesized alumina powder (e).

4.3.2 Adsorption of diuron on bare alumina

In the study of diuron removal by adsolubilization on SDS-modified alumina, comparison between the synthesized alumina and commercial alumina powder was studied. Nevertheless, the adsorption of diuron on bare alumina was firstly investigated. The alumina powder was immerged into an aqueous solution of diuron at concentration of 10 ppm. The amount of alumina was 50 mg/ 10 ml of diuron solution prepared at pH value of 3 and 11. The mixture was stirred for 2 h, which had been proved experimentally to be long enough for the adsorption to reach equilibrium. The results are shown in Figure 4.11.

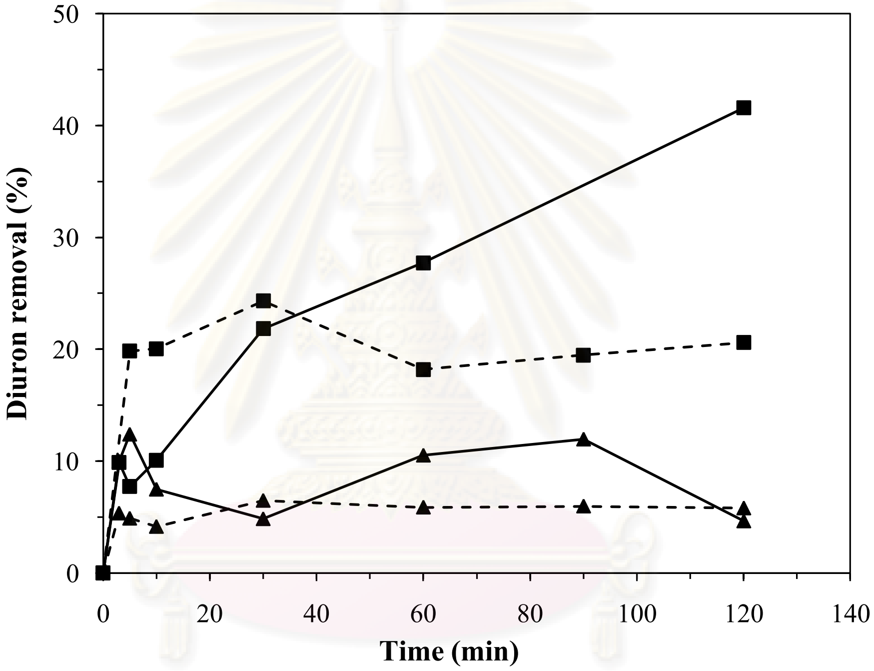


Figure 4.11 Adsorption of diuron on bare synthesized alumina (▲) and bare commercial alumina (■) at pH 3 (—) and 11 (---).

According to Figure 4.11, it is found that the amount of diuron removed by bare commercial alumina is higher than synthesized alumina, although the specific surface area and pore volume of the commercial alumina are lower than the synthesized alumina. The different ability in removal of diuron may cause not only by dispersion force of diuron molecules to alumina surface but also by surface charge. The results from Figure 4.11 show that the adsorptions at pH 3 and 11 of the synthesized alumina are not significantly different. According to the surface morphology of alumina shown in Figure 4.2, the synthesized alumina has more complex structure than commercial alumina. The synthesized alumina has more complex porosity and surface, so the charge site might be in their complex structure.

4.3.3 Effect of pH for the adsolubilization of diuron

One of the most important factors affecting the adsolubilizaion of diuron is pH of the solution. In this work, pH was adjusted by using either HCl or NaOH to the value that covered the point of zero charge (PZC) of alumina (c.a. 8.5-9.1). Figure 4.12 shows the effectiveness of diuron removal via adsolubilization at pH 3 and 11. The synthesized alumina powders were modified with SDS in the concentration corresponding to its CMC. It should be noted that the modification of alumina surface by SDS was done at pH 3. However, the capacity was found to depend upon the pH of diuron solution, which suggests different adsolubilization mechanism. The charge of diuron would be changed with respect to pH of the solution and interacts with the surface of alumina differently. Further study is needed to verify details of adsolubilization mechanism. Figure 4.12 reveals that the diuron uptake is different at different pH. For all surfactant-modified alumina, the amount of diuron removal at pH 3 is higher than pH 11 regardless of SDS content. The maximum capacity of diuron removal is achieved from adsolubilization by using surfactant-modified alumina with 1%CMC of SDS concentration. The highest removal for diuron is 55%

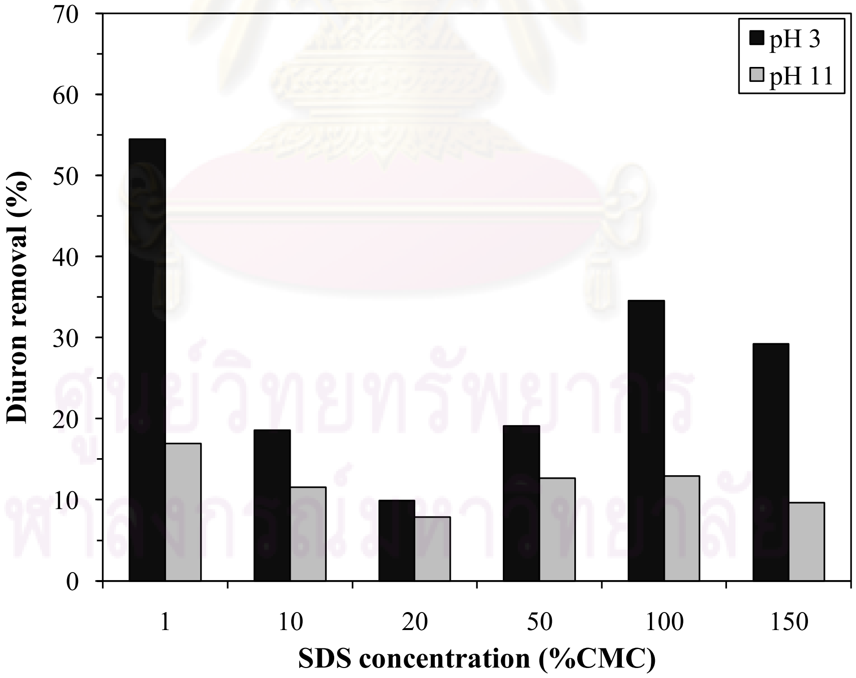


Figure 4.12 Effect of pH on diuron removal at different SDS concentrations.

