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จุฬาลงกรณ์มหาวิทยาลัย

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ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

PREPARATION OF SILICA ADSORBENT
FROM RICE HUSK ASH

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สถาบันวิทยบริการ
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งานวิจัยนี้เป็นการพัฒนาวิธีการเตรียมตัวดูดซับซิลิกาคุณภาพสูงจากเถ้าแกลบ โดยวิธีการสกัดด้วยโซเดียมไฮดรอกไซด์และทำให้เกิดเจลโดยการปรับค่าความเป็นกรด-เบส (pH) ด้วยกรดซัลฟูริก ศึกษาผลของการแช่เจลที่ค่าความเป็นกรด-เบส 1, 3, 7, 9 และทำการพิสูจน์เอกลักษณ์ พบว่าการแช่เจลที่ค่าความเป็นกรด-เบสเท่ากับ 3 ให้ปริมาณผลิตภัณฑ์สูงที่สุดถึงร้อยละ 85.19 ผลจากไนโตรเจนแอมมोनียม พบว่าตัวดูดซับทั้งหมดที่เตรียมได้มีลักษณะเป็นมีโซพอร์ส โดยที่ซิลิกาเจลที่ถูกแช่ที่ค่าความเป็นกรด-เบสเท่ากับ 1 ให้ค่าพื้นที่ผิวมากที่สุดถึง 662.68 ตารางเมตร/กรัม และให้ความบริสุทธิ์ของซิลิกาสูงที่สุดถึงร้อยละ 99.96 เมื่อตรวจสอบด้วยเทคนิคเอ็กซ์เรย์ฟลูออเรสเซนซ์ และพบว่าซิลิกาเจลที่เตรียมขึ้นทั้งหมดอยู่ในรูปอสัญฐาน จากเทคนิคอินฟราเรดสเปกโทรสโคปีพบความแตกต่างเล็กน้อยที่เลขคลื่น 951 (เซนติเมตร)⁻¹ จากนั้นนำซิลิกาเจลที่เตรียมขึ้นไปศึกษาขนาดอนุภาคและทดสอบประสิทธิภาพการแยกสารทางโครมาโทกราฟี 2 เทคนิค คือคอลัมน์โครมาโทกราฟีและซินเลเซอร์โครมาโทกราฟี พบว่าซิลิกาเจลที่แช่ที่ค่าความเป็นกรด-เบสเท่ากับ 1 ให้ประสิทธิภาพการแยกได้ดีที่สุดทั้งสองเทคนิค และมีค่าเรตโซลูชันสูงที่สุดถึง 1.69 เมื่อทดสอบด้วยเทคนิคคอลัมน์โครมาโทกราฟี เมื่อเปรียบเทียบกับตัวดูดซับ 2 ชนิดทางการค้าพบว่ามีประสิทธิภาพในการแยกสารใกล้เคียงกัน

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์

ลายมือชื่อนิสิต.....

วชิราภรณ์ กนกสิทธิ์

ปีการศึกษา

2551.....

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PRACHYA WATASIT: PREPARATION OF SILICA GEL ADSORBENT FROM RICE HUSK ASH. ADVISOR: PROF. SOPHON ROENGSUMRAN, Ph.D., 117 pp.

This research developed a high grade silica adsorbent from rice husk ash. It was extracted by sodium hydroxide solution and formed gel by adjustment pH with sulfuric acid. Effect of aging silica gel at pH 1, 3, 7 and 9 were investigated and characterized. Aging silica gel at pH 3 gave the highest yield, 85.19% of product. Results from nitrogen adsorption indicated that all synthesized adsorbents were mesoporous. Synthesized silica at aging pH 1 presented the highest specific surface area of 662.68 m²/g. Data from X-ray fluorescent showed that synthesized silica at aging pH 1 gave the highest purity of silica of 99.96%. X-ray diffraction technique confirmed that all synthesized silica gel were amorphous form. Results from infrared spectroscopy showed a little different at wavelength 951 cm⁻¹. Then silica products were controlled particle size and tested efficiency of separation of compounds using 2 techniques of chromatography namely column chromatography and thin-layer chromatography. Synthesized silica at aging pH 1 showed the best results for efficiency of separation and gave the highest resolution of 1.69 when tested with column technique. When compared with commercial adsorbents, it was found that silica product had efficiency of separation close to commercial adsorbents.

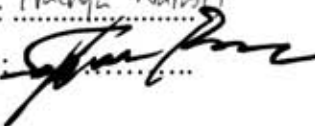
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จุฬาลงกรณ์มหาวิทยาลัย

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LIST OF ABBREVIATIONS

RHA	rice husk ash
°C	degree celsius
SEM	scanning electron microscope
AES	atomic emission spectroscopy
ρ	density
ppm	parts per million
PZC	point of zero charge
IEP	isoelectric point
nm	nanometer
GLC	gas-liquid chromatography
GSC	gas-solid chromatography
LLC	liquid-liquid chromatography
LSC	liquid-solid chromatography
K	equilibrium constant
t_R	retention time
R	resolution
min	minute
g	gram
μm	micrometer
TEOS	tetraethoxysilane
TEM	transmission electron microscopy
Å	angstrom
XRF	x-ray fluorescence
XRD	x-ray diffraction
FT-IR	fourier transform infrared spectroscopy
ASTM	american standard test method
N	normality
ml	milliter
h	hour
TLC	thin-layer chromatography
LC	liquid chromatography

cm	centimeter
R _f	retention factor
IUPAC	international union of pure and applied chemistry
cm ⁻¹	wavenumber



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CHAPTER I

INTRODUCTION

1.1 Introduction

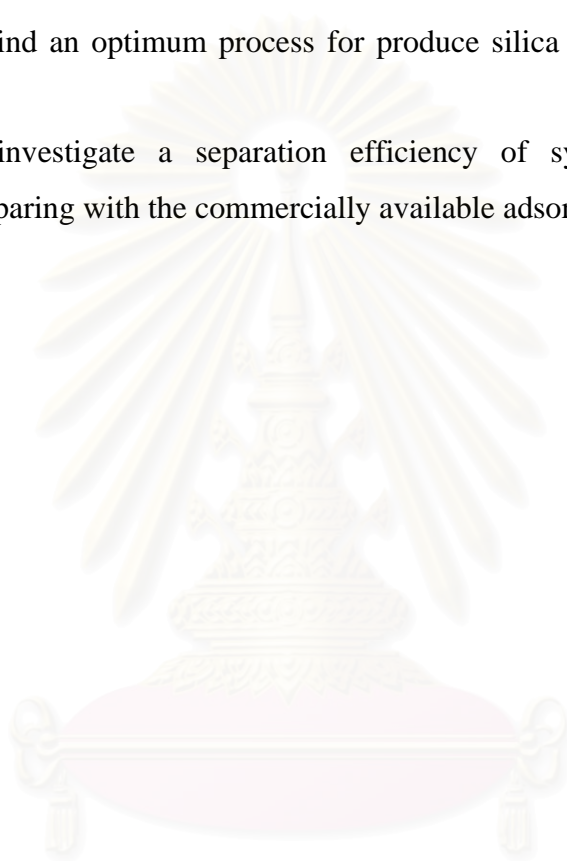
Rice husk ash (RHA) is a by-product waste from rice mill. It is generated together with electric energy when rice husk is burned. In each year several million tons of RHA is produced especially in agricultural countries such as Thailand [1]. Some ash is generally used as fertilizer or filler in concrete which the remainder is exported in the form of low-grade black husk ash [2]. Until now it has not been applied in special utilization in the country. But it is well known that RHA contain a lot of silica (silicon dioxide), more than 90% [3]. The easy method to produce silica from RHA is alkaline extraction following gelation with acid. Then many authors have concluded that rice husk ash is an excellent source of high-grade amorphous silica [4]

Silica gel is the one form of amorphous silica. It has wide applications in industrial and agricultural fields. Depending on the textural properties of silica gel, its applications include as a desiccant, a molecular sieve, a catalyst support, an abrasive, an additive, an adsorbent, etc. [5]. Silica adsorbent is one of products that important for many industries. It is a porous material and with a high surface area that can adsorb substances onto its surface. From this reason, it is used in drying and purification of natural gas and petrochemical. In field of packaging, it is used to adsorb moisture in various products such as pharmaceuticals, nutraceutical, diagnostic, optical and electronic devices. Then high grade of silica adsorbent is applied in separation and purification in chromatography fields. Thailand has to import the adsorbent (in form silicon dioxide) from abroad to support demand in the country which is increased year after year [6]. Furthermore, conventional methods for preparation of silica adsorbent requires the use of high temperature (in excess of 1500°C) and pressure for extracting silicon in pure form from natural deposits of quartzite rock or quartz sand [7]. This process consumes high energy therefore it makes high production cost.

In order to demanding of imported silica adsorbent from abroad and to improve value of rice husk ash including reduce consumption energy of conventional method. This research related to preparation of high grade silica adsorbent from rice husk ash.

1.2 Objectives of the study

1. To find an optimum process for produce silica adsorbent from rice husk ash.
2. To investigate a separation efficiency of synthesized adsorbent by comparing with the commercially available adsorbent.



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CHAPTER II

THEORETICAL

2.1 Rice husk and rice husk ash

Rice husk is an agricultural waste material abundantly available in rice-growing countries. They are the natural sheaths that form on rice grains during their growth. Removed during the refining of rice, these husks have no commercial interest [4]. It is reported that every ton of rice produced, ~ 0.23 tons of rice husk is formed [8]. Every year the annual world rice production amounts to approximate 400 million ton therefore about 92 million ton is husk [4]. The chemical composition of rice husk is found to vary from sample to sample. The differences in the type of paddy, crop year, climatic and geographical conditions could be the reason for this variation. Gavindarao, in an extensive review has analyzed all the reported data on the chemical composition of rice husk from various counties including western world and Asia and gives an average composition on dry basis in table 2.1 [8].

Table 2.1 Chemical compositions of dry rice husk

Compositions	Contents
Ash	20 %
Lignin	22 %
Cellulose	38 %
Pentosans	18 %
Other organic	2 %

The presence of silica in rice husk has been known since 1938 [8]. In rice husk, it shows the highest amount when compare the others plant as shown in table 2.2. Then the chemical composition of rice husk ash is listed in table 2.3 because of the high silicon content in rice husk ash, the utilization of ash has been significantly widened in the past few decades. At present, rice husk ash is the raw materials for the

production of a series of silicon-based materials, including silicon carbide, silica, silicon nitride, silicon tetrachloride, pure silicon and zeolite [9].

Table 2.2 Contents of ash and silica in plants [10]

plants	fraction	Ash (%)	Silica (%)
rice husk	-	22.1	93.0
wheat	leaf	10.5	90.5
millet	leaf	12.5	88.7
straw	-	14.6	82.0
breadfruit	trunk	8.6	81.0
bagasse	-	14.7	73.0
corn	leaf	12.1	64.3
bamboo	knot	1.5	57.4
sunflower	trunk, leaf	11.5	25.3
lantana	trunk, leaf	11.2	23.3

Table 2.3 Chemical compositions of rice husk ash [9]

Component	Content (%)
SiO ₂	86.9-97.3
K ₂ O	0.58-2.5
Na ₂ O	0.0-1.75
CaO	0.2-1.5
MgO	0.12-1.96
Fe ₂ O ₃	trace-0.54
P ₂ O ₅	0.2-2.85
Cl	trace-0.42

Silicon enters the rice plant through its root in a soluble form, probably as a silicate or monosilicic acid, and then moves to the outer surface of the plant, where it becomes concentrated by evaporation and polymerization to form a cellulose silica membrane (Figure 2.1). There is quite general agreement that the silica is

predominantly in inorganic linkages, but some of the silica is also bonded covalently to the organic compound. This portion of the silica cannot be dissolved in alkali and can withstand very high temperature. Characterizations by SEM, energy-dispersive X-ray analysis, AES, etc., suggest that the silica is mainly localized in the tough interlayer (epidermis) of the rice husk and that it also fills in the spaces between the epidermal cells [9].

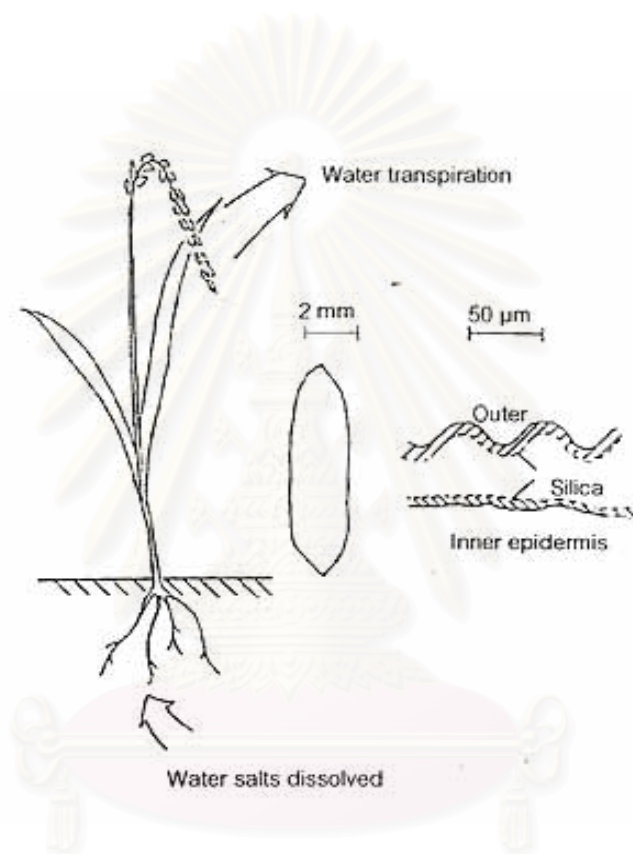


Figure 2.1 Absorption and collection of silica in rice plant [10].

2.2 Silica chemistry

The term silica denotes the compound silicon dioxide. Silicon dioxide is the most common binary compound of silicon and oxygen, the two elements of greatest terrestrial abundance. It constitutes ca. 60 wt. % of the earth's crust, occurring alone or combined with other oxides in silicates. Generally, silica can be separated in 2 types, crystalline and amorphous. Commercially, crystalline silica is the source of element silicon and is used in large quantities as a constituent of building materials. In various amorphous forms it is used as a desiccant, adsorbent, reinforcing agent, filler and catalyst component. It has numerous specialized applications such as piezoelectric crystals, vitreous-silica, optical element and glass ware. Silica is a basic material of the glass, ceramic and refractory industries and an important raw material for the production of soluble silicates, silicon and its alloys, silicon carbides, silicon-base chemicals and silicones [2].

Structure of silica is based on the silicate tetrahedron, SiO_4 (Figure 2.2). This consists of a silicon atom bound to four oxygen atoms, evenly distributed in space around the Si center, which results in a tetrahedron structure. Silicon atoms joined together with oxygen atoms by siloxane bonds (Si-O-Si). On the surface of each primary particle, uncondensed hydroxyl groups from the original polymeric silicic acid remain. These residual hydroxyl groups are weak acids therefore they are reactive for chemical reaction. Then they are classified to free silanol, geminal silanol, and vicinal silanol [11].

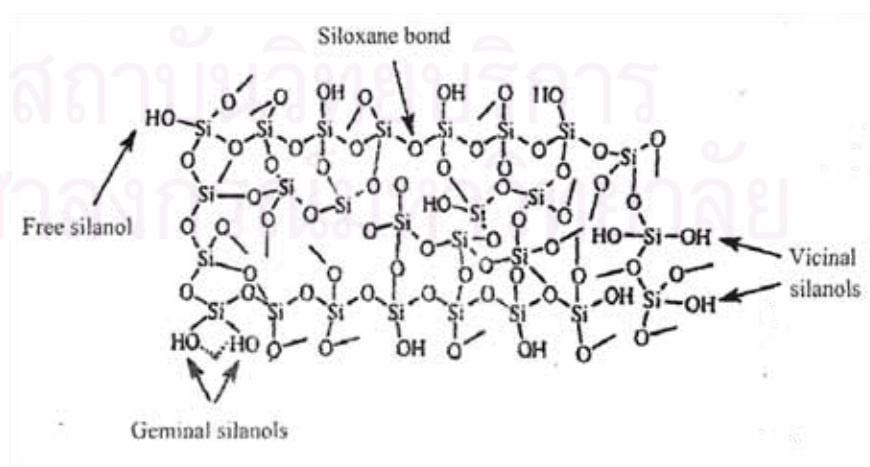
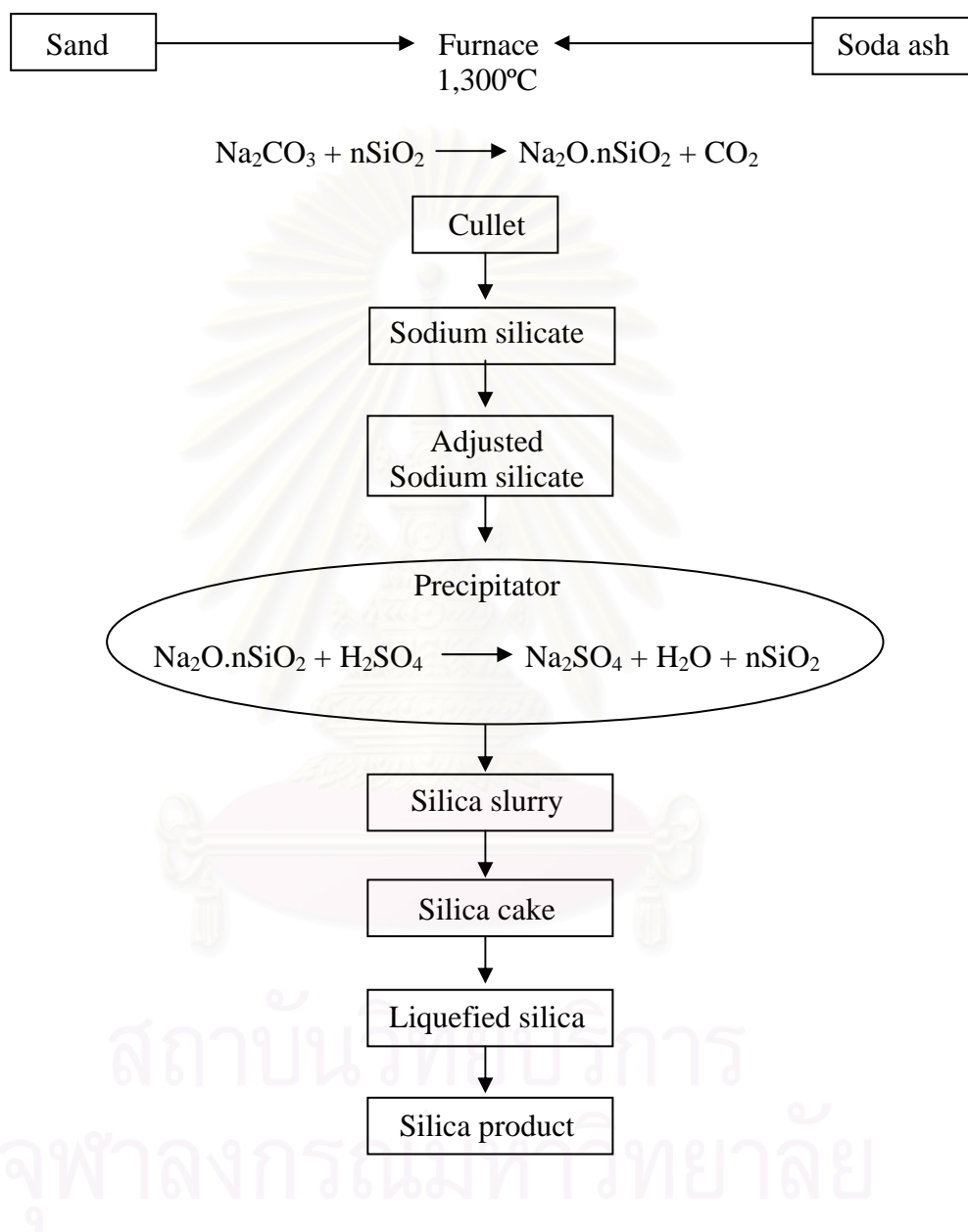


Figure 2.2 Structure of silica [12].

Generally, silica is produced from reaction between sand (silica source) and soda ash (sodium carbonate) at high temperature as shown in Scheme 2.1.



Scheme 2.1 Silica production processes [3].

At ordinary temperatures, silica is chemically resistant to many common reagents. Acids do not attack silica, except for hydrofluoric acid which forms fluorosilicate anions, *i.e.*, SiF_6^{2-} or volatile SiF_4 . The rate at which the various forms (low-T modifications) of silica are dissolved by aqueous HF decreases with increasing of density (ρ) in the sequence: vitreous silica ($\rho = 2.2 \text{ g/cm}^3$) < tridymite ($\rho = 2.22 \text{ g/cm}^3$) ~ cristobalite ($\rho = 2.33 \text{ g/cm}^3$) < quartz ($\rho = 2.65 \text{ g/cm}^3$). Coesite ($\rho = 3.01 \text{ g/cm}^3$) is practically insoluble in aqueous HF. Stishovite ($\rho = 4.35 \text{ g/cm}^3$) is even less soluble. Phosphoric acid attacks vitreous silica at elevated temperatures, forming crystalline silicophosphate. The solubility of silica is greater in dilute than concentrated aqueous phosphoric acid. Quartz and vitreous silica are affected only slightly by aqueous alkali at room temperature. The attack is fast at higher temperature. Precipitated amorphous silica is more reactive than vitreous silica, which in turn is more reactive than quartz.

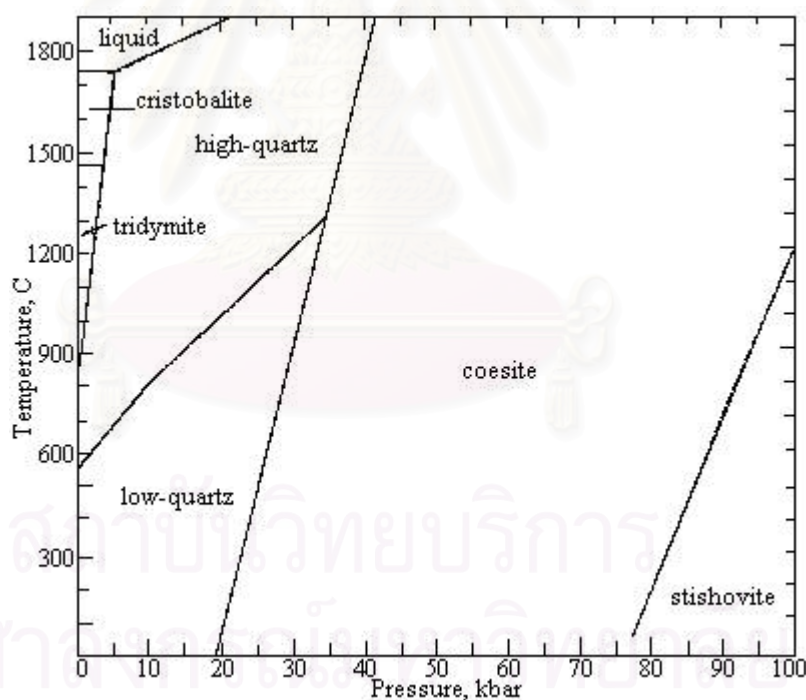
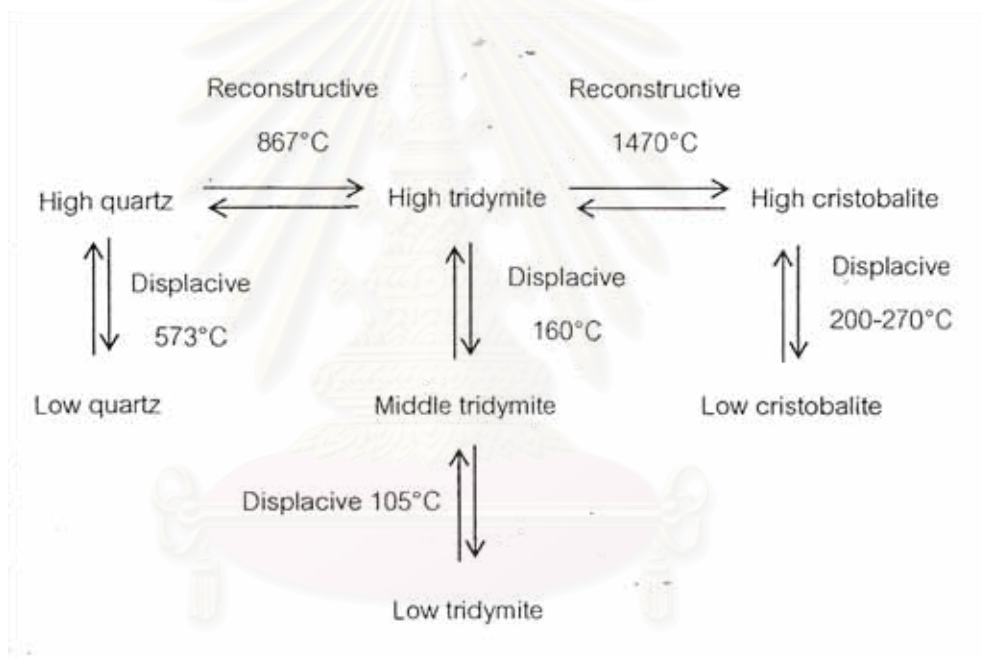


Figure 2.3 Phase diagram of silica forms.

2.3 Form of silica

2.3.1 Crystalline silica

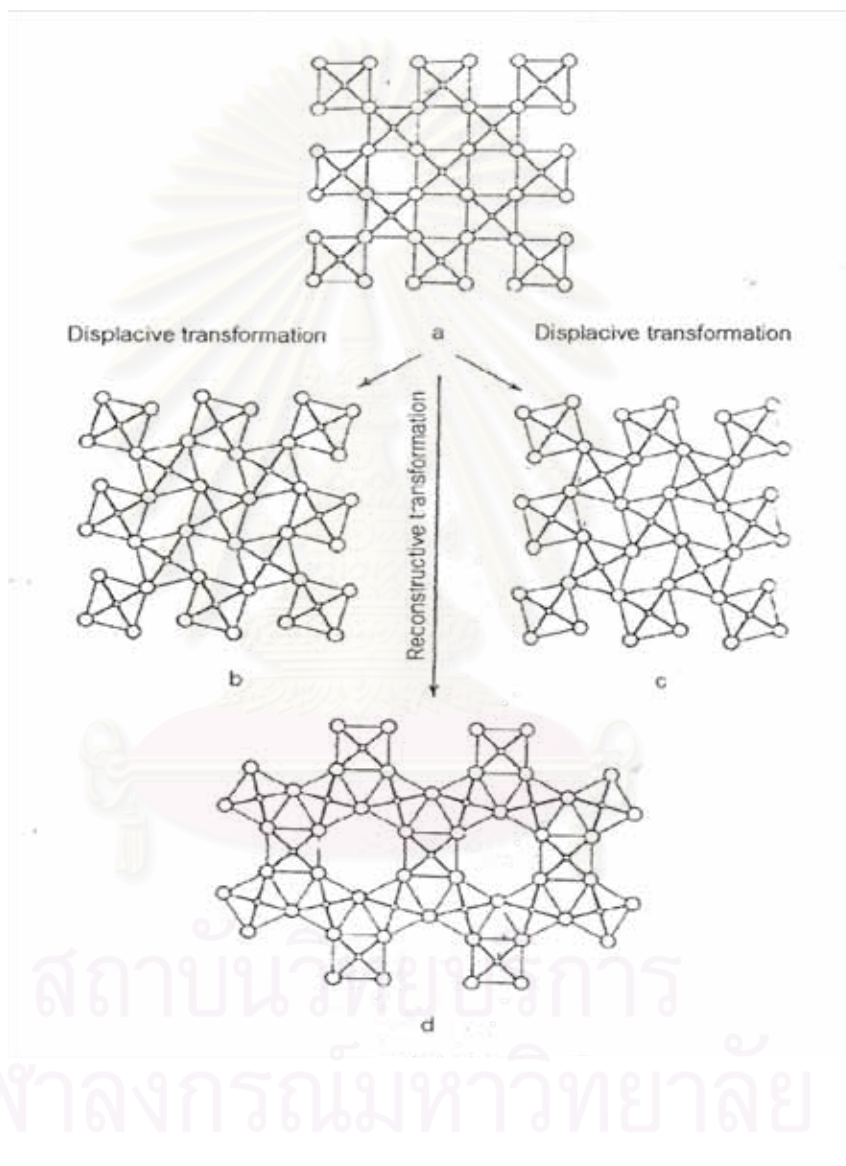
Silica exists in a variety of polymorphic crystalline form. According to the conventional view of the polymorphism of silica, there are 3 main form at atmospheric pressure (Figure 2.3): quartz, stable at below 867°C; tridymite, stable from 867-1470°C; and cristobalite, stable from 1470°C to the melting point at 1723°C (Scheme 2.2). In all these form, the structures are based on $[\text{SiO}_4]$ tetrahedral linked in such a way that every oxygen atom is share between two silicon atom.



Scheme 2.2 Polymorphic transformations in silica [13].

All the temperature limits of their stability ranges, these forms interconvert. The transformations involve a change in the secondary (non-nearest-neighbor) coordination and require the breaking and reformation of Si-O bonds. The transformation processes, known as reconstructive polymorphic transformation, are slow, as show by the fact that the high temperature polymorphs can persist outside their normal stability range. The transformations are aided by or may require the presence of impurities or added mineralizer such as alkali metal oxides. Indeed, it has been suggested that tridymite cannot be formed at all in the absence of impurities. In

addition to the reconstructive transformation, each of the main forms of silica undergoes one or more transformations of a different sort, the so-called high-low, displacive, or martensitic transformations. These involve relatively small structure rearrangement such as mirror rotations of the tetrahedral without bond-breaking. In general, they are quick and reversible as shown in Scheme 2.3.



Scheme 2.3 The structure “a” changes to collapsed forms “b” and “c” by displacive transformation and reconstructive form “d” [14].

2.3.2 Noncrystalline silica

The noncrystalline forms of silica include bulk vitreous silica and a variety of other amorphous types.

Vitreous silica (silica glass) is essentially a super-cooled frozen-in liquid traditionally formed by fusion and subsequent cooling of crystalline silica. It is hardly found in nature except for some exotic species, *i.e.*, fused bodies resulting from lightning striking sand, or Libyan Desert glass. Liquid silica is highly viscous, and freezing-in to the glassy form occurs readily at approximate 1,100°C. In practice, vitreous silica is prepared by fusion of crystalline quartz or quartz sand. Vitreous silica is also made by flame or plasma hydrolysis of silicon tetrachloride, by thermal decomposition of silicate asters, or by flame-fusion process may contain significant amounts (>1,000 ppm) of hydroxyl impurity which affect optical transmission as well as thermal and mechanical properties.

The structure of vitreous silica is a continuous network of [SiO₄] tetrahedral with a lower degree of order than the crystalline phase. The structure itself is subject to many speculations, involving microcrystal theories and a complete random approach. The following is generally accepted: silica glass differ from crystalline silica in having a broader distribution of Si-O-Si bond angles, and a less negative Gibb's free energy of formation, ΔG of vitreous silica is -849.05 kJ/mole; ΔG of low-T cristobalite is -849.76 kJ/mole; ΔG of low-T tridymite is -852.18 kJ/mole; ΔG of low-T quartz is -857.08 kJ/mole. This means silica glass and cristobalite are closer to each other thermodynamically than any other two silica species. From the width of the main broad diffraction peak in the glass diffraction pattern, the "crystallite size" in the case of silica glass was estimated at about 0.8 nm. Since the size of a unit cell of cristobalite is also about 0.8 nm, any crystallites would be only a single unit cell in extent; at such a scale, the terms amorphous and crystalline cease to make sense.

The properties of high quality vitreous silica which determine its uses include high chemical resistance, low coefficient of thermal expansion ($0.5-0.8 \times 10^{-6} \text{K}^{-1}$), high thermal shock resistance, high electrical resistivity, and high optical transmission, especially in the ultraviolet. Bulk vitreous silica is difficult to work because of the absence of network-modifying ions present in common glass. The traditional melting process requires temperatures of 2,000°C and more.

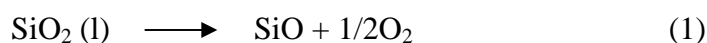
Amorphous silica exists also in a variety of forms, which are composed of small particles, possibly aggregated. Commonly encountered products include colloidal silica, silica gels, precipitated silica, and fumed or pyrogenic silica. Amorphous silicas are characterized by small ultimate particle size and high specific surface area. Their surface may be substantially anhydrous or may contain silanol (Si-OH) groups. They are frequently viewed as condensation polymers of silicic acid, $\text{Si}(\text{OH})_4$. Colloidal silicas (silica sols) are stable dispersions of amorphous silica particles in water.

Silica gels contain three-dimensional networks of aggregated silica particles of colloidal dimension. As formed, the pores are filled with the medium in which the gel is prepared. The medium gives the name to the product, e.g., hydrogel for water, alcogel for alcohols, etc. Simple removal of the liquid results in extensive shrinkage owing to surface-tension forces. Silica gels dried this way are termed xerogels. If the liquid in the pores is replaced by a substance which can be processed in the supercritical range (e.g., certain alcohol, or CO_2) and the gel is heated under pressure above the critical temperature of the liquid, resulting in the disappearance of the liquid-vapor interface, surface-tension effects are absent and a very voluminous dry silica gel (aerogel) is obtained.

Precipitated silicas are powders obtained by coagulation of silica particles from an aqueous medium under the influence of high salt concentrations or other coagulants.

Fumed silicas (aerosols, pyrogenic silica) are produced by vapor-phase processes, generally by the vapor-phase hydrolysis of silicon tetrahalides. Other methods include vaporization of SiO_2 , vaporization and oxidation of Si, and high temperature oxidation and hydrolysis of silicon compound such as silicate esters.

Vaporization silica vaporized principally by dissociation to gaseous SiO and O_2 ; these are the predominant vapor species, which some contribution from atomic oxygen and gaseous SiO_2 . The total vapor pressure over the liquid at the melting point is in the range 1-10 Pa (10^{-5} - 10^{-4} bar). The boiling of silica is estimated as $2,797 \pm 75^\circ\text{C}$. The heat of vaporization of SiO_2 at the melting point is given as 560 kJ/mole, whereas the heat of the reaction is 750 kJ/mole.



Biogenic silicas are natural amorphous silicas. They occur from small organisms in water (diatom) and in plant cells. Dissolved silica is absorbed by the diatom or plant to form a silica skeleton. Diatomite (silica from diatom structure) is usually used as filler or filter medium. Silica in plant has little industrial use.