For further study, commercial alumina and the synthesized alumina were modified by surfactant at SDS concentration of 1% CMC at pH 3 and 11. Then the obtained SMA was used in adsolubilization of diuron from water at pH 3 and 11. Figure 4.13 shows the similar phenomena of the adsolubilization by using different types of alumina with different conditions in preparation. For all conditions, SMA shows rapid action toward the removal of diuron and reaches its adsolubilization capacity within 20 min. The efficiency of diuron removal by using SMA from commercial alumina is the lowest. It was confirmed by Figure 4.14 that the SDS contents on alumina surface of the commercial alumina is greater than synthesized alumina. This result indicates that the large amount of SDS on commercial alumina surface dose not have a great ability toward diuron removal. It might be resulted from the bilayer structure of SDS formed on commercial alumina surface that causes the obstacle to diuron molecule to get into the hydrophobic part of SDS. In adsolubilization process by using SMA from synthesized alumina, the amount of diuron uptake from water at pH 3 is greater than at pH 11, regardless of the pH for the preparation of SMA.

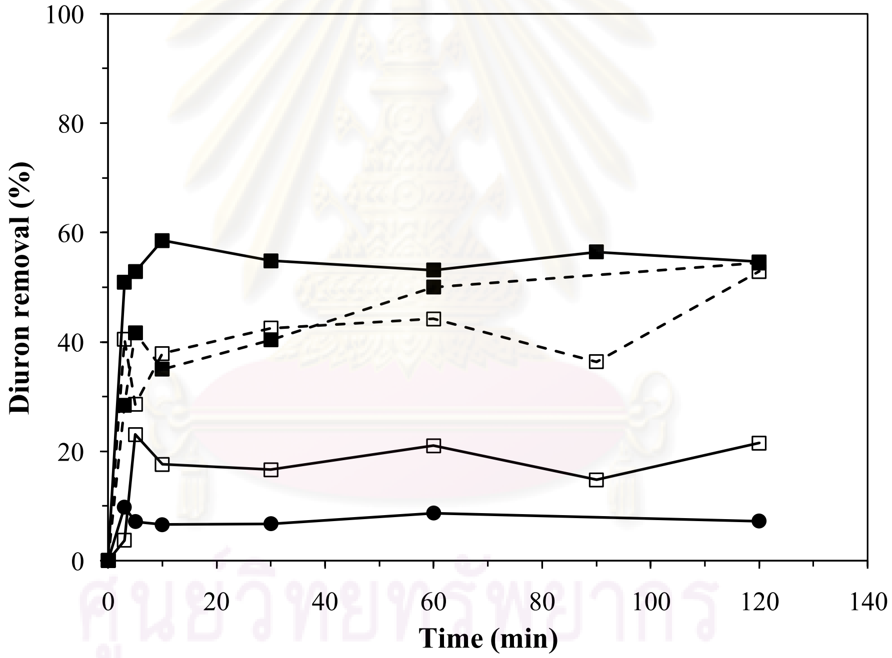


Figure 4.13 Adsolubilization of diuron by using SMA with SDS concentration 1% CMC at different pH: synthesized alumina (■) and commercial alumina (●); the adsorption of SDS at pH 3 (—) and 11 (---); the adsolubilization at pH 3 (■) and pH 11 (□).

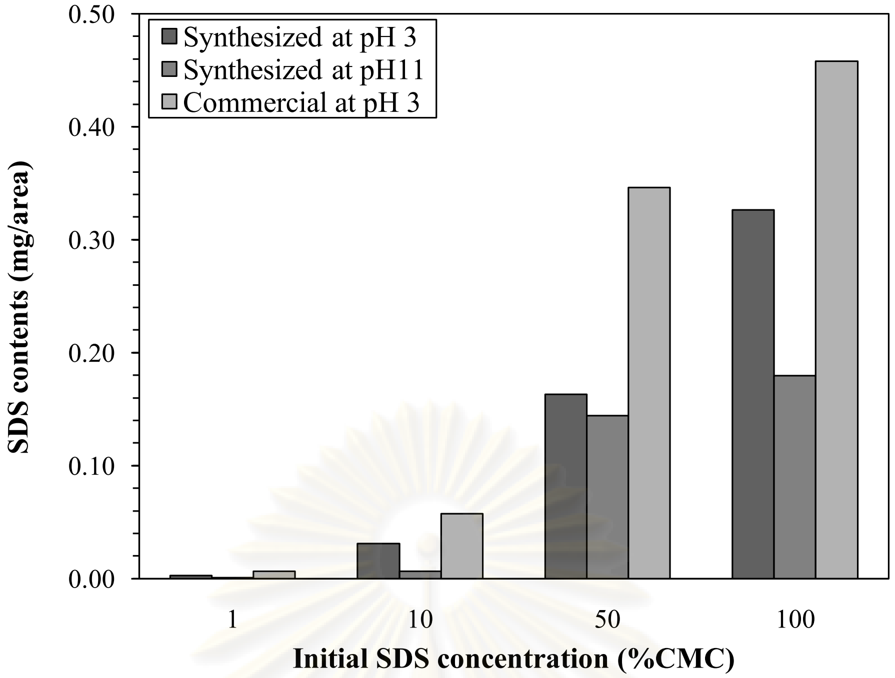


Figure 4.14 SDS contents on synthesized alumina and commercial alumina at pH 3 and 11.

As discussed earlier, the SMA prepared at pH 3 has higher SDS content adsorbed on the surface of alumina than the one prepared at pH 11. Therefore, when this SMA is used in adsolubilization, the capacity of diuron removal is much higher. At pH 11, the charge of alumina surface becomes negative, so SDS on the surface desorbs and brings diuron out from the alumina particle. Moreover, the electrostatic force repels the anions in the solution, so the molecules of diuron and SDS can not adsorb. Figure 4.15 also confirms that SDS is found in the diuron solution after the adsolubilization at pH 11. The SDS contents from the solution of adsolubilization by using SMA at pH 3-11 are higher than at pH 11-11 because the adsorbed SDS at pH 3-11 are more than pH 11-11. Nevertheless, SDS can adsorb onto alumina surface in small amount at pH 11. So diuron removal by the SMA prepared at pH 11 is not significantly different even though the pH of diuron solution is changed. The amount of SDS in the solution at pH 3 is so small in amount that it can be neglected.

Figure 4.14 shows the SDS content on alumina surface. It can be found that commercial alumina contains higher SDS content than the synthesized alumina. However, the synthesized alumina can more remove diuron than commercial alumina in adsolubilization. It is suggested that SDS was adsorbed onto alumina surface in different form. The high SDS amount on the surface of commercial alumina may be in admicelles form. In lower SDS content, SDS on the synthesized alumina surface can form hemimicelles structure. Diuron molecules can be solubilized into hydrophobic tail of SDS on the monolayer SDS of synthesized alumina easier than bilayer structure on the commercial alumina. In other words, the high SDS contents on alumina surface results in difficult access of diuron molecules into tail of SDS.