2.4 Aqueous chemistry of silica [15]

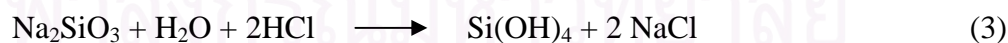
The +4 oxidation state ($z = 4$) is the only important one in the chemistry of silicon in naturally occurring systems, and the coordination number of silicon, N , is most often four. Compared to transition metals, silicon is generally less electropositive, eg., the partial positive charge on silicon $\delta(\text{Si})$ in $\text{Si}(\text{OH})_4$ is + 0.32, whereas $\delta(\text{Ti}) = + 0.63$ and $\delta(\text{Zr}) = + 0.65$ in $\text{Ti}(\text{OH})_4$ and $\text{Zr}(\text{OH})_4$, respectively. The reduced $\delta(\text{M})$ makes silicon comparatively less susceptible to nucleophilic attack with nucleophilic reagents. These factors make the kinetics of hydrolysis and condensation considerably slower than observed in transition metal system or in Group III systems.

Silicon is hydrolyzed even in dilute acid, as expected from its small ionic radius (0.42 Å), and $\text{Si}(\text{OH})_4$ is the predominant mononuclear solution species below ca pH 7 (Figure 2.7). Above pH 7, further hydrolysis produces anionic species:

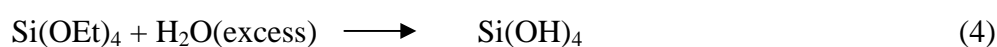


where $\text{SiO}(\text{OH})_3^-$ ($x = 1$ in Eq. (2)) is the predominant mononuclear species above ca pH 7. Because $\text{SiO}(\text{OH})_3^-$ is a very weak acid, $\text{SiO}_2(\text{OH})_2^{2-}$ is observed in appreciable quantities only above pH 12 (Figure 2.4).

Freundlich made silicic acid by acidifying a soluble silicate:



or hydrolyzing the ester:



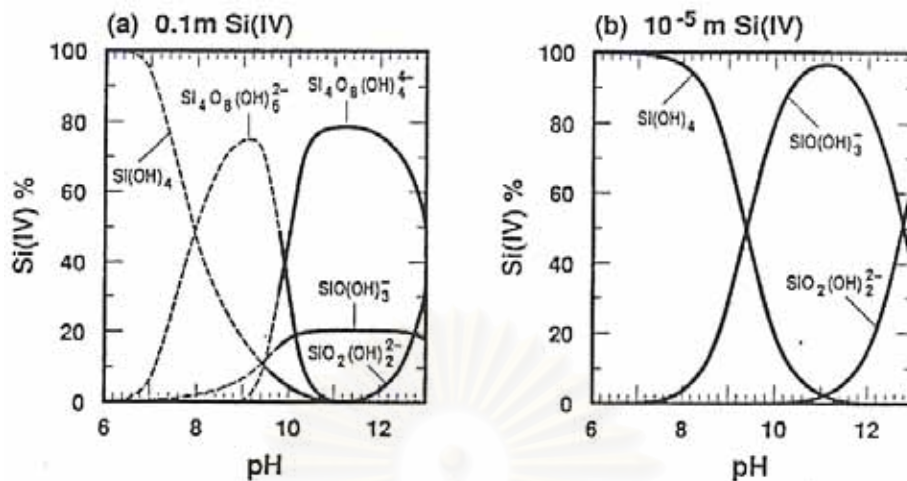


Figure 2.4 Distribution of aqueous silicate species at 25°C in (a) 0.01-m Si(IV) and (b) 10^{-5} -m Si(IV). Ionic strength, $I = 3$ m.

2.5 Polymerization of silica

The formation of silica gel can be regarded as taking place in two stages. In the first, initially formed Si(OH)_4 condenses to form colloidal particles. In dilute solution, a further slow increase in particle size is the only subsequent change, but at a concentration of about 1 percent silica, these primary particles are able to condense together to give a very open but continuous structure, extending throughout the medium, thus bestowing a certain degree of rigidity upon it. In both stages of polymerization, the mechanism is the same, that is, condensation to form Si-O-Si links, but in the first stage, condensation leads to particles of massive silica, while in the second, since it is not possible to fit two particles accurately together over a common face, the number of Si-O-Si linkages between particle is fewer in number than those within the particles themselves. They are merely sufficient to bind adjacent particles together, in a fixed position relative to one another, and thereby lead to a rigid, highly porous, tangled network of branching chain [16].

In polymerization process, there are many factors that can affect silica particle morphology such as temperature, concentration of the silicate solution, neutralizing acid solution, pH gradient, ionic strength, final pH, delay time for gel ageing, effect of

additives (e.g., ammonia acts as a coagulant) and the stirring energy or other external pressure or forces applied to the reactor [17]. Effects of pH gradient and ionic strength are shown in Figure 2.5.

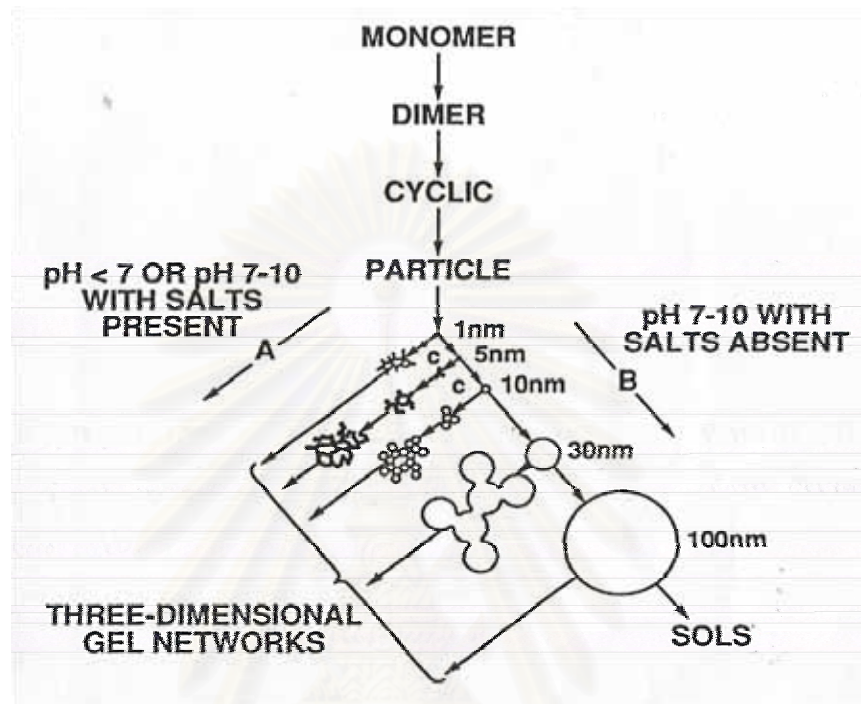
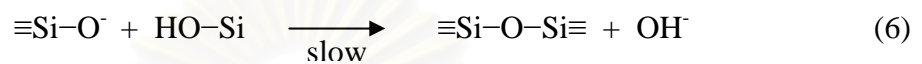
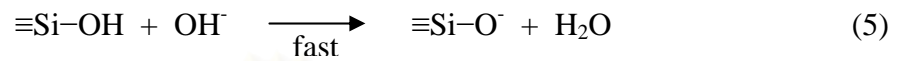


Figure 2.5 Effect of ionic strength and pH gradient on the structure of silica obtained.

Iler divides the polymerization process into three approximate pH domains: < pH 2, pH 2-7 and > pH 7. pH 2 appears as a boundary, since the point of zero charge (PZC), where the surface charge is zero, and the isoelectric point (IEP), where the electrical mobility of the silica particle is zero, both are in the range pH 1-3. pH 7 appears as a boundary because both the silica solubility and dissolution rates maximized at or above pH 7 and because the silica particles are appreciably ionized above pH 7 so that particle growth occurs without aggregation or gelation (Figure 2.6).

2.5.1 Polymerization at pH 2-7

Since the gel time decrease steadily between pH 2 and ca pH 6, it is generally assumed that above the IEP the condensation rate is proportional to $[\text{OH}^-]$ as in the following reaction sequence:



Growth of silica occurs by continued addition of low-molecular-weight species to more highly condensed species and by aggregation of the condensed species to form chains and network. Near the IEP where there is no electrostatic particle repulsion, the growth and aggregation processes occur together and may be indistinguishable. In any case, since the solubility of silica is low in this pH range, particle growth stops when the particles reach 2-4 nm where the solubility and size-dependence of solubility is greatly reduced.

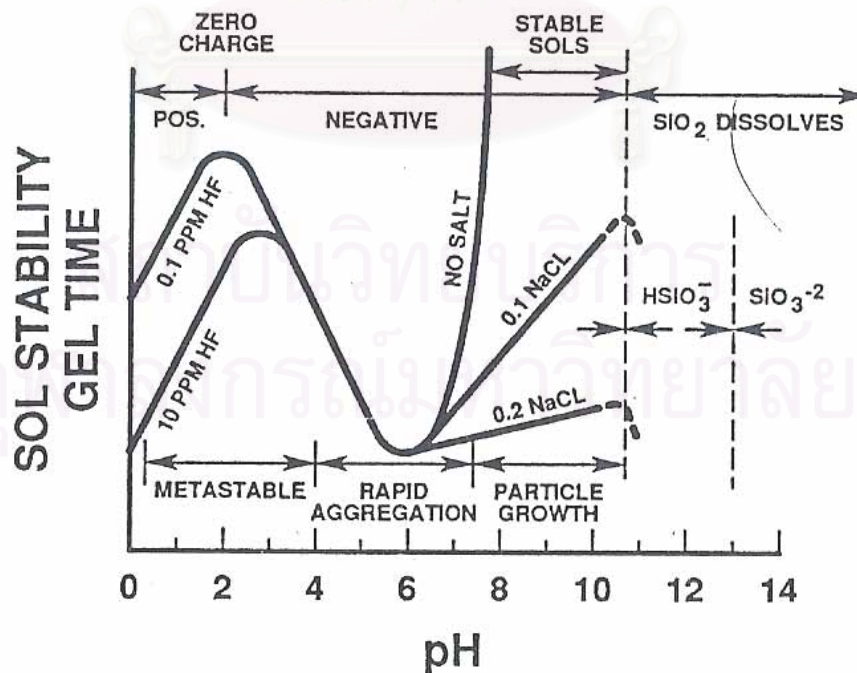


Figure 2.6 Effect of pH in the colloidal silica-water system.

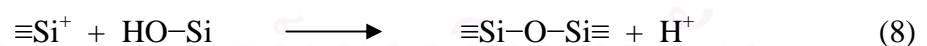
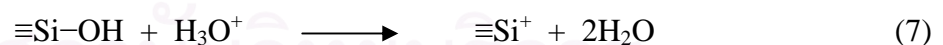
2.5.2 Polymerization above pH 7

Above pH 7, polymerization occurs by the same nucleophilic mechanism as pH 2-7 (Eqs. 1 and 2). However, because all the condensed species are more likely to be ionized and therefore mutually repulsive, growth occurs primarily by the addition of monomer to more highly condensed particles rather than by particle aggregation. Due to the greater solubility of silica and the greater size-dependence of solubility above pH 7, growth of the primary particle continues by Ostwald ripening. Particles grow rapidly to a size that depends mainly on the temperature. Higher temperatures produce large particles due to greater silica solubility. Since growth occurs by the dissolution of smaller particles and deposition of soluble silica on larger particles, the growth rate depends on the particle-size distribution.

In the absence of salt, no chaining or aggregation occur, because the particles are mutually repulsive. Stable sols of large particle sizes can be prepared and concentrated for industrial use. The addition of salt reduces the thickness of the double layer at a given pH, dramatically reducing the gel time.

2.5.3 Polymerization below pH 2

Below pH 2, the polymerization rate is proportional to $[H^+]$. Although Iler and others propose that the acid-catalyzed polymerization mechanism involves a siliconium ion inter-mediate ($\equiv Si^+$):



In the absence of fluoride ion, the solubility of silica below 2 is quite low and at the moderate acidities (pH 0-2) silicate species should not be highly ionized. For these reasons it is likely that the formation and aggregation of primary particles occur together. Traces of F^- or the addition of HF decrease the gel times and produce gels similar to those formed above pH 2.

2.6 Chromatographic theory

Chromatography is a technique in which the components of a mixture are separated based upon the rates at which they are carried through a stationary phase by a gaseous or liquid mobile phase. It was invented by the Russian botanist Mikhail Tswett. He used the technique to separate various plant pigments, such as chlorophylls and xanthophylls, by passing solutions of them through glass column packed with finely divided calcium carbonate [18].

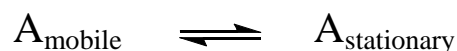
All chromatographic separations are carried out using a mobile and a stationary phase. As a result of this prerequisite, the primary classification of chromatography is based on the physical nature of the mobile phase. Thus, all separation process that utilizes a gas as the mobile phase are classed as gas chromatography. Conversely, all separation processes that utilize a liquid as the mobile phase are classified as liquid chromatography. In a similar manner the subclasses of chromatography are defined on a basis of the physical nature of the stationary phase. Consequently, if the mobile phase is a gas and the stationary phase is a liquid, then the technique is call gas-liquid chromatography (GLC) and if the mobile phase is a gas and the stationary phase is a solid, then the technique is called gas-solid chromatography (GSC). If the mobile phase is liquid, then there will be two complimentary sub-classes of liquid chromatography, that is, liquid-liquid chromatography (LLC) and liquid-solid chromatography (LSC). Table 2.4 presented the classification of chromatography in tabular form [3].

Table 2.4 Classification of chromatographic technique

Mobile phase	Gas		Liquid	
Stationary phase	Liquid	Solid	Liquid	Solid
Chromatographic technique	Gas-Liquid Chromatography	Gas-Solid Chromatography	Liquid-Liquid Chromatography	Liquid-Solid Chromatography

2.6.1 Distribution of analyst between phases

The distribution of analytes between phase can often be described quite simply. An analyte is in equilibrium between the two phases;



The equilibrium constant, K is termed the partition coefficient; defined as the molar concentration of analyte in the stationary phase divided by the molar concentration of the analyte in the mobile phase. The time between sample injection and an analyte peak reaching a detector at the end of the column is termed the retention time (t_R). Each analyte in a sample will have a different retention time. The time taken for the mobile phase to pass through the column is called t_M [19] as shown in Figure 2.7.

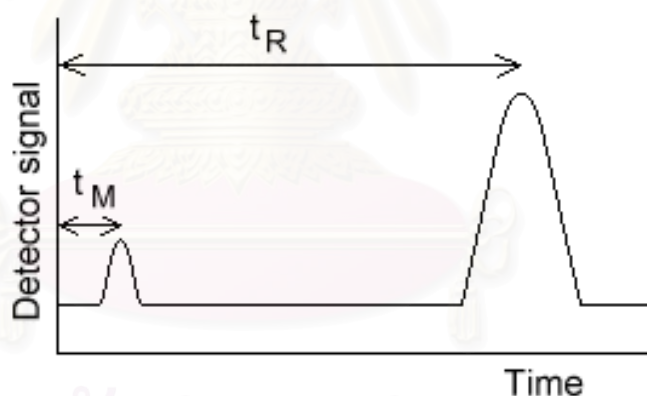


Figure 2.7 Definition of various chromatographic parameters.

A term called the retention factor, k' , is often used to describe the migration rate of an analyte on a column. You may also find it called the capacity factor. The retention factor for analyte A is defined as;

$$k'_A = \frac{(t_R - t_M)}{t_M} \quad (9)$$

t_R and t_M are easily obtained from a chromatogram. When an analyte's retention factor is less than one, elution is so fast that accurate determination of the retention time is very difficult. High retention factors (greater than 20) mean that elution takes a very long time. Ideally, the retention factor for an analyte is between one and five. We define a quantity called the selectivity factor, α , which describes the separation of two species (A and B) on the column;

$$\alpha = \frac{k'_B}{k'_A} \quad (10)$$

When calculating the selectivity factor, species A elutes than species B. The selectivity factor is always greater than one.

2.6.2 Band broadening and column efficiency

To obtain optimal separation, sharp, symmetrical chromatographic peaks must be obtained. This means that band broadening must be limited. It is also beneficial to measure the efficiency of the column.

2.6.2.1 The theoretical plate model of chromatography

The plate model supposes that the chromatographic column contains a large number of separate layers, called theoretical plates (Figure 2.8). Separate equilibrations of the sample between the stationary and mobile phase occur in these "plates". The analyte moves down the column by transfer of equilibrated mobile phase from one plate to the next.

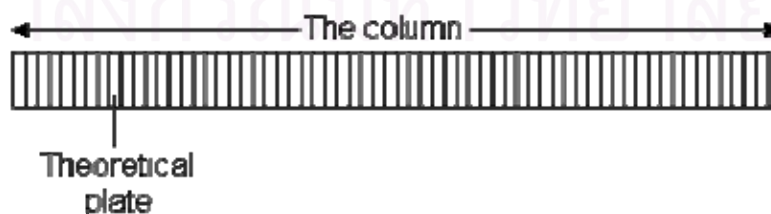


Figure 2.8 Theoretical plate model.

It is important to remember that the plates do not really exist; they are a figment of the imagination that helps us understand the processes at work in the column. They also serve as a way of measuring column efficiency, either by stating the number of theoretical plates in a column, N (the more plates the better), or by stating the plate height; the Height Equivalent to a Theoretical Plate (the smaller the better). If the length of the column is L , then the HETP is

$$HETP = \frac{L}{N} \quad (11)$$

The number of theoretical plates that a real column possesses can be found by examining a chromatographic peak after elution;

$$N = \frac{5.55t_R^2}{w_{1/2}^2} = \frac{16t_R^2}{W_b^2} \quad (12)$$

Where $w_{1/2}$ and w_b are the peak width at half-height and at the base peak, respectively. As can be seen from this equation, column behaves as if they have difference number of plates for difference solutes in a mixture.