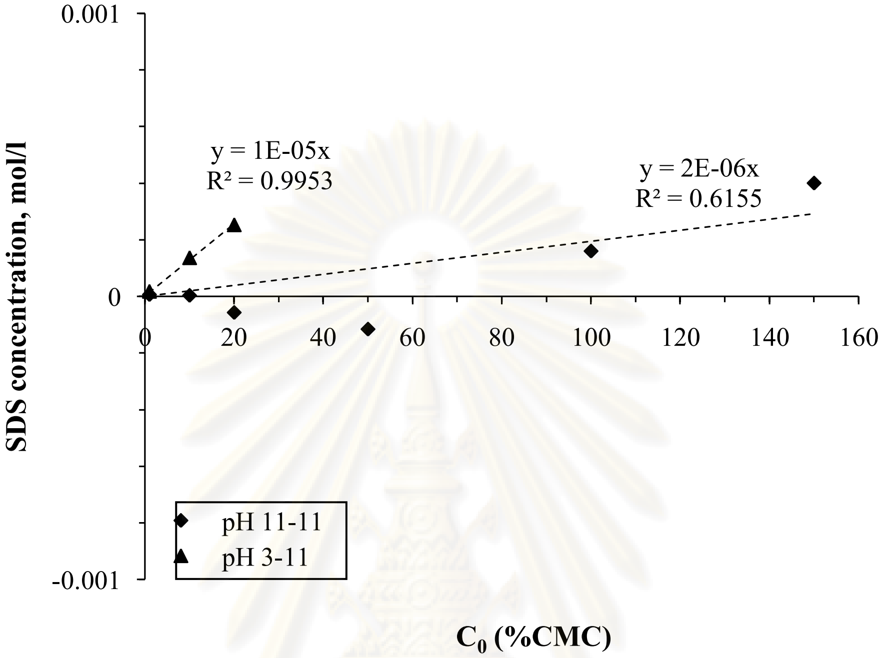


Figure 4.15 SDS content in solution after adsolubilization: pH A-B; ―A" is pH value of SDS adsorption and ―B" is pH value of adsolubilization.

The pH of an aqueous medium is an important factor that may influence the uptake of the adsorbate. The chemical characteristics of both adsorbate and adsorbent vary with pH. Studies were carried out to see the effect of pH in the range of 3–11. The pH of the solutions was maintained by adding HCl or NaOH. However, because the synthesized alumina used in the part of pH study has different physical properties from the previous synthesized alumina, it results in the decrease in diuron removal efficiency ng5from 55% to 20%.

Figure 4.16 shows that the removal of diuron decreases with the increase in pH. At pH below PZC (i.e. 10.0), the positive charge on alumina surface cause the surfactant adsorbed onto the surface. It has been reported that in case of adsorption of SDS on alumina surface, aqueous concentration at which hemimicelles are formed decreases as the pH decreases from higher to lower range. It has also been reported that at lower pH amount of SDS adsorbed concentration is much greater than at very high pH as shown in Figure 4.8. This may lead to considerable amount of solubilization of diuron in SDS aggregates formed at solid/liquid interface at lower pH value. Adsorption of diuron is mainly due to surfactant adsorption because a positively charged oxide surface with an adsorbed anionic surfactant layer on its surface, act as an adsorbent for organic compounds. At pH higher than pH value of 10, SDS molecules are desorbed from the alumina surface and cause reduction in the removal of diuron. As the pH increases, gradual decrease in adsorption occurs with respect to change in pH. Therefore, the extent of diuron solubilized in surfactant aggregates at solid/liquid interface decreases and corresponding decrease in adsorption at higher pH value is observed.

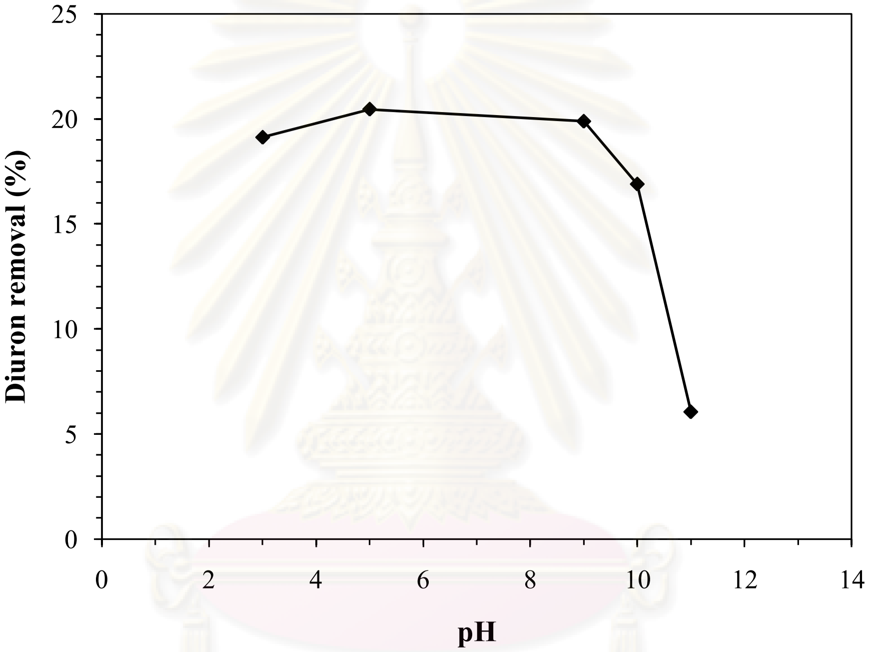


Figure 4.16 Effect of pH on diuron removal by SMA.

4.3.4 Effect of surfactant content on alumina surface

After the modification of alumina by SDS, the obtained powder (i.e., SMA) was used for the adsolubilization of diuron in water. In this section, experiments were conducted to see the effect of surfactant coverage on alumina on the removal of diuron. The concentration of diuron was fixed at 10 ppm, while the amount of SMA used was 50 mg/ 10 ml of diuron solution.

In order to investigate the mechanism of diuron adsolubilization onto the adsorbent, the amount of SDS adsorbed on alumina was varied. In this section, SMA was prepared from SDS solution with different concentration, in the range of 8.1×10^{-5} to 1.22×10^{-2} mol/l (i.e., 1% to 150% of its CMC), using the same procedure previously described. The results are shown in Figure 4.17 - 4.22. It could be seen that the removal of diuron via adsolubilization takes place rapidly. Majority of the prepared SMAs reach their adsolubilization capacity within less than 10 min, which is much faster than the results from other degradation technologies. Nevertheless, the fraction of diuron removed from the solution is limited by small content of SMA employed. The maximum diuron removal is obtained when the alumina powder modified with SDS in the amount corresponding to its CMC is employed.