2.6.2.2 The rate theory of chromatography

A more realistic description of the processes at work inside a column takes account of the time taken for the solute to equilibrate between the stationary and mobile phase (unlike the plate model, which assumes that equilibration is infinitely fast). The resulting band shape of a chromatographic peak is therefore affected by the rate of elution. It is also affected by the different paths available to solute molecules as they travel between particles of stationary phase. If we consider the various mechanisms which contribute to band broadening, we arrive at the Van Deemter equation for the plate height;

$$HETP = A + \frac{B}{u} + Cu \quad (13)$$

Where u is the average velocity of the mobile phase. A, B, and C are factors which contribute to band broadening.

(a) A-Eddy diffusion

The mobile phase moves through the column which is packed with stationary phase. Solute molecules will take different paths through the stationary phase at random. This will cause broadening of the solute band, because different paths are of different lengths.

(b) B-Longitudinal diffusion

The concentration of analyte is less at the edges of the band than at the center. Analyte diffuses out from the center to the edges. This causes band broadening. If the velocity of the mobile phase is high then the analyte spends less time on the column, which decrease the effects of longitudinal diffusion.

(c) C-Resistance to mass transfer

The analyte takes a certain amount of time to equilibrate between the stationary and mobile phase. If the velocity of the mobile phase is high, and the analyte has a strong affinity for the stationary phase, then the analyte in the mobile phase will move ahead of the analyte in the stationary phase. The band of analyte is broadened. The higher velocity of mobile phase, the worse the broadening becomes.

2.6.2.3 Van Deemter Plots

A plot of plate height vs. average linear velocity of mobile phase. Such plots are of considerable use in determining the optimum mobile phase flow rate (Figure 2.9).

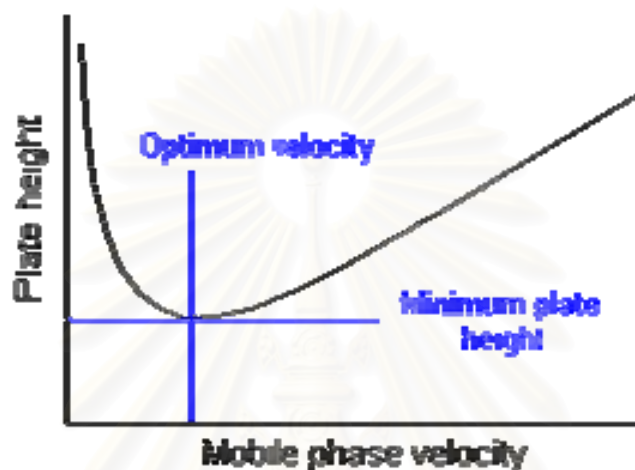


Figure 2.9 A typical of Van Deemter plot.

2.6.2.4 Resolution

Although the selectivity factor, α , describes the separation of band centers, it does not take into account peak widths. Another measure of how well species have been separated is provided by measurement of the resolution. The resolution of two species, A and B, is defined as

$$R = \frac{2[(t_R)_B - (t_R)_A]}{w_A + w_B} \quad (14)$$

Baseline resolution is achieved when $R = 1.5$. It is useful to relate the resolution to the number of plates in the column, the selectivity factor and the retention factors of the two solutes;

$$R = \frac{\sqrt{N}}{4} \left(\frac{\alpha - 1}{\alpha} \right) \left(\frac{1 + k'_B}{k'_B} \right) \quad (15)$$

To obtain high resolution, the three term must be maximized. An increase in N , the number of theoretical plates, by lengthening the column leads to an increase in retention time and increased band broadening – which may not be desirable. Instead, to increase the number of plate, the height equivalent to a theoretical plate can be reduced by reducing the size of the stationary phase particles. It is often found that by controlling the capacity factor, k' , separations can be greatly improved. This can be achieved by changing the temperature (in Gas Chromatography) or the composition of the mobile phase (in Liquid Chromatography).

2.7 Adsorbent

An adsorbent is a substance, usually porous in nature and with a high surface area that can adsorb substances onto its surface by intermolecular forces. Only at very low concentrations is the adsorption isotherm linear, at higher concentrations the adsorption isotherm may be Langmuir or Freundlich in nature. Due to the fact that solutes can distribute between the adsorbent surface and a mobile phase, adsorbents are used as a stationary phases in gas-solid and liquid-solid chromatography. Adsorbents are also used for extraction purposes removing traces of organic materials from large volumes of water very efficiently (cf solid phase extraction devices). Typical adsorbents used in gas-solid chromatography are silica gel, alumina, carbon and bonded phases. These are mostly used in the separation of the permanent gases and the low molecular weight hydrocarbon gasses. Adsorbents used in liquid solid chromatography are mostly silica gel and various types of bonded phases. Adsorbents in liquid-solid chromatography have a very wide variety of application areas [20]. Mode of separation for each adsorbent and their application are listed in Table 2.5.

Table 2.5 Adsorbents and mode of separation [21]

Adsorbents	Chromatographic Mechanism	Typical Application
Silica gel	Adsorption	Steroids, amino acids, alcohols, hydrocarbons, lipids, aflatoxins, bile acids, vitamins, alkaloids
Silica gel RP	Reversed phase	Fatty acids, vitamins, steroids, hormones, carotenoids
Cellulose, kieselguhr	Partition	Carbohydrates, sugar, alcohols, amino acids, carboxylic acids, fatty acids
Aluminum oxide	Adsorption	Amines, alcohols, steroids, lipids, aflatoxins, bile acids, vitamins, alkaloids
PEI cellulose	Ion exchange	Nucleic acids, nucleotides, nucleosides, purines, pyrimidines
Magnesium silicate	Adsorption	Steroids, pesticides, lipids, alkaloids

2.8 Literature reviews

In 1992 Leela-Adisorn [2] prepared the nano-structure silica from rice husk. Husk samples were submitted to a chemical pre-treatment using cellulase enzyme and different inorganic acids. Subsequently, samples were burned at 600°C for 6 h under static atmosphere. The results revealed that pre-treatment rice husk using HCl (1:4) or H₂SO₄ (1:4) gave silica product with properties intermediate to those of fumed silica and xerogel. The specific surface area was 250 m²/g, the purity was 99.4% silica.

In 1994 Kuotung *et al.* [22] studied the effect of solvents on ageing of silica gel. The sol was prepared by mixing in a molar ratio of TEOS : H₂O : HNO₃ = 1 : 10 : 0.4. Gelation of the sol was carried out at 60°C and then the gel was aged in various solvents. From the results, it was found that surface area can be related to the polarity parameter of the ageing solvent. Density of the dried gel after solvent ageing is

closely related to the surface area of the gel and tends to decrease as the surface increases. The results from SEM showed aged gel having a slit-shaped micropore, narrow pore-size distribution, and homogeneous microstructure.

In 1995 Fungsin [10] improved purity of silica using cellulase incorporated into silica preparation system. The optimum condition for cellulase hydrolysis was: 9%(w/v) of rice husk pretreated with acid in deionized water, 0.02%(w/v) EDTA, 0.1%(v/v) Tween 80 pH 4.5-4.8 with agitation rate of 200 rpm at room temperature. This incorporation of cellulase could enhance the whiteness of silica after ashing in comparison to those without enzyme. The best combination observed was the use of cellulase on husk treated with HCl 1:5, by which a 99% purity was obtained.

In 1995 Nualsuwan [23] investigated the addition of silica from rice husk to natural rubber. Rice husk was treated with 0.4 M HCl and burned at 600°C for 6 h. After burning, the ash contained 99.6% silica. The rubber compound that mixed with the ash was compared with rubber compounds without reinforcing agent, with Hi-sil 255 (commercial silica used in rubber industry), and with carbon black. The results indicated that reinforcing with rice ash had several advantages over the other products such as good abrasion resistance and good compression set.

In 1997 Khunthon *et al.* [24] prepared silica gel from rice husk ash as adsorbent for thin-layer chromatography. RHA sample was refluxed with sodium hydroxide and formed gel by adding sulfuric acid. The highest percentage yield of 81.39 was obtained using 10% NaOH with refluxed for 3 h. After milling, silica sample gave surface area was 661.21 m²/g, the purity was 99.93% silica. The R_f value of triptamitin was 0.77 which was similar to using adsorbent from Merck Company.

In 2000 Kalapathy *et al.* [25] prepared silica xerogel from rice husk ash by alkali extraction followed by acid precipitation. In this research they tried to remove impurities such as Na, and K. Effect of washing rice husk ash with acid prior to alkali extraction and washing dried silica gel with water were investigated. The initial acid washing of rice husk ash resulted in a lower Ca content (<200 ppm) while the final washing of the xerogel led to a silica product with lower Na, and K content (Na<200 ppm, K<400 ppm).

In 2002 Kalapathy *et al.* [26] prepared silica from rice husk ash using the improved method to remove Na contaminant. This method was performed by adding silicate solution to hydrochloric, citric acid, or oxalic acid solutions until the pH 4.0 and 7.0 were reached. The results revealed that silica produced at pH 4.0 had lower

sodium content than that produced at pH 7.0 while the silica precipitated using citric and oxalic acid solution had lower sodium content than the silica produced using hydrochloric acid.

In 2002 Della *et al.* [27] prepared active silica from rice husk ash. The first rice husk ash was burned at several temperatures to increase the relative amount of silica. The next step silica was grinded to decrease mean particle size and increase specific surface area. It was found that 95% silica powder could be produced after heat-treating at 700°C for 6 h. The specific surface area of particle was increased after wet milling from 54 to 81 m²/g.

In 2004 Tzong-Horng Liou [28] investigated morphology of silica from rice husk. Rice husk was treated with hydrochloric acid after that it was burned using tubular reactor which was inserted into a furnace. At a heating rate of 5 K/min, the specific surface area of silica powder was 235 m²/g, the average pore diameter was 5.4 nm, and average particle size was 60 nm. The products obtained from various heating rate were all amorphous. From thermogravimetric analysis, a mechanism including two reaction stages was observed. The first stage is the loss of volatile compounds and the second stage is further oxidation of carbon to form carbon dioxide.

In 2004 Jal *et al.* [29] prepared nanosilica by precipitation method. Commercial silica gel was made iron free by reflux with hydrochloric acid then it was dissolved in NaOH solution. Then conc.H₂SO₄ was added to alkaline silicate solution to form gel. From TEM silica particles were found to have almost spherical shape with dimension of ~50 nm. The surface area was found to be of 560 m²/g and density 2.2 g/cm³. From TGA the total silanol density in the silica was found to be 7.68 nm⁻². The number of reactive silanols that forms hydrogen bond with water molecules was found to be 2.48.

In 2004 Jadsadapattarakul [3] investigated using rice husk to produce silica particles for high performance liquid chromatography (HPLC) and gas chromatography (GC). Rice husk was burned at 700°C for 1 h. After that it was refluxed with 10% NaOH, and then precipitated with hydrochloric acid. The obtained silica products have purity above 99% and amorphous form. After that, silica particles were synthesized into silica-ODS (C18). The HPLC column packing was performed using wet packing technique while GC column was packed using dry packing technique. For HPLC column, carbon loading of 17.72%, average particle size of

14.92 μm and theoretical plate height minimum value (H) of 0.0467 cm at 0.3 ml/min of 100% methanol. For GC column, H minimum value of 0.100 cm at carrier gas flow-rate of 6.76 ml/min.

In 2005 Chandrasekhar *et al.* [30] investigated effect of acid treatment on properties of rice husk silica. Two rice husk samples of different origin in India, APRH and KRH were leached in various acid of different concentration before were burned at 700°C. The APRH was found to be inferior to the KRH ash in all properties. Pretreatment of the husks with the organic acids improved the properties of silica such as purity, reactivity, brightness, surface area and pore volume. High surface area, 270.50 m^2/g was obtained by treated KPH ash by 0.1 N oxalic acid.

In 2005 Tang *et al.* [31] prepared silica aerogel from rice hull ash by supercritical carbon dioxide drying. Rice hull ash was extracted using sodium hydroxide solution. The solution was neutralized with sulfuric acid solution to form a silica gel. The aged gel was dried to produce aerogel using supercritical carbon dioxide drying. The prepared silica was characterized using SEM, TEM and BET measurement. The specific surface area of silica aerogel was as high as 597.7 m^2/g with bulk density of 38.0 kg/m^3 . The diameters of the pores inside the aerogel are between 10 and 60 nm.

In 2006 Possamai *et al.* [32] investigated the effect of acid leaching of rice husk before thermal treatment. The best leaching result was obtained using 10% hydrochloric acid followed by washing with water. Then rice husk was performed by thermal treatment, calcinations of RHA at 700°C for 6 h follow by grinding for 80 min. Silica obtained from acid leaching was about 97% amorphous, had a 17.37 μm mean particle size, and specific surface area of 296 m^2/g . On the other hand, for silica obtained from only thermal treatment the values were about 95% amorphous material 0.68 μm , and 81 m^2/g .

In 2006 Smitha *et al.* [33] prepared silica aerogels from tetraethoxysilane (TEOS) by subcritical drying method. Effect of concentration and time of ageing solution on the porosity characteristics of silica aerogels was investigated. The results revealed that specific surface area, pore size and pore volume increase in concentration of TEOS in the ageing solution. With an 80% TEOS in isopropanol at 50°C, a surface area of 1098 m^2/g , pore volume 1.3 cm^3/g and an average pore size of 47.7 Å were obtained.

CHAPTER III

EXPERIMENTAL

3.1 Chemicals

1-naphthylamine, Fluka Chemies, Switzerland
Ammonium hydroxide, J. T. Baker, USA
Barium sulfate, BHD, England
Calcium sulfate, BHD, England
Chloroform, LAB SCAN. Thailand
Dichloromethane, LAB SCAN. Thailand
Diphenylamine, Fluka Chemies, Switzerland
Hexane, LAB SCAN. Thailand
Magnesium sulfate, Fluka Chemies, Switzerland
Naphthalene, Merck, Germany
Silica gel 60, Merck, Germany
Silica gel 60G, Merck, Germany
Sodium hydroxide, Ajax Finechem, Australia.
Sodium sulfate, Merck, Germany
Sulfuric acid, J. T. Baker, USA
 α -naphthol, Fluka Chemies, Switzerland

3.2 Instruments and apparatus

All equipments, used in the preparation and characterization silica gel, were listed as follows:

Absorbance detector : UA-6 ISCO
CombiFlash : Graduate ISCO
FT-IR : Perkin Elmer, Nicolet (Impact 410)
Mechanical stirrer : Janke & kunkel, RE 16
Laser particle size analyzer : Mastersizer 2000 Ver.5.22

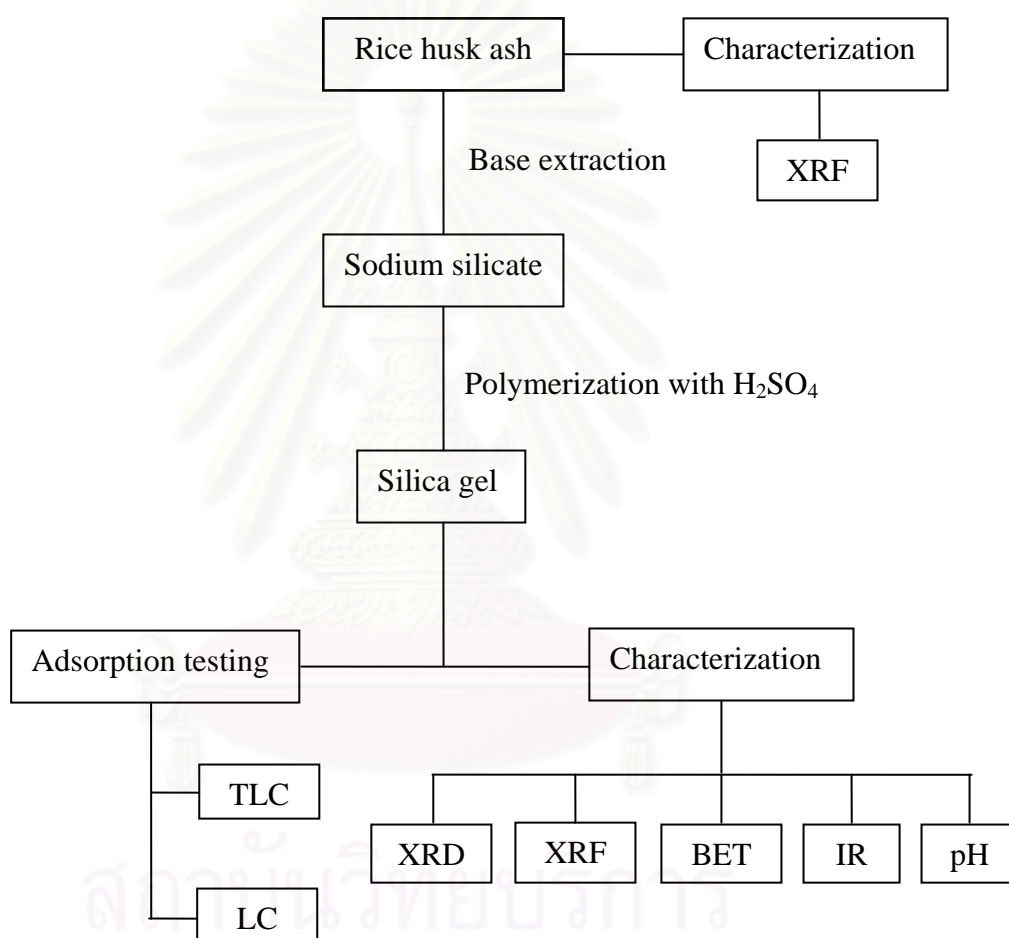
Sieve shaker : Retsch AS 200

Surface area analyzer : Micromeritics FlowSorb II 2300

X-ray diffractometer : PW3710 Xpert, Philips

X-ray fluorescent : EDXRF 2000

3.3 Experimental procedure of silica gel



Scheme 3.1 Scope of preparation silica gel.