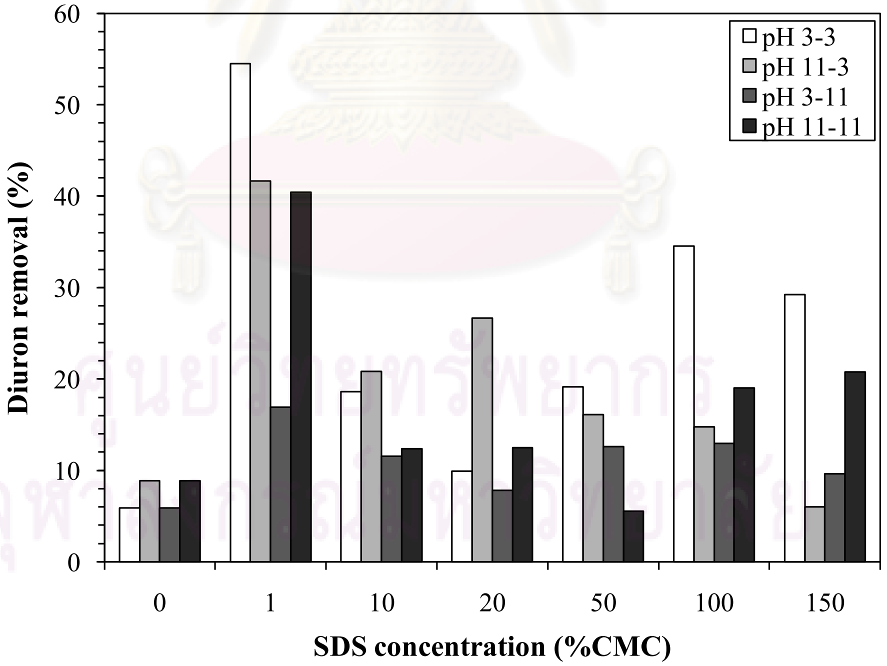


Figure 4.17 Diuron removal efficiency of alumina modified with SDS in various contents: pH A-B; –A” is pH value of SDS adsorption and –B” is pH value of adsolubilization.

Figure 4.17 shows the diuron removal at different concentration of SDS. The maximum diuron removal was obtained from SMA prepared with 1% CMC of SDS concentration. It can be confirmed by the adsorption isotherm in Figure 4.6 that at 1% CMC of SDS concentration, the structure of SDS on alumina surface is in mixed-micelle structure (consists of hemimicelles and admicellles). Since the SDS concentration at 1% CMC has a small number of the admicellle structure on the surface of alumina, majority of alumina surface becomes hydrophobic. Diuron is also hydrophobic with benzene ring in molecular structure, so it can be dissolved into the long chain of SDS on alumina surface. At higher SDS concentration, more admicelle structure aggregates on alumina surface, the head group of SDS are extruded into the solution, so the alumina surface becomes more hydrophilic. This phenomenon results in decreasing the amounts of dissolved diuron. Moreover, the negatively charged might block diuron molecules into the long chain of SDS, so the diuron removal decreases.

Figure 4.18 to 4.22 show the nature of adsolubilization on SDS-modified alumina at pH 3 and 11. It can be seen that the efficiency of diuron removal by the adsolubilization at pH 3 with different SDS concentrations differ significantly, while those in pH 11 do not.

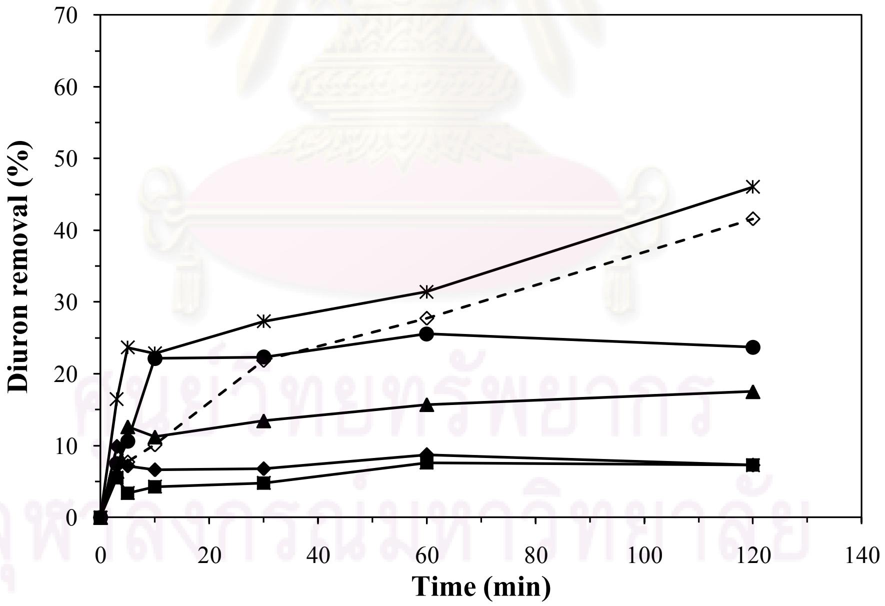


Figure 4.18 Adsolubilization of diuron at pH 3 by using SMA from commercial alumina at pH 3 with different SDS concentrations: bare commercial alumina (---), modified commercial alumina (—); SDS concentration 1% CMC (◆), 10% CMC (■), 50% CMC (▲), 100% CMC (∗) and 150% CMC (●).

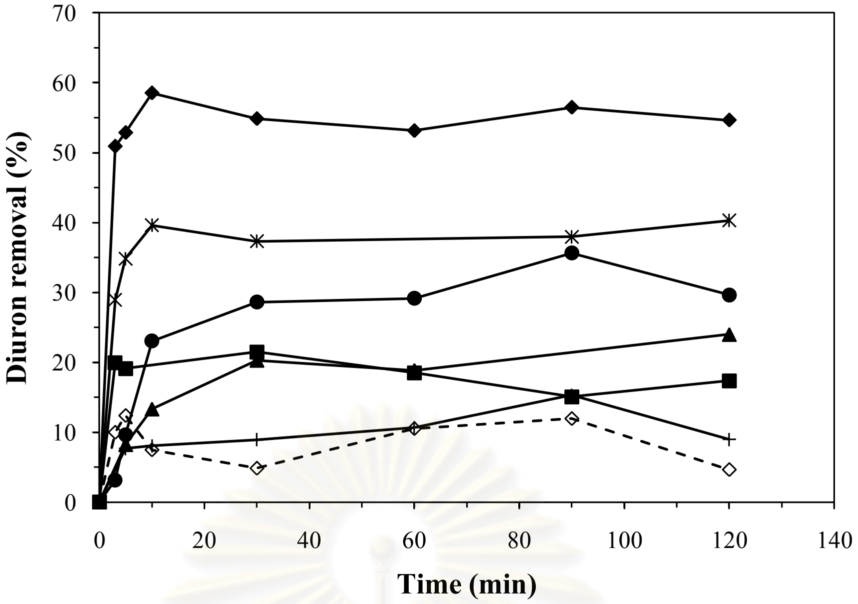


Figure 4.19 Adsolubilization of diuron at pH 3 by using SMA from synthesized alumina at pH 3 with different SDS concentrations: bare synthesized alumina (---), modified synthesized alumina (—); SDS concentration 1% CMC (◆), 10% CMC (■), 20% CMC (+), 50% CMC (▲), 100% CMC (∗) and 150% CMC (●).

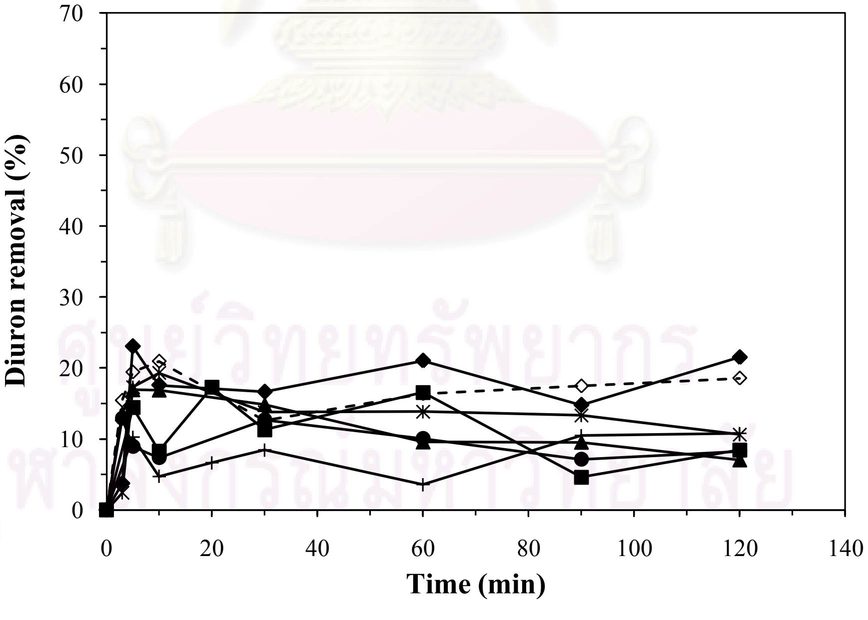


Figure 4.20 Adsolubilization of diuron at pH 11 by using SMA from synthesized alumina at pH 3 with different SDS concentrations: bare synthesized alumina (---), modified synthesized alumina (—); SDS concentration 1% CMC (◆), 10% CMC (■), 20% CMC (+), 50% CMC (▲), 100% CMC (∗) and 150% CMC (●).

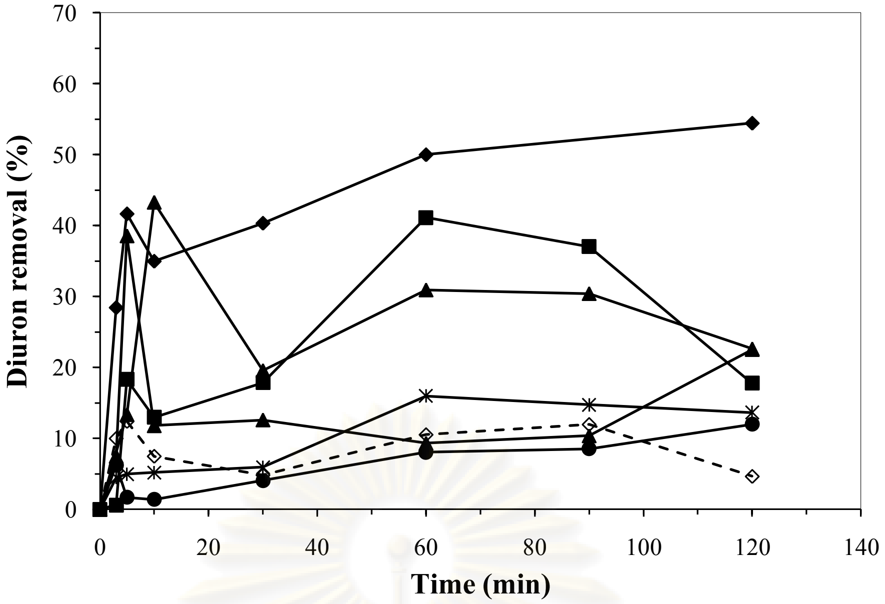


Figure 4.21 Adsolubilization of diuron at pH 3 by using SMA from synthesized alumina at pH 11 with different SDS concentrations: bare synthesized alumina (---), modified synthesized alumina (—); SDS concentration 1% CMC (◆), 10% CMC (■), 20% CMC (+), 50% CMC (▲), 100% CMC (∗) and 150% CMC (●).

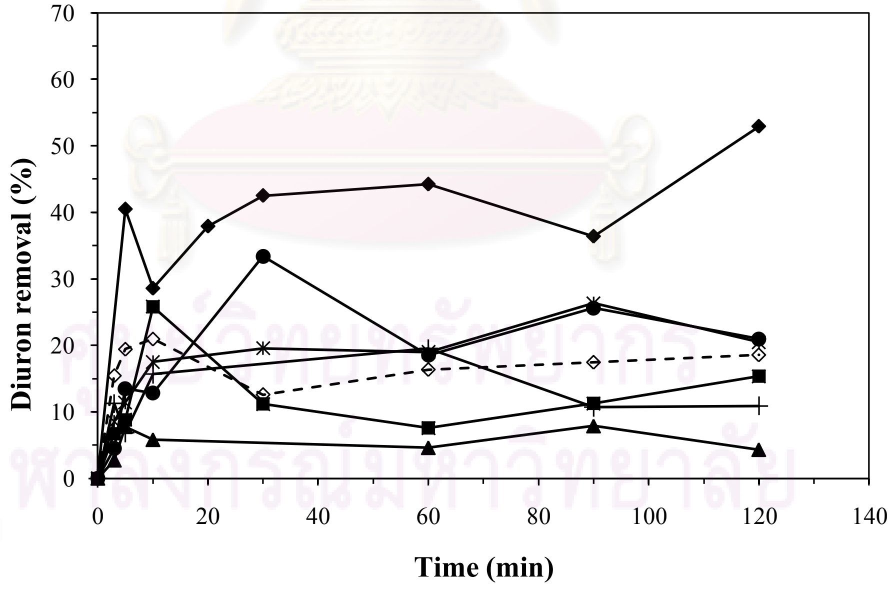


Figure 4.22 Adsolubilization of diuron at pH 11 by using SMA from synthesized alumina at pH 11 with different SDS concentrations: bare synthesized alumina (---), modified synthesized alumina (—); SDS concentration 1% CMC (◆), 10% CMC (■), 20% CMC (+), 50% CMC (▲), 100% CMC (∗) and 150% CMC (●).