Silica gel was synthesized using the method of Khunthon [23]. This method gave the suitable condition for preparation of high yield silica gel.

3.3.1 Preparation of starting material

Rice husk ash (RHA) from rice mill was sieved through the test sieve aperture 100 mesh (149 μm , ASTM) to remove unburned husk and any impurities. Then it was dried in hot air oven at 110°C for 24 hours to remove the moisture.

3.3.2 Extraction of silica from RHA

Eight hundred milliliter of 10% NaOH was added to 100 g of dried ash. The mixture was heated up to its boiling point for 3 hours with the reflux. After refluxed, the orange-brown color solution was obtained. Then the mixture was filtered through Whatman No.1 filter paper using suction filtration, and adjusted the volume by adding deionized water to give 800 ml of sodium silicate solution. Finally it was allowed to cool to room temperature.

3.3.3 Synthesis of silica gel

The sulfuric acid solution (5N) was added to the sodium silicate solution by drop-wise to decrease the pH of this solution less than 12 and H_2SO_4 (5N) solution was added continuously by drop-wise to the solution and continuously stirred using mechanically stirrer until reaching the desired pH (such as pH 1) and the reaction mixture was continuously stirring for 30 minutes at room temperature. Then the formed gel was soaked in this pH (pH 1) solution (or was aged in pH 1) for 3 hours. After that the gel was filtered by suction filtration. The obtained silica gel was washed with excess deionized water 2 times. Next the collected gel was dried in hot air oven at 110°C for 24 hours to form the xerogel. The xerogel was milled by mortar and pestle to give small particle. The milled silica was rewashed again with excess deionized water 2 times. Finally the silica was dried in hot air oven at 110°C for 48 hours. (this prepared silica gel was called silica gel aging pH 1)

3.3.3.1 Effect of aging pH

The effect of aging pH was investigated *via* preparation of silica gel by aging the gelling silica solution at various pHs at 1, 3, 7, and 9, respectively, for 3 hours. The silica gel aging at each pH was collected and ready for the further investigation in the next step.

3.4 Characterization of silica gel

3.4.1 Specific surface area

Specific surface area of silica was determined using a micromeritics adsorbentometer, model Flowsorb 2300. The principle is adsorption of particular molecular species from gas N₂ onto the surface. Based upon one adsorbed layer, the quantity of adsorbed material gave directly the total surface area of the sample.

3.4.2 X-Ray Fluorescence (XRF)

Quantitative chemical analyses of RHA and silica were accomplished using an Energy Dispersive X-Ray Fluorescence (EDXRF) serviced by the Scientific and Technology Research Equipment Center (STREC), Chulalongkorn University.

3.4.3 X-Ray Diffraction (XRD)

XRD measurement was performed using a PW3710 Xpert X-ray powder diffractometer with a monochromator and Cu K_α radiation (40 Kv, 30 mA). The 2θ angle was ranged from 5 to 60 degree. This technique was serviced by the Metallurgy and Materials Science Research Institute, Chulalongkorn University.

3.4.4 Fourier Transform Infrared Spectroscopy (FT-IR)

FT-IR analysis was obtained from Perkin Elmer system 200 FT-IR spectroscopy (Impact 410, Nicolet). The frequency range of 4000-400 cm⁻¹ was observed using transmittance, Perkin Elmer, Nicolet (Impact 410) model. Silica was

mixed with potassium bromide in agate mortar and pestle. The mixture was then transferred to a hydraulic pressing machine and pressed into a thin disc for FT-IR analysis.

3.4.5 Particle size analyzer

Particle size distribution of silica was measured by laser diffraction (Mastersizer 2000) serviced by Department of Imaging Printing Technology, Faculty of Science, Chulalongkorn University.

3.4.6 pH of silica

pH of silica was determined according to standard method ASTM : D 6739-01

3.5 Particle size separation of silica gel

Milled silica was sieved using sieve shaker (Retsch AS 200) that connected with the sieve number 325, 200, and 80 mesh as shown in figure 3.1. Degree of shaking was 50 amplitudes and during time for shaking was 20 min.

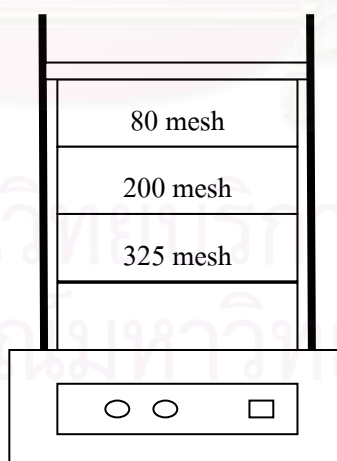


Figure 3.1 The order of passed plate sieve support.

3.6 Chromatographic testing of silica gel

In this research, chromatographic testing of silica was compared with two silica gel commercial grades from Merck; silica gel 60 G for thin-layer chromatography and silica gel 60 for column chromatography.

3.6.1 Thin-layer chromatography

For preparing TLC plates, 6 g of silica gel was mixed with deionized water. The mixture was coated on glass plates (5 x 20 cm) using preparative TLC instrument. The thickness for each coating was 0.25 mm. Then the coated plates were first allowed to dry at room temperature and then in an oven at 110°C for 2 h. After that the plates were allowed to cool to room temperature. The distance for development of each plate was 15 cm. 1000 ppm of α -naphthol, diphenylamine and 1-naphthylamine in ethyl acetate were used as the standard compounds for chromatographic testing. 100% chloroform was selected as mobile phase. Test solutions were spotted onto the plates with a fine capillary. The solvent was removed by air drying and the plates were developed in glass jar (23 x 25 cm). After the development finished, the spots were visualized by staining with iodine vapor and then marked the position of standard compound and determined the R_f values.

The retention factor, or R_f , is defined as the distance traveled by the compound divided by the distance traveled by the solvent.

$$R_f = \frac{\text{distance traveled by the compound}}{\text{distance traveled by the solvent front}} \quad (3.1)$$

3.6.1.1 Effect of metal salts as binder

Four types of metal sulfate (Na_2SO_4 , CaSO_4 , MgSO_4 , and BaSO_4) were selected as binder. 10% of metal sulfate was prepared by mixing 0.60 g of metal salt with 5.40 g of synthesis silica. The mixture was dissolved in deionized water and coated on glass plates.

3.6.2 Column chromatography

Silica gel 5 g was mixed with mobile phase (50% dichloromethane in hexane) after that the mixture was packed in glass column (1 x 30 cm). This column was joined to Combi flash column which combined with uv-visible detector. The wavelength was set at 254 nm. Before testing, solvent was flowed in system to equilibrate column for 30 min. Mixed standard compounds for separating investigation were 5000 ppm of naphthalene and α -naphthol. All experiment 0.4 ml of standard mixtures was injected in flash column. Sensitivity was set to 2.0 and chart speed was 15 cm/h. Suitable flow rate was 15 ml/min. Finally, resolution values of standard compounds were determined.

$$R = \frac{2[(t_R)_B - (t_R)_A]}{w_A + w_B} \quad (3.2)$$

where

R = resolution

t_R = retention time

w = full width at half maximum of peak

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CHAPTER IV

RESULTS AND DISCUSSIONS

In this research, silica gel was prepared from rice husk ash (RHA) by base extraction and sol-gel method, respectively. Effect of aging pH in gel formation was investigated. Then silica gel was characterized with various techniques including X-Ray Fluorescence (XRF), X-Ray Diffraction (XRD), Fourier Transform Infrared spectroscopy (FT-IR) and BET surface area. After that silica gel was controlled particle size and tested as adsorbent for compounds separation in chromatography with two techniques namely column chromatography and thin-layer chromatography. For thin-layer chromatography effect of binder was also studied.

4.1 Chemical composition of rice husk ash

Starting material, RHA was obtained from rice mill. It was black with gray particles and contaminated with unburned rice husk. Therefore, it has to be sieved before using in the next steps. The chemical compositions of RHA were determined by XRF technique. The results are showed in Table 4.1. From the table, it was found that RHA contained about 85% of silica. It also contained small amount of other elements that was considered as impurities such as potassium, calcium, magnesium, iron and manganese. Then ash from each source showed difference in chemical compositions. This different may occur due to geographical factors for example, type of ground, year of harvest, sample preparation and analysis methods [34]. From the Table 4.1, the remainder of percent concentration in RHA was expected as black carbon and some moisture (Table 4.2).

Table 4.1 Chemical compositions of rice husk ash sample

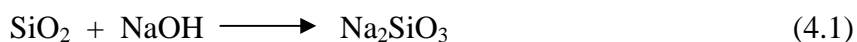
Compounds	Concentration (%)
SiO ₂	85.087
MgO	0.219
Al ₂ O ₃	0.082
P ₂ O ₅	0.388
SO ₃	0.077
Cl	0.125
K ₂ O	0.929
CaO	0.471
MnO ₂	0.144
Fe ₂ O ₃	0.079

Table 4.2 Moisture content in rice husk ash sample

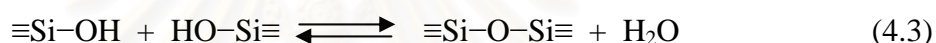
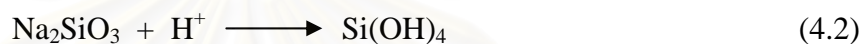
Samples	Ash (g)	Moisture (g)	% Moisture
1	1.0037	0.9902	1.3550
2	1.0024	0.9929	0.9477
3	1.0023	0.9900	1.2272
Average			1.1766±0.2108

4.2 Synthesis of sodium silicate and silica gel

Sodium silicate was produced by extraction of RHA with sodium hydroxide. In this research, the reaction was heated with reflux for 3 hours. Finally the orange-brown solution product was obtained. This color may result from impurities which also dissolved in basic solution. The chemical equation of the reaction was represented as follows:



Then sodium silicate solution was used as starting material for synthesis of silica gel. Sulfuric acid (5N) was added to the solution of sodium silicate to initiate gelation. The white soft gel initially occurred when the pH decreased to 12. In this step, acid reacted with sodium silicate to form silicic acid, $\text{Si}(\text{OH})_4$. After that, silicic acid condensed to form a polymeric network of gel. In this step, hydrolysis and condensation polymerization reaction occurred simultaneously [16]. The chemical reactions were showed as follows:



4.2.1 Effect of aging pH on percentage yield of silica

Percentage yield of silica was measured by weight of dried silica gel. This gel obtained after it was heated at 110°C for 48 hours. The results are listed in Table 4.3. It was found that the silica gel aging at pH 3 gave the highest yield of 85.19% whereas the silica was prepared by aging at pH 1 gave the yield quite similar amount to that which aging at pH 3 with a little lower percentage yield. The percentage of product which was prepared by aging at pH higher such as at pH 7 and 9 resulted the yield lower by about 79% and 73%, respectively. These results indicated that silica which was prepared by aging at pH higher than 3 the silica product might be dissolved better at higher pH solution that caused decreasing of percentage yield of silica gel product. The results in Table 4.3 indicated that the optimal yield of silica gel should be prepared by aging at pH 3.

Table 4.3 Percentage yield of silica gel from RHA

pH aging	Silica gel (g)/100g ash			Average (%)
	No.1	No.2	No.3	
1	84.22	84.10	83.52	83.95±0.37
3	84.97	85.06	85.55	85.19±0.31
7	78.85	77.91	78.58	78.45±0.48
9	72.86	73.60	73.93	73.46±0.55

4.3 Characterization of silica gel

The silica gel products at aging pH 1, 3, 7 and 9 were characterized for physical properties using various techniques including BET surface area, Fourier transform infrared spectroscopy (FT-IR), X-ray fluorescence (XRF), X-ray diffraction (XRD), and pH-values followed ASTM : D 6739-01.

4.3.1 Effect of aging pH on specific surface area

The surface area of each silica gel sample which prepared by variation of aging pH (pH 1, 3, 7 and 9) was measured by nitrogen adsorption using BET equation. The results of surface area analysis are showed in Table 4.4. The results indicated that the sample with highest surface area was obtained when prepared by aging at pH 1. The surface area of silica gel decreased when the sample was prepared by aging at higher pH. These results can be explained by Iler theory [16] including the polymerization of silica. In dilute solution, SiO₂ was soluble and stable in a form of silicic acid monomer. When the concentration of SiO₂ higher than the solubility of amorphous silica, then it started to polymerize by condensation to form dimer and resulted a higher molecular weight such as cyclic structure and a particle. After that, two processes occurred simultaneously which including the addition of monomer to a particle leading to particles of massive silica and the other process, the particle was linked together to form a large three dimensional molecules lead to highly porous and higher surface area. In both stages of polymerization which occurred by the same

mechanism including a condensation to form Si-O-Si links. At the pH of solution above 7, a small particle of silica was easily soluble and then it was deposited on the large particle. In addition, at the high pH, silica particles were negatively charge and repelling each other to result a particle growth continuing without aggregation. Hence at pH solution above 7, silica formed particles with lower surface area.

Table 4.4 Physical properties of silica gel which prepared at various aging pHs.

Aging pH	Surface area (m ² /g)	Total pore volume (cm ³ /g)	Average pore diameter (nm)
1	627.10	1.10	7.01
3	404.52	1.21	11.96
7	87.01	0.21	9.79
9	72.98	0.16	8.64

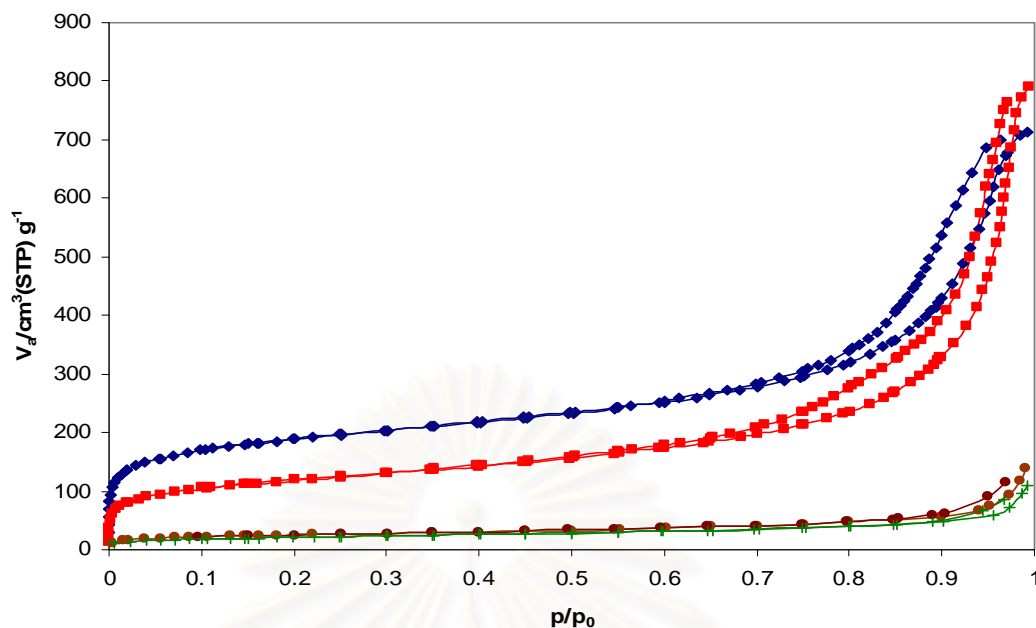


Figure 4.1 N₂ adsorption-desorption isotherm of synthesized silica gel which was prepared at various pH aging; (♦) aging at pH 1, (■) aging at pH 3, (●) aging at pH 7, (+) aging at pH 9.

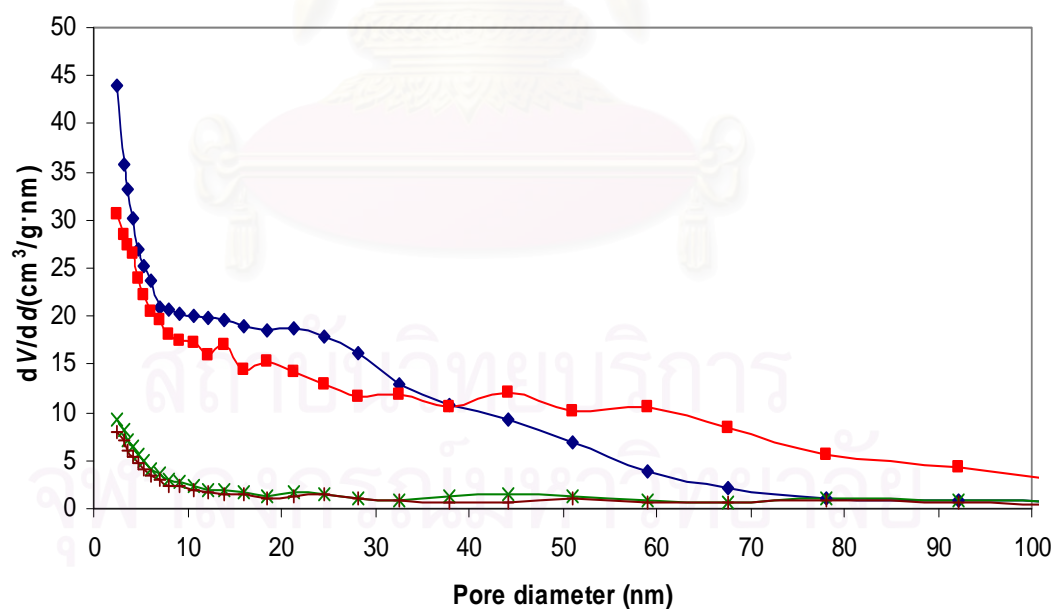


Figure 4.2 Pore size distribution of synthesized silica gel which was prepared at various pH aging; (♦) aging at pH 1, (■) aging at pH 3, (x) aging at pH 7, (+) aging at pH 9.

Total pore volume and average pore diameter are also presented in Table 4.4. It was found that total pore volume decreased when silica gel was aged in higher pH solution. Then it was observed that all synthesized silica gel gave the average pore diameter in the range 2-50 nm which was classified as mesoporous following by IUPAC classification [11]. Nitrogen adsorption-desorption isotherm of all synthesized silica samples are showed in Figure 4.1. It was found that all samples showed the hysteresis loop at high values of P/P_0 which resembled type IV of IUPAC classification [11]. This hysteresis loop indicated mesoporous property associated with capillary condensation [5]. Figure 4.2 shows a plot of the increment of pore volume per increment in pore size, versus pore size. This result was determined by the Barrett-Joyner-Halenda (BJH) method. It was found that all silica products had a wide distribution of pore and showed a high pore volume in range of small pore and decreased when pore size increased. Prepared silica at low pH aging gave a high pore volume more than prepared silica at high pH aging as the same pore diameter.

4.3.2 Effect of aging pH on purities of silica

The purities of silica gel samples, which were prepared at various pH aging, were determined by XRF technique. The results are presented in Table 4.5. The results indicated that silica gel prepared from rice husk ash by this process gave high purity of product. Generally, the purity of silica gel prepared by this method depended on a washing step. It was found that the washing of dried silica (xerogel) with deionized water is more effective than washing the silica gel (aquagel) prior drying, in removing contaminated minerals from silica [25]. This could be due to an entrapment of metal ions in the silica gel network, which might not be leached out by water washing. Drying silica gel to a very low moisture content level might be resulted in disruption of the silica gel network structure and would free the trapped mineral ions. These ions might be easily leached out by washing of dried silica gel with water.

The results in Table 4.5 indicated that prepared silica by aging at pH 1 gave the highest purity of product. It was due to differences in the silica gel network resulting from the effect of pH on the chemical form of silica. When pH of aging decreased, the major form of silica would change from SiO_2 to $\text{Si}(\text{OH})_4$. Since SiO_2 was responsible for siloxane ($-\text{Si}-\text{O}-\text{Si}-$) bonding, the decrease in pH could lead to a decrease in the extent of siloxane bonding [26]. This effect made the gel

comparatively softer (as reflected by lack of firmness) than aging at high pH. In the soft gel, metal ions could diffuse out of the gel very well when the gel dispersed in water. In high pH solution, metal ions were trapped in the gel by siloxane bonding and metal impurities liked to form metal oxide precipitate which hard to remove out of gel. Therefore low metal ions contaminate obtained when aging the gel at low pH.

4.3.3 Effect of aging pH on morphology of silica

The XRD patterns of silica sample prepared at various aging pH are showed in Figure 4.3. The results showed that XRD patterns of all aging pH were similar. They showed a broad perk centered at 2θ angle of 22° which confirmed the amorphous nature of silica. Because of all silica was formed by sol-gel technique and drying temperature was not higher than transformation temperature between amorphous and another crystalline forms. From the data, it was also indicated that the aging pH of silica did not effect on morphology of silica gel.

Table 4.5 Purities of synthesized silica which prepared at various aging pH

Aging pH	Contents (%)				
	SiO ₂	Al ₂ O ₃	Na ₂ O	SO ₃	K ₂ O
1	99.962	0.038			
3	99.769	0.096	0.053	0.081	
7	98.725	0.068	0.792	0.204	0.211
9	98.491	0.052	1.043	0.120	0.294

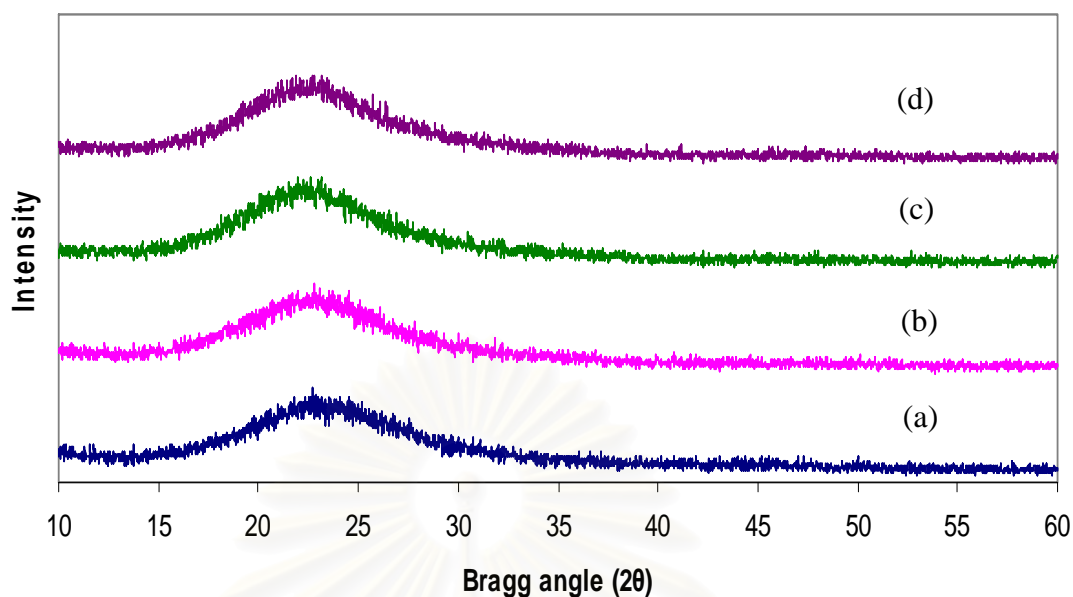


Figure 4.3 X-ray diffraction patterns of silica prepared at various aging pHs (a) pH 1, (b) pH 3, (c) pH 7, and (d) pH 9.

4.3.4 Effect of aging pH on functional groups

The major functional groups present in silica which preparation at the desired aging pH were identified by the FT-IR spectra as showed in Figure 4.4 to 4.7. The IR spectral assignments of the silica aging at pH 1 are present in Table 4.6. Presence of adsorbed water and free surface silanol groups as well as siloxane linkages can easily be conceived from the IR spectra of silica in the range 400-4000 cm^{-1} . In the spectra the broad band located in the range 3000-3700 cm^{-1} corresponds to the fundamental stretching vibration of different hydroxyl groups. The broadness of this band suggests different local environments of the OH groups. The band at 1631 cm^{-1} is assigned to the deformation mode of water molecules, which are probably trapped inside the voids. In the range 400-1500 cm^{-1} the spectrum has several bands. Band located about 459, 798 and 1084 cm^{-1} were the bond rocking, bond bending and bond stretching vibrations of the Si-O-Si units.

From IR spectra, it was observed that all spectra of silica at the desired pH aging showed the similar pattern with a small difference at intensity of 951 cm^{-1}

which presented Si–OH bond stretching. Silica aging at pH 1 gave the highest peak intensity. When aging pH was increased, intensity of Si–OH bond stretching decreased. This could be due to at low pH aging the solution had numerous proton (H^+) therefore oxygen atom on surface of silica could bond with proton very well due to high silanol group. In base solution, hydroxide ion (OH^-) competed to react with proton of silanol group on surface of silica. Consequently, the amount of silanol group on surface of silica was decreased. Therefore Si–OH bond stretching at 951 cm^{-1} disappeared at high pH aging.

Table 4.6 Assignment of IR spectral data of silica prepared by aging at pH 1

Frequency (cm^{-1})	Functional group assignment	Literature value [29]
459	Si–O bond rocking	475-465
798	OH bending (silanol)	870-800
951	Si–OH bond str.	980-935
1084	Asymmetric Si–O–Si str. in SiO_4 tetrahedral	1115-1050
1632	O–H bending (molecular water)	1625
3000-3700	O–H str. and adsorbed water	3000-3800

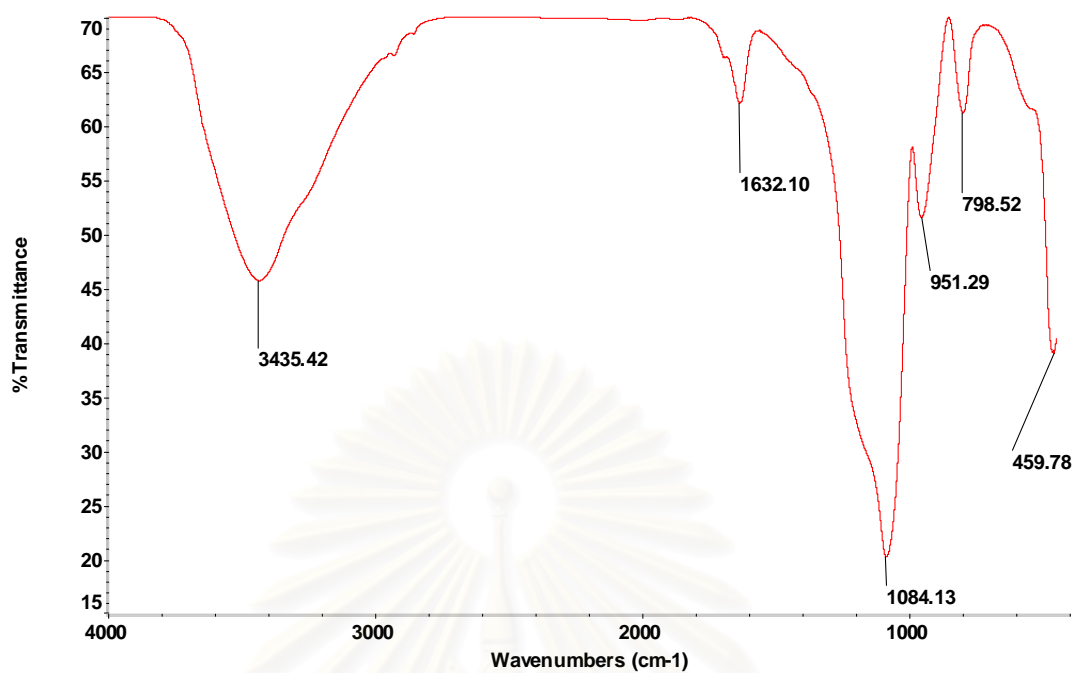


Figure 4.4 Fourier transform infrared spectrum of silica as aging at pH 1.

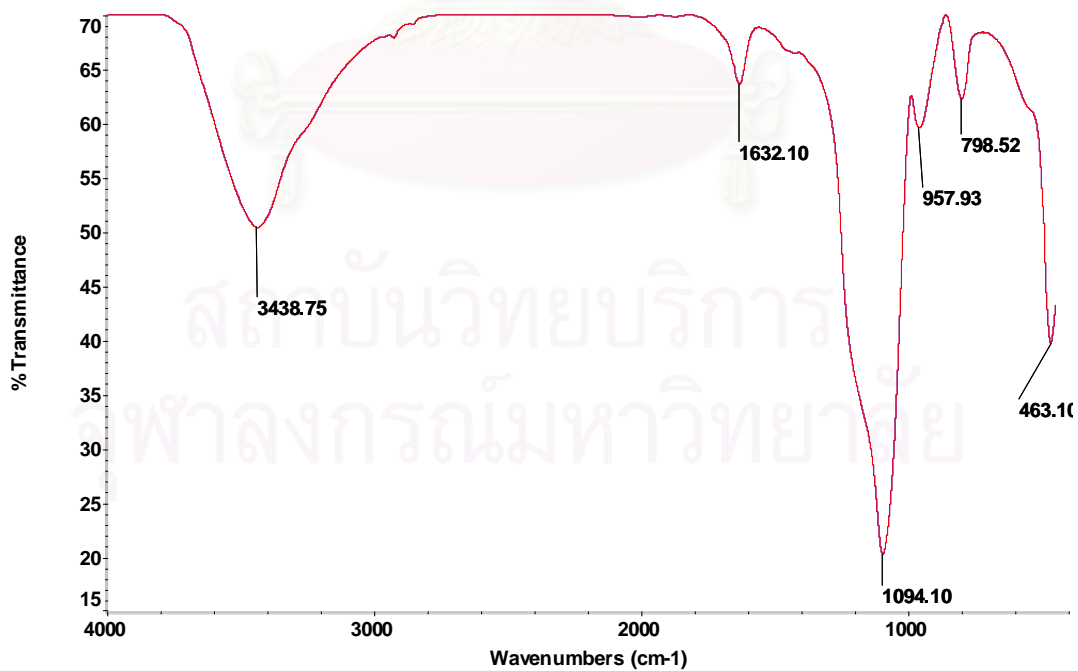


Figure 4.5 Fourier transform infrared spectrum of silica as aging at pH 3.

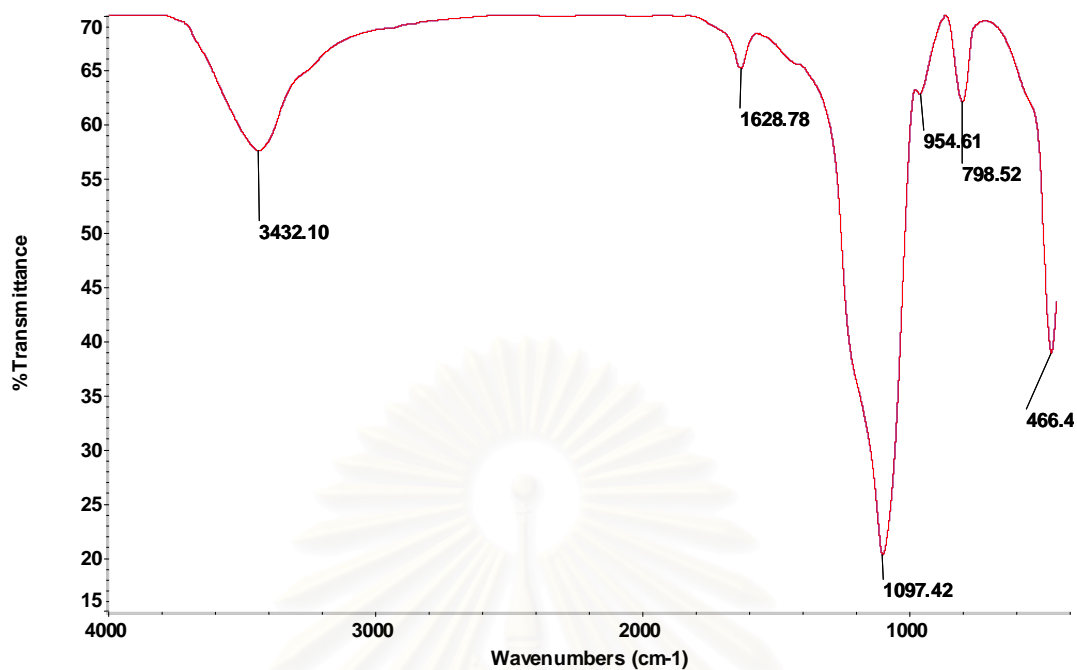


Figure 4.6 Fourier transform infrared spectrum of silica as aging at pH 7.

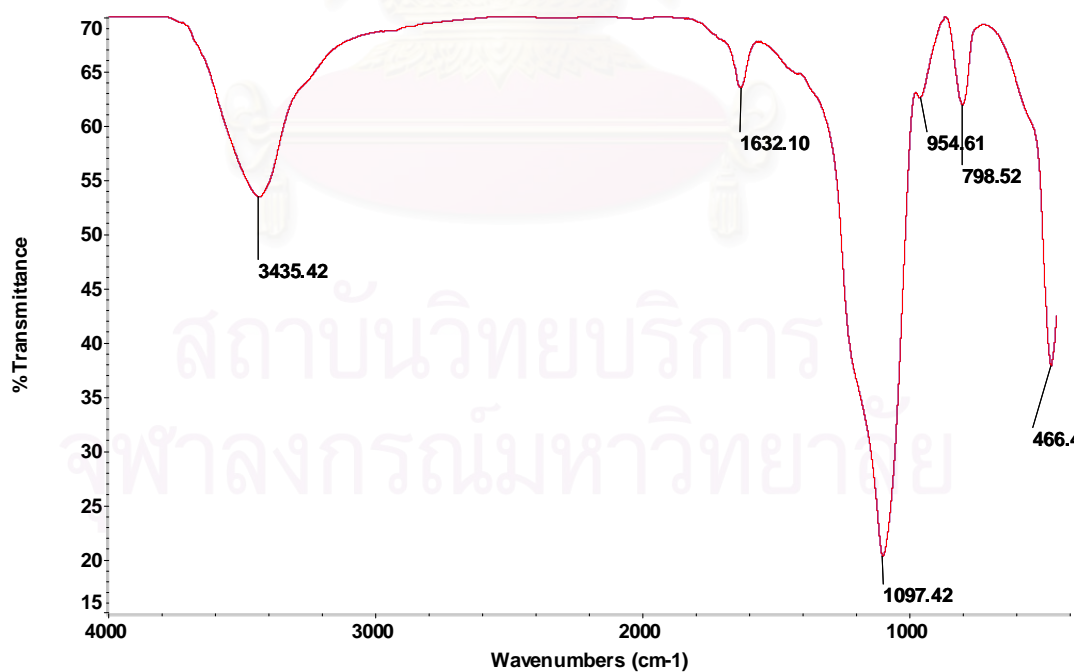


Figure 4.7 Fourier transform infrared spectrum of silica as aging at pH 9.