4.3.5 Effect of initial diuron concentration

To investigate the effect of initial diuron concentration, adsolubilization was study at initial diuron concentration at 1, 5, 10, 15, 20 and 30 ppm. The adsorption of diuron on SDS coated alumina was fitted to Freundlich Isotherm equation as given by Eq. (2.2) as follows;

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \qquad (2.2)$$

Where C_e = equilibrium concentration, q_e = amount adsorbent at equilibrium, k_f = Freundlich constant related to adsorption capacity and $\frac{1}{n}$ = adsorption intensity.

Figure 4.23 shows that the Freundlich isotherm fits the adsorption of diuron onto SDS modified alumina with 1%CMC of SDS concentration at pH 3. It is suggested that the adsorbed diuron on the adsorbent increases when the diuron concentration in solution increased. The values of K_f can be used as alternative measure of adsorption capacity, while $\frac{1}{n}$ determines the adsorption intensity. From Figure 4.23, it was found that K_f , $\frac{1}{n}$ and R^2 are 2.289, 1.1387 and 0.9355, respectively. The value of the Freundlich constant K_f for adsorption of diuron by SMA reveals that the behavior of diuron in alumina-water system with micelle forming surfactant mainly depends on the degree of hydrophobicity of diuron [53].

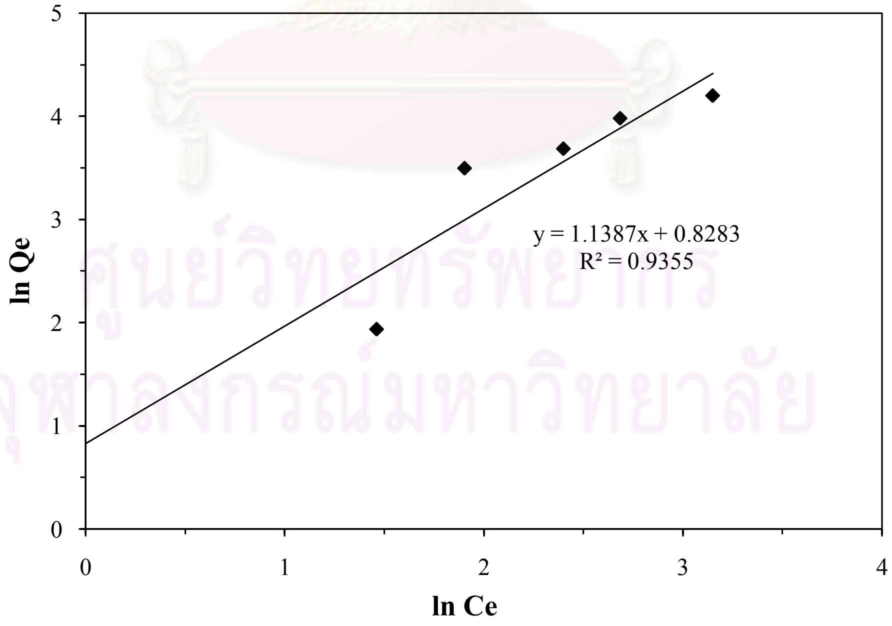


Figure 4.23 Freundlich isotherms for the adsorption of diuron onto SDS modified alumina with 1%CMC of SDS concentration at pH 3.

4.3.6 Effect of Amount of Adsorbent on Adsolubilization

Since the adsorbent dose has significant effect on the diuron removal, the effect of this parameter was studied by changing the mass of adsorbent from 10 to 50 mg/ 10 ml of diuron solution. The pH of solution was adjusted to pH 3 by adding HCl and the results are shown in Figure 4.24. From this study, it can be observed that amount of diuron removed increases when mass of the adsorbent is increased. A large amount of adsorbent increases the sites of adsolubilization. So, more diuron molecules can access into the surfactant structure.

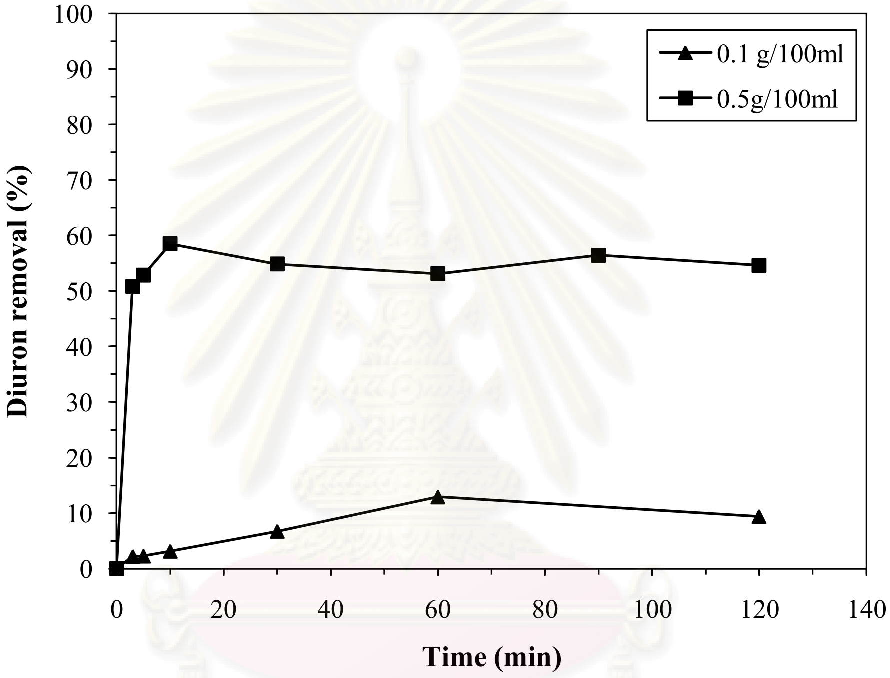


Figure 4.24 Removed diuron by using different adsorbent dose.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The conclusions of the present research are following:

1. Mesoporous porous alumina powders can be prepared via sol-gel method assisted by resorcinol/formaldehyde gel technique. Specific surface area of obtained alumina powders is 194.2 m^2 g^{-1}, average pore size diameter is 2.1 nm and average pore volume is 0.5526 cm^3 g^{-1}.

2. Surfactants can be successfully adsorbed onto the surface of alumina, whereas the adsorption is controlled by pH and initial concentration of the surfactant. From the SDS adsorption study, the maximum adsorption capacity is found to be 186.2 mg/g at the initial SDS concentration of 11,664 mg/l (500 % CMC).

3. The adsolubilization of diuron via surfactant-modified alumina enhance the efficiency of diuron removal. Adsolubilization of diuron is controlled by pH of solution, mass of absorbance and initial concentration of diuron.

4. The synthesized alumina modified with SDS has greater efficiency in diuron removal than commercial alumina. The greatest efficiency in diuron removal via adsolubilization was found to be 55% by using SMA with 1% CMC of SDS.

5.2 Recommendations for the Future Studies

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

1. Effect of other types of herbicide in adsolubilization ability should be investigated.
2. Effect of other types of surfactant in adsorption on the alumina surface should be investigated and should be tested for diuron adsolubilization capability.
3. Other methods of alumina synthesis should be investigated for adsorbent.
4. The other applications for surfactant-modified alumina should be also investigated.
5. The regeneration techniques for the used alumina should be investigated.

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APPENDICES

APPENDIX A

CALIBRATION CURVE OF SDS

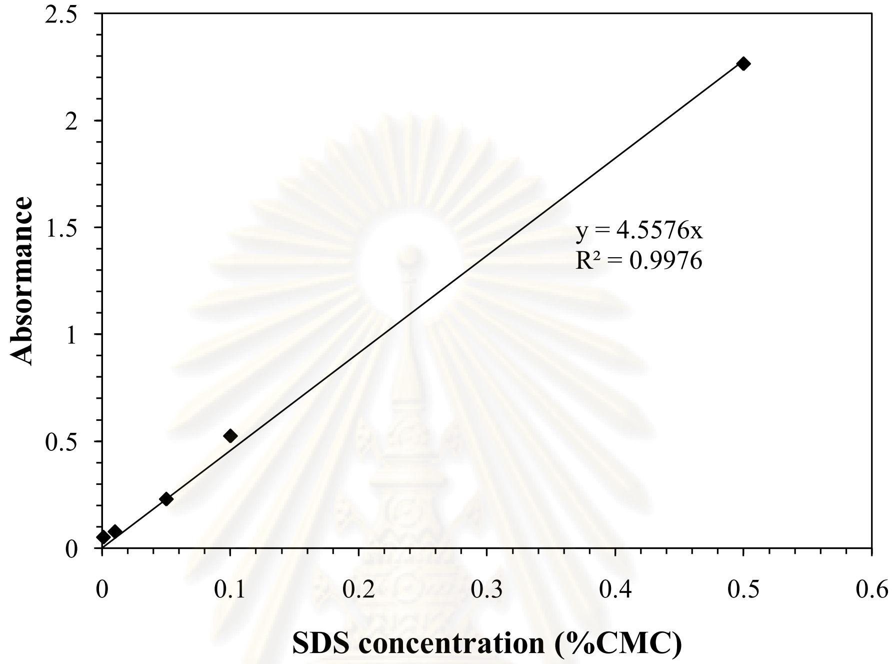


Figure A.1 The calibration curve of SDS at concentration from 0.001 to 0.5%CMC.

APPENDIX B

CALIBRATION CURVE OF DIURON

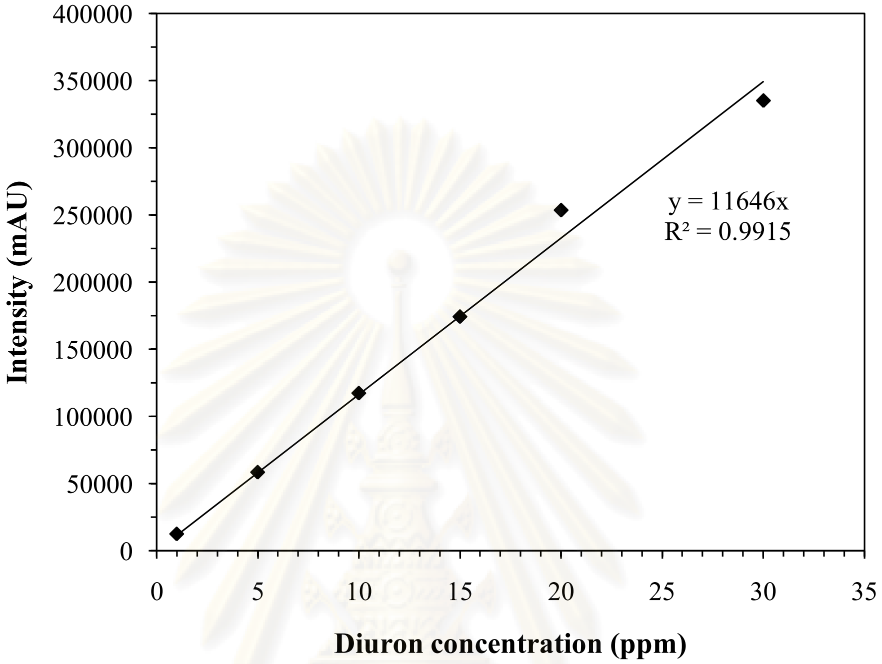


Figure B.1 The calibration curve of diuron.