4.3.5 pH of dried silica gel

pH value of dried silica was determined following ASTM : D 6739-01 (Standard test method for silica-pH value). This method was performed by addition silica gel to deionized water with continuously stirred and then measured pH value. The results are presented in Table 4.7. It was found that all silica products gave pH values higher more than aging pH. This could be due to silica products adsorbed H^+ and OH^- in gel when were prepared in acid and base solution, respectively. Then it was eluted by water when silica products were measured pH values. Therefore, pH values of silica products were higher more than aging pH while silica gel 60 and silica gel 60G from Merck Company gave a pH value of 6.85 and 6.12, respectively.

Table 4.7 pH of dried silica gel which preparation at the desired aging pH and commercial adsorbents

Samples	No.1	No.2	No.3	Average
Aging pH 1	4.25	4.39	4.36	4.33±0.06
Aging pH 3	6.58	6.60	6.60	6.59±0.01
Aging pH 7	10.84	10.86	10.87	10.86±0.01
Aging pH 9	11.24	11.23	11.24	11.24±0.01
Silica gel 60	6.85	6.84	6.85	6.85±0.01
Silica gel 60G	6.12	6.11	6.13	6.12±0.01

4.4 Separation efficiency testing

Activity testing of silica samples was selected from separation efficiency of compounds using silica gel as adsorbent. In this research, column chromatography and thin-layer chromatography were selected to test for separation efficiency by comparing with two silica gel standard from commercially available of the Merck company namely silica gel 60 and silica gel 60 G for column chromatography and thin-layer chromatography, respectively.

Before testing for activity and/or separation efficiency, all of silica gel samples which were prepared from RHA by aging at desired pH, were grinded and sieved using sieve shaker instrument. After that it was measured particle size distribution. The results are presented in Figure 4.8. It was found that silica passed through the sieve number 325 mesh had mean particle sized close to the silica gel 60G for TLC of Merck company whereas silica passed through the sieve number 200 mesh presented mean particle size close to particle size of silica gel 60 for column chromatography. Therefore synthesized silica gel that passed through sieve number 325 and 200 were selected for activity and separation efficiency testing.

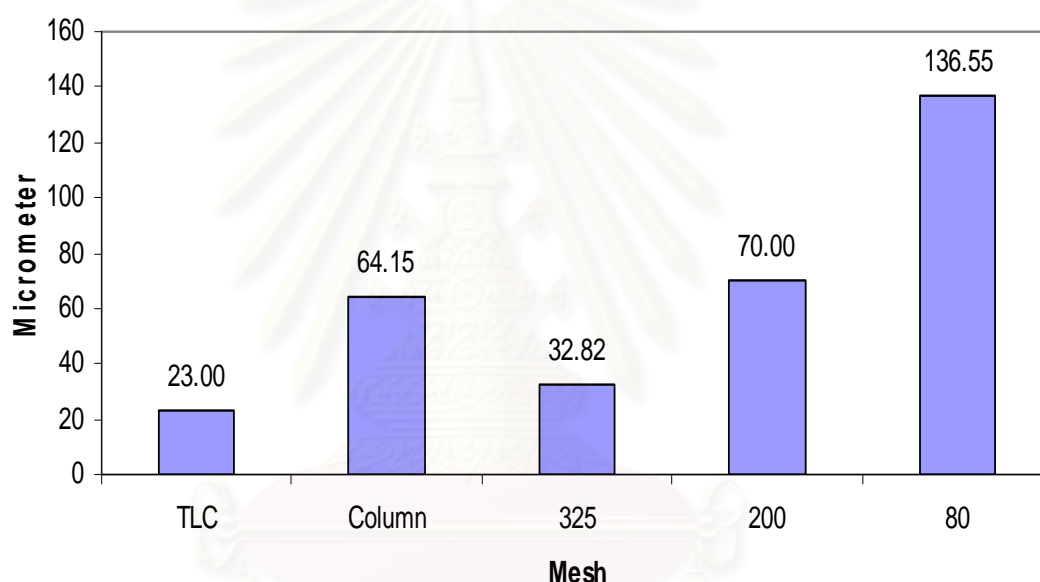


Figure 4.8 Particle size of commercials available and synthesized silica samples.

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Table 4.8 Surface area, total pore volume and average pore diameter of commercial adsorbents and synthesized adsorbents passed through the sieve number 325 and 200 mesh

Samples	Surface area (m ² /g)	Total pore volume (cm ³ /g)	Average pore diameter (nm)
Silica gel 60	441.51	0.74	6.73
Silica gel 60G	354.28	0.65	7.33
325 mesh			
Aging at pH 1	662.68	1.17	7.03
Aging at pH 3	428.60	1.27	11.87
Aging at pH 7	88.71	0.61	27.64
Aging at pH 9	74.25	0.56	29.92
200 mesh			
Aging at pH 1	622.06	1.12	7.23
Aging at pH 3	298.18	1.37	18.42
Aging at pH 7	82.98	0.79	38.04
Aging at pH 9	72.31	0.60	33.43

Surface area, total pore volume and average pore diameter of commercial adsorbents and sieved silica gel are showed in Table 4.8. Silica gel 60 had a specific surface area higher than silica gel 60G but total pore volume and average pore diameter of them was similar. Adsorption isotherms of two commercial adsorbents are presented in Appendix A25 and A27. Chemical compositions of commercial adsorbents are showed in Table 4.9. It was found that silica gel 60 had purities of silica higher than silica gel 60G. Since silica gel 60G was mixed with binder (CaSO₄) to help holding between silica and glass plates. Generally, it was added to silica gel at 10 % by weights.

Table 4.9 Chemical compositions of commercial adsorbents and synthesized silica gel

Compounds	Concentration (%)		
	Silica gel 60	Silica gel 60G	Synthesized silica gel at pH 1
SiO ₂	99.640	87.705	99.962
Na ₂ O	-	0.113	-
MgO	-	0.042	-
Al ₂ O ₃	-	0.041	0.038
SO ₃	0.100	7.547	-
CaO	0.140	4.474	-
TiO ₂	0.060	0.027	-
Fe ₂ O ₃	-	0.044	-
SrO	-	0.005	-
ZrO ₂	-	0.003	-

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4.4.1 The separation efficiency of synthesized silica sample using column chromatography technique

Activity and/or separation efficiency testing of synthesized silica gel samples were performed using flash-column chromatography and detected by UV absorption at 254 nm. The mixed solution of naphthalene (5000 ppm) and α -naphthol (5000 ppm) in ethyl acetate was selected for the separation efficiency testing because the two compounds were similar structure and showed a different of polarity. Furthermore, they contained conjugated double bonds which were detected by UV absorption. A mobile phase was a solvent mixture of hexane in dichloromethane (50:50). The testing results were presented in a form of chromatograms (Figures 4.9-4.13). The separation efficiency was reported in term of resolution value which was calculated from chromatogram using equation 3.2 (in page 33). The resolution values of the silica gel samples are presented in Figure 4.14. The resolution value was used for evaluation of separation efficiency. In general, high resolution value yielded better separation efficiency. In addition, the mixed compounds could be completely separated when resolution value should be equal to be or more than 1.5 [18]. When consider only synthesized adsorbents, it was found that synthesized silica at pH aging 1 gave the highest resolution of 1.69 and showed completely separation. Synthesized silica samples prepared at pH 3, 7 and 9 to result the resolution value of 1.19, 1.07 and 0.99, respectively. These results demonstrated that the synthesized silica samples which were prepared at lower pH aging gave higher resolution value, which corresponding to that silica sample with higher specific surface area to result a higher resolution value. When compared with silica gel 60 from Merck Company, it was found that commercial silica gave the resolution of 1.97 with a little higher than synthesized silica at aging pH 1. From Table 4.8, it was found that specific surface area of silica gel 60 had a lower surface area than synthesized silica at aging pH 1 but gave a better resolution. It may be due to pore size distribution as showed in Figure 4.15. Silica gel 60 gave a narrow pore size distribution in range 0-20 nm whereas our synthesized silica showed a wide pore size distribution. Then range 0-20 nm may be suitable for separation of compounds. Therefore, silica gel 60 had a high resolution value than our silica gel.

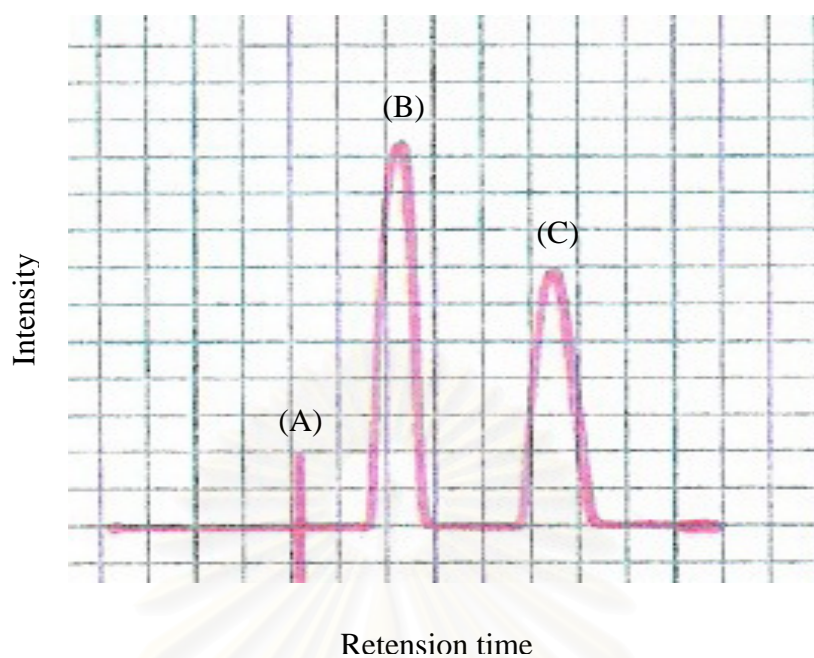


Figure 4.9 Chromatogram of silica gel 60 from Merck (A) injection point, (B) naphthalene, and (C) α -naphthol.

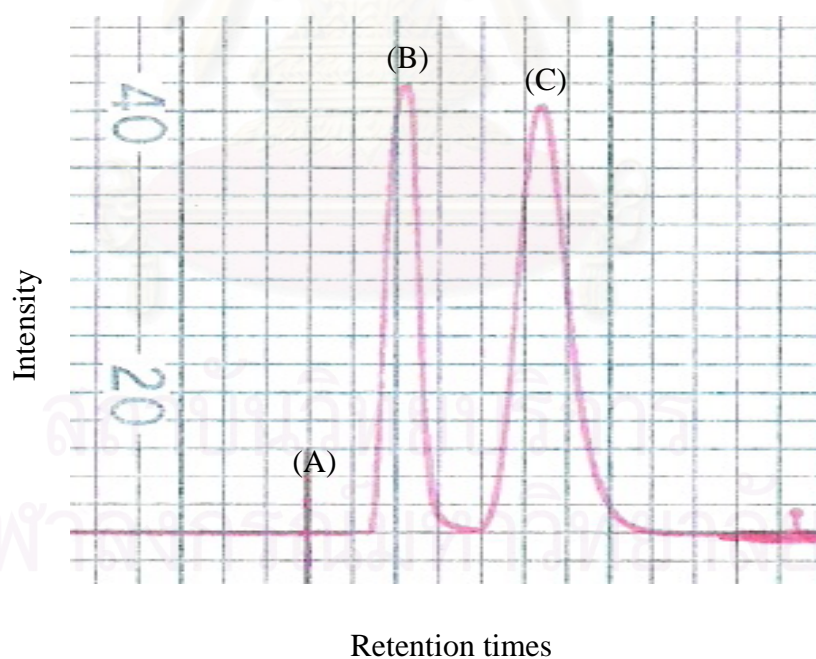


Figure 4.10 Chromatogram of silica gel which was prepared at aging at pH 1 (A) injection point, (B) naphthalene, and (C) α -naphthol.

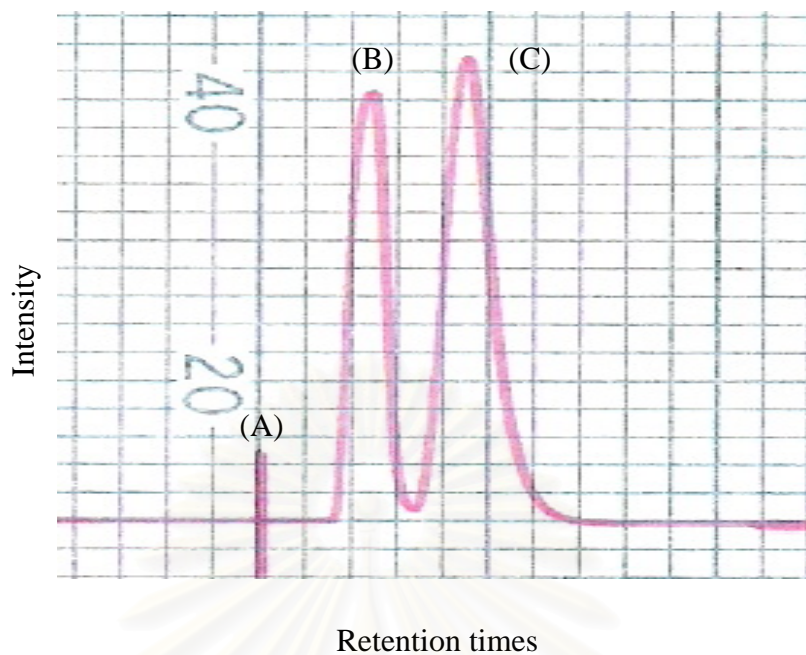


Figure 4.11 Chromatogram of silica gel which was prepared at aging at pH 3, (A) injection point, (B) naphthalene, and (C) α -naphthol.

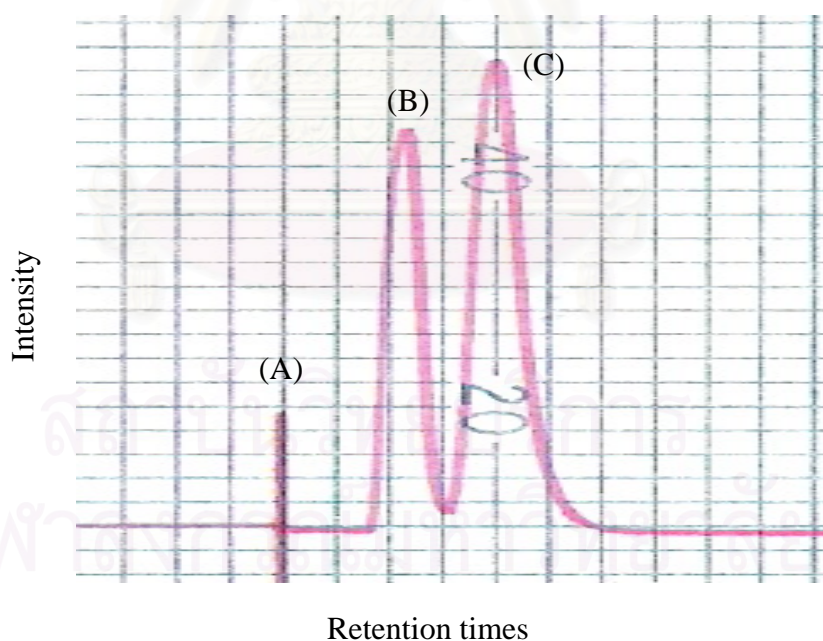


Figure 4.12 Chromatogram of silica gel which was prepared at aging at pH 7, (A) injection point, (B) naphthalene, and (C) α -naphthol.

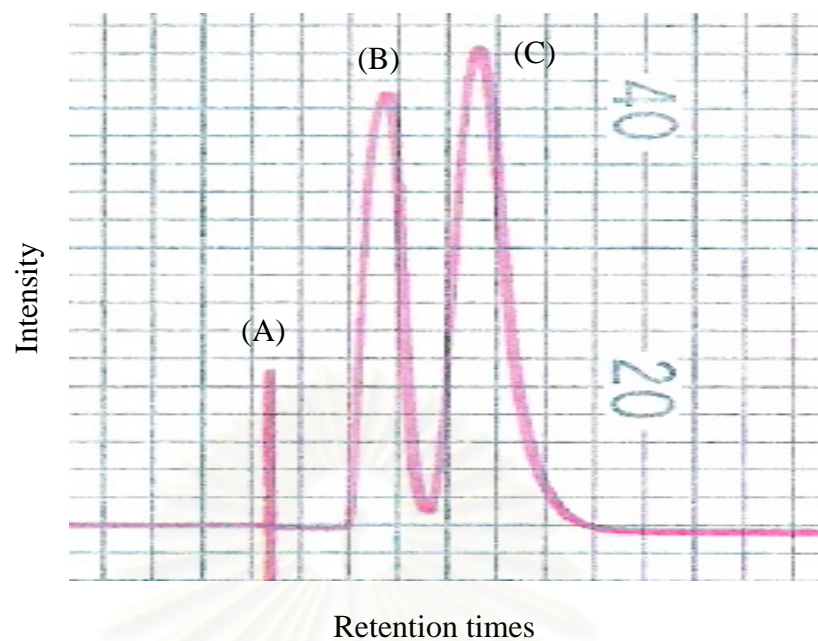


Figure 4.13 Chromatogram of silica gel which was prepared at aging at pH 9 (A) injection point, (B) naphthalene, and (C) α -naphthol.