APPENDIX C

ADSORPTION OF FILTER TEST

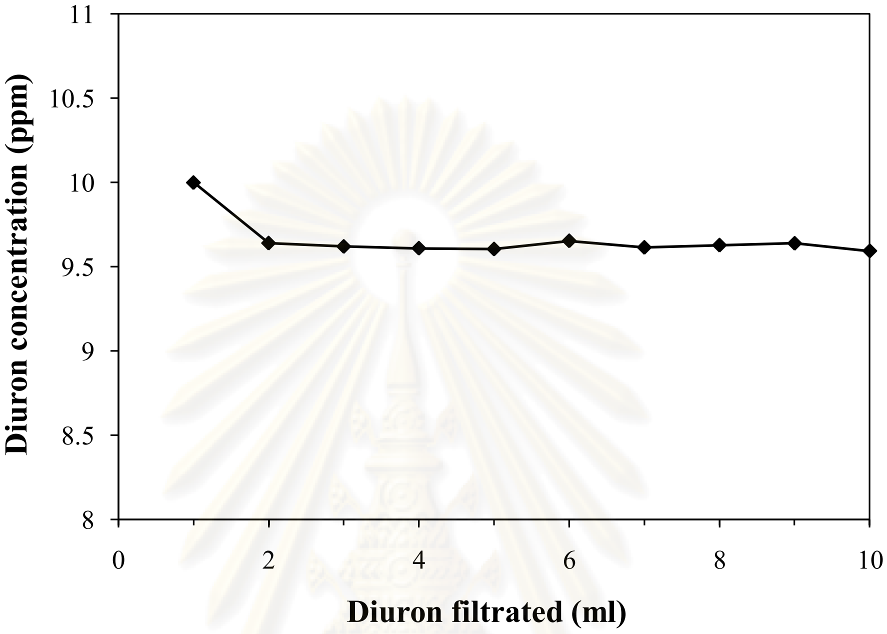
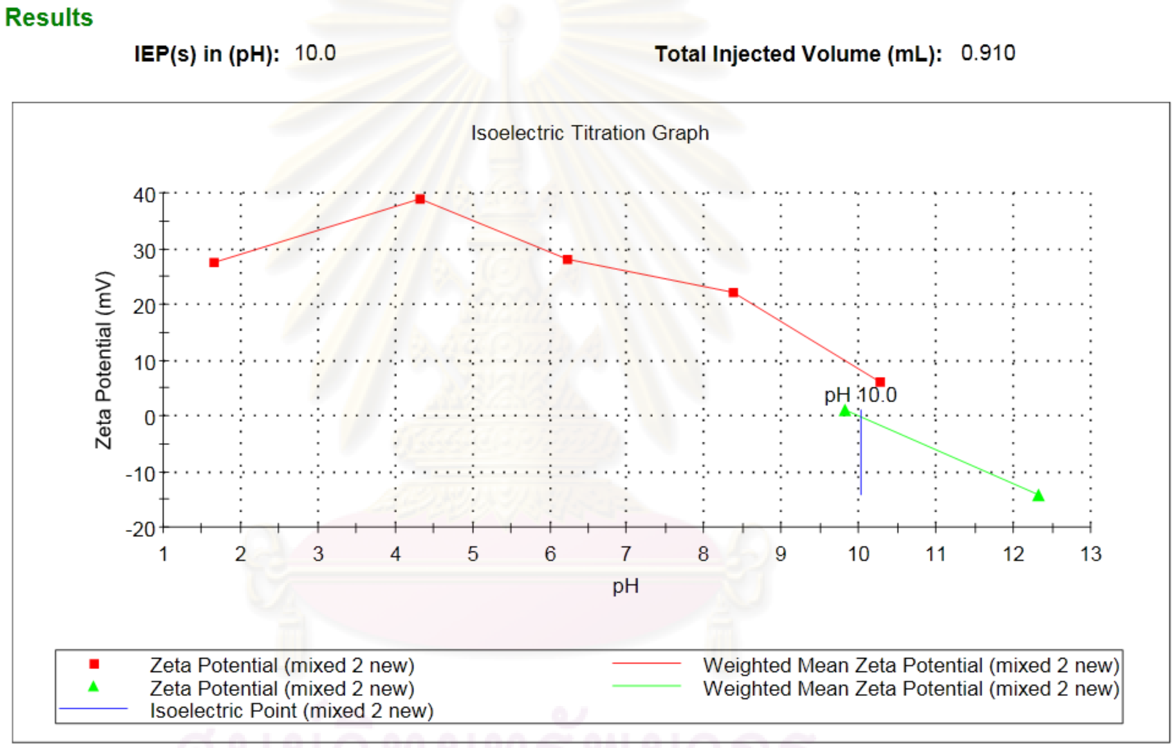


Figure C.1 Adsorption of diuron on filter.

APPENDIX D

ISOELECTRIC POINT OF SYNTHESIZED ALUMINA POWDER

To determine the isoelectric point of synthesized alumina, the powder was analyzed by using Zetasizer (Malvern Instruments Ltd.). The result shows that the isoelectric point of synthesized alumina is about pH value of 10 as shown in Figure D.1.



Results

IEP(s) in (pH): 10.0

Total Injected Volume (mL): 0.910

Figure D.1 Isoelectric point of synthesized alumina powder.

APPENDIX E

EFFECT OF AMOUNT OF ADSORBENT

Figure E.1 shows the effect of adsorbent dose to removed diuron content. Diuron concentration in the solution was controlled to 10 ppm at pH 3. SMA was varied from 0.1 to 2.0 g/ 100 ml of diuron solution. The result shows that the removed diuron increase when adsorbent amount increase.

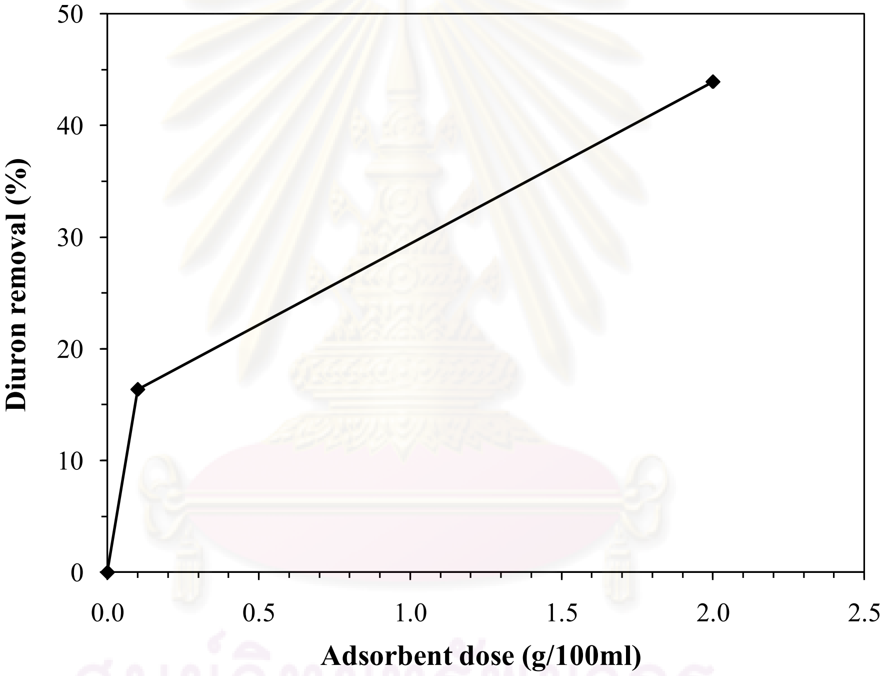


Figure E.1 Effect of adsorbent dose to diuron removal.

APPENDIX F

LIST OF PUBLICATION

1. Sawitta Trimit, Pamornrat Chantam, Alisa S. Vangnai and Varong Pavarajarn. —Formation of Mesoporous Alumina Assisted by Resorcinol/Formaldehyde Gel for Applicationin Diuron Removal via Adsolubilization”. The 17th Regional Symposium on Chemical Engineering, Bangkok, Thailand, November 22-23, 2010.

VITA

Miss. Sawitta Trimit was born on 11th March, 1986, in Nakornpathom Province, Thailand. She received the Bachelor's Degree of Engineering with a major in Chemical Engineering from Chulalongkorn University, Bangkok, Thailand in March 2009. She entered the Master of Engineering in Chemical Engineering at Chulalongkorn University, Bangkok, Thailand in May 2009.