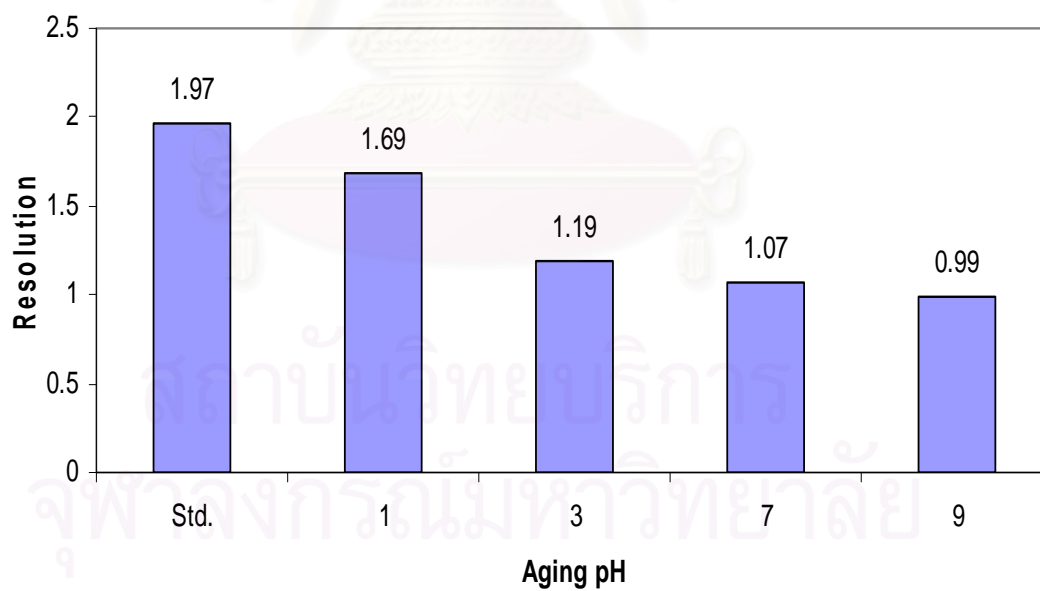


Figure 4.14 Resolution of silica gel samples which were prepared at the desired aging pH.

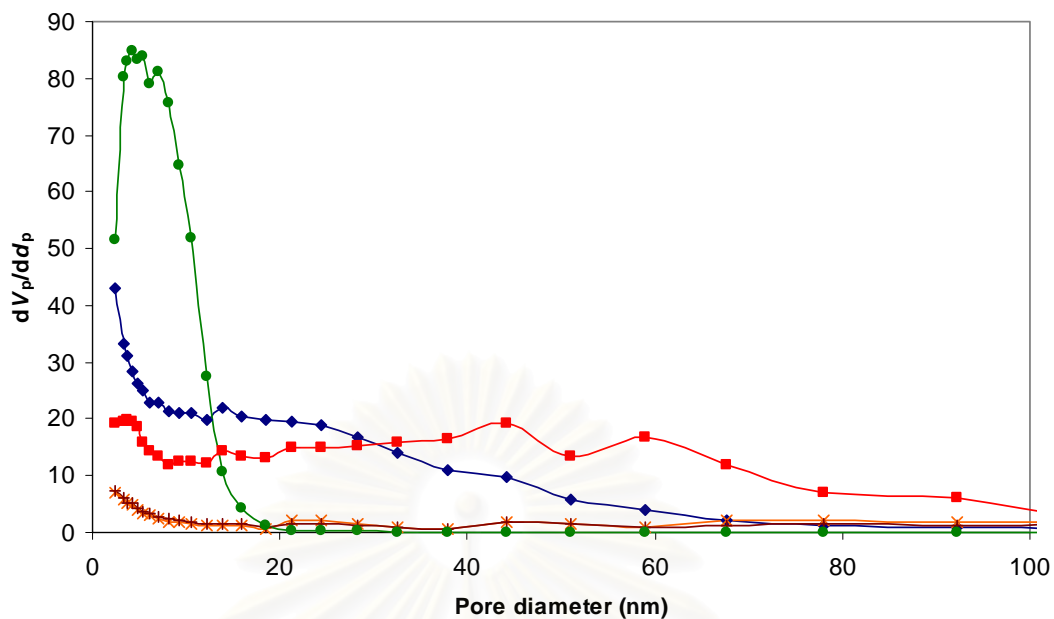


Figure 4.15 Pore size distribution of synthesized silica gel which was sieved through 200 mesh at the desired aging pH; (♦) aging at pH 1, (■) aging at pH 3, (x) aging at pH 7, (+) aging at pH 9, (●) silica gel 60.

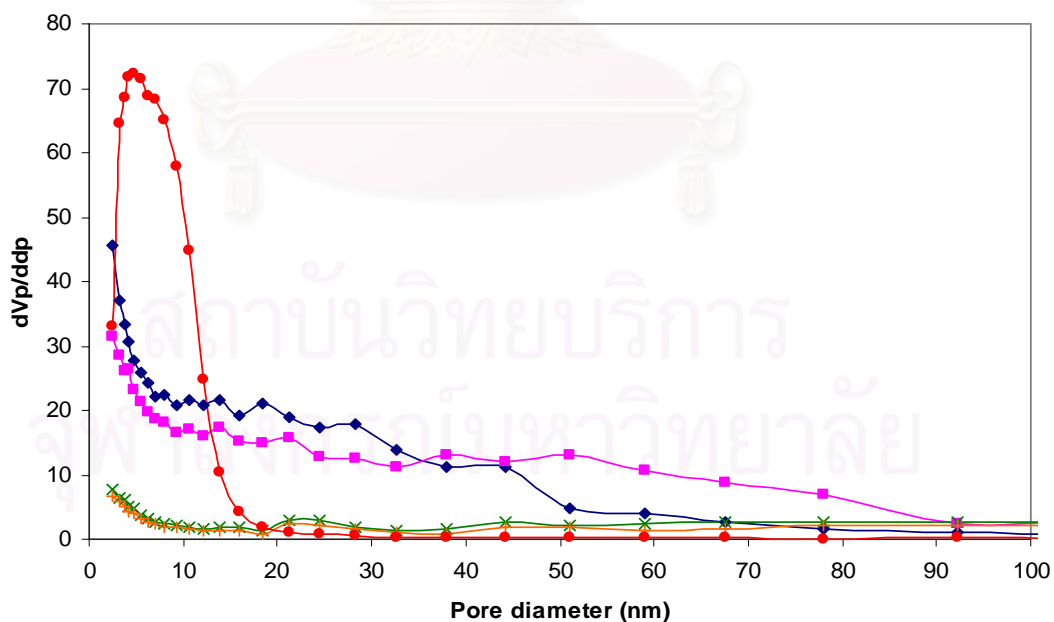


Figure 4.16 Pore size distribution of synthesized silica gel was sieved through 325 mesh at the desired aging pH; (♦) aging at pH 1, (■) aging at pH 3, (x) aging at pH 7, (+) aging at pH 9, (●) silica gel 60.

4.4.2 The separation efficiency of synthesized silica samples using TLC-technique

The separation efficiency (resolution) of the synthesized silica gel samples were also evaluated by thin-layer chromatography technique. The TLC-plates of each synthesized silica and standard silica of the Merck Company were prepared by coating on glass plates (5x20cm) [35]. These standard compounds, α -naphthol, diphenylamine and 1-naphthylamine, were used for separation efficiency testing. The TLC plates testing were spotted with standard mixture. These spotted TLC plates were developed with 100% chloroform in TLC-tank. After that the position of each standard compound in developed TLC plate was detected by iodine vapor and then the R_f value of each compound was calculated. The results are presented in Figure 4.17, 4.18 and Table 4.10.

Figure 4.17 showed the separation efficiency of TLC plate coated with silica gel 60G from Merck Company. The result indicated that when the commercially available silica was used in TLC plate gave excellent resolution. The R_f value of α -naphthol, diphenylamine and 1-naphthylamine were 0.36, 0.71 and 0.55, respectively.

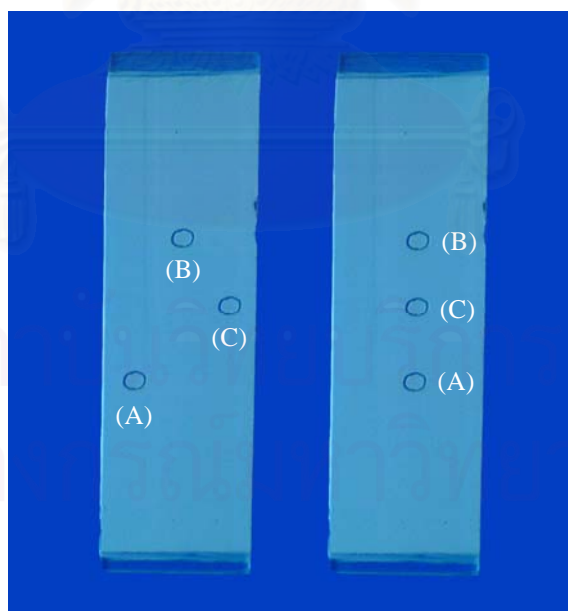


Figure 4.17 TLC of three standards; (A) α -naphthol, (B) diphenylamine and (C) 1-naphthylamine using silica gel 60 G as adsorbent (a) individual spot (b) one mixed spot.

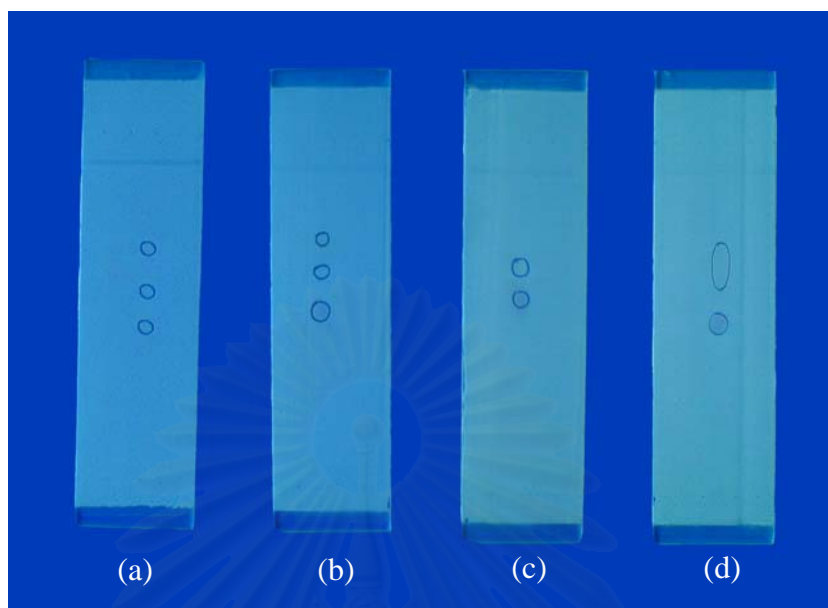


Figure 4.18 TLC testing of various aging pHs; (a) pH 1 (b) pH 3 (c) pH 7 and (d) pH 9.

Table 4.10 R_f values from various types of stationary phase

Samples	R_f		
	α -naphthol	Diphenylamine	1-naphthylamine
Silica gel 60 G	0.36	0.71	0.55
Aging pH 1	0.45	0.68	0.55
Aging pH 3	0.51	0.71	0.62
Aging pH 7	0.55		0.64
Aging pH 9	0.48		0.65

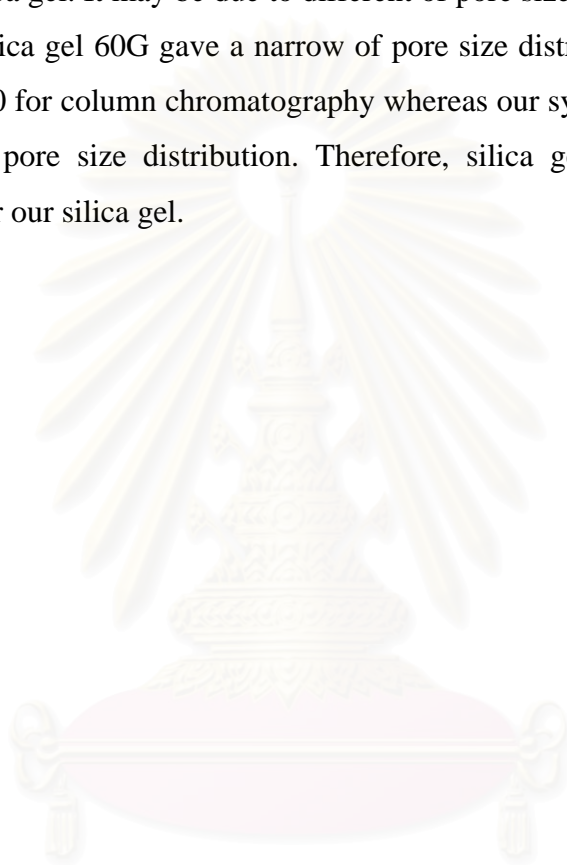
Then the synthesized silica gel samples from our research were performed the TLC technique experiment in identical to the former experiment. The results are presented in Figure 4.18, and the calculated R_f values of each testing experiment was summarized in Table 4.10. These results demonstrated that the silica gel samples prepared at aging pH 1 and 3 gave the better resolution than samples which were prepared at aging pH 7 and 9. From these results also indicated that the resolution of each silica gel sample was better on specific surface area and also particle sized of silica adsorbent. When compared the resolution of these experiment to that of commercially available in plate a and plate b in Figure 4.17 hence the resolution poorer than silica gel of Merck silica. It might due to the effect of binding material for improving of silica adhere to the glass plate. And then silica gel 60G contained 10% of CaSO_4 as a binder but there was not any binder in our silica samples. Therefore we have to observe the effect of binding material on the resolution of our synthesized silica gel samples.

4.4.2.1 Effect of binder types on separation efficiency

The binder effecting on separation efficiency of our synthesized silica gel samples was observed by adding 10% of various types of binder including CaSO_4 , BaSO_4 , MgSO_4 and Na_2SO_4 . Then TLC-plates of each silica gel plus binder were prepared by the technique that identical to the former experiment. The separation efficiency of prepared TLC-plates was performed in identical condition and mobile phase with the former experiment (4.2.2). The separation efficiency of TLC-plates with CaSO_4 , BaSO_4 , MgSO_4 and Na_2SO_4 as binder are presented in Figure 4.19, 4.20, 4.21 and 4.22, respectively. The resolution of TLC-plates with different binder (CaSO_4 , BaSO_4 , MgSO_4 and Na_2SO_4) was reported in term of R_f value which were summarized in the Table 4.11, 4.12, 4.13 and 4.14, respectively.

These results indicated that prepared silica gel by aging at pH 1 was mixed with various binders to give the better separation efficiency than the silica gel samples which were prepared at aging pH higher. These results also indicated that when the silica gel sample at aging pH 1 was mixed with four different binders (CaSO_4 , BaSO_4 , MgSO_4 and Na_2SO_4), the silica gel sample with CaSO_4 binder gave a better separation efficiency than the other types of binder as showed in Figure 4.23 and Table 4.15. It might due to the effect of humidity in prepared TLC-plates which obstructed

adsorption capability of silica gel. The selected binders showed a different of humidity adsorption. CaSO_4 has lower humidity adsorption ability than among the other type of binder (BaSO_4 , Na_2SO_4 and MgSO_4) [36]. Adhering between silica gel and glass plate was important factor which also affected to separation efficiency. Then CaSO_4 showed adhering capability better than the others binder. The results also demonstrated that the silica gel 60G gave a litter better resolution than our synthesized silica gel. It may be due to different of pore size distribution as showed in Figure 4.16. Silica gel 60G gave a narrow of pore size distribution in range 0-20 nm like silica gel 60 for column chromatography whereas our synthesized silica showed a wide range of pore size distribution. Therefore, silica gel 60G had a separation efficiency better our silica gel.



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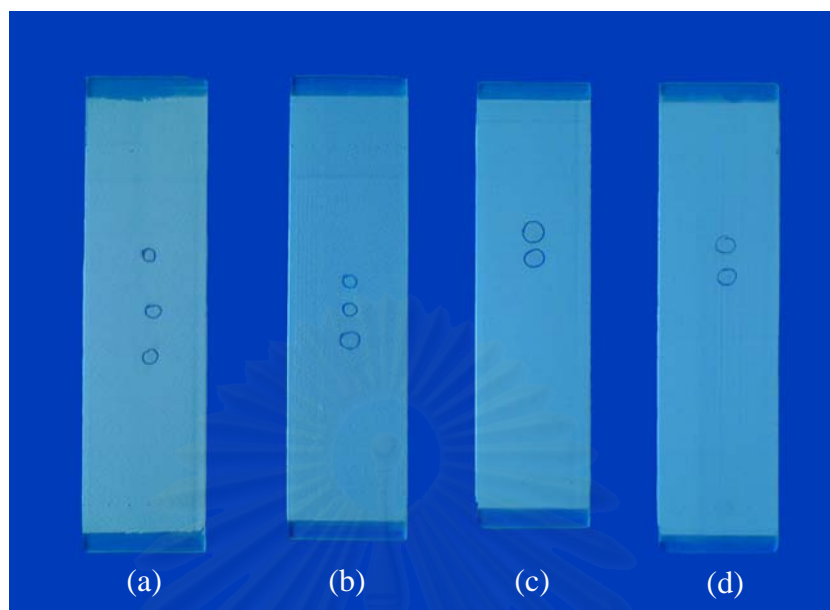


Figure 4.19 TLC testing of various aging pH mixed with 10% CaSO₄; (a) pH 1 (b) pH 3 (c) pH 7 and (d) pH 9.

Table 4.11 R_f values of desired aging pH mixed with CaSO₄ binder

pH	R _f		
	α-naphthol	Diphenylamine	1-naphthylamine
1	0.46	0.71	0.60
3	0.45	0.63	0.54
7	0.68		0.75
9	0.65		0.75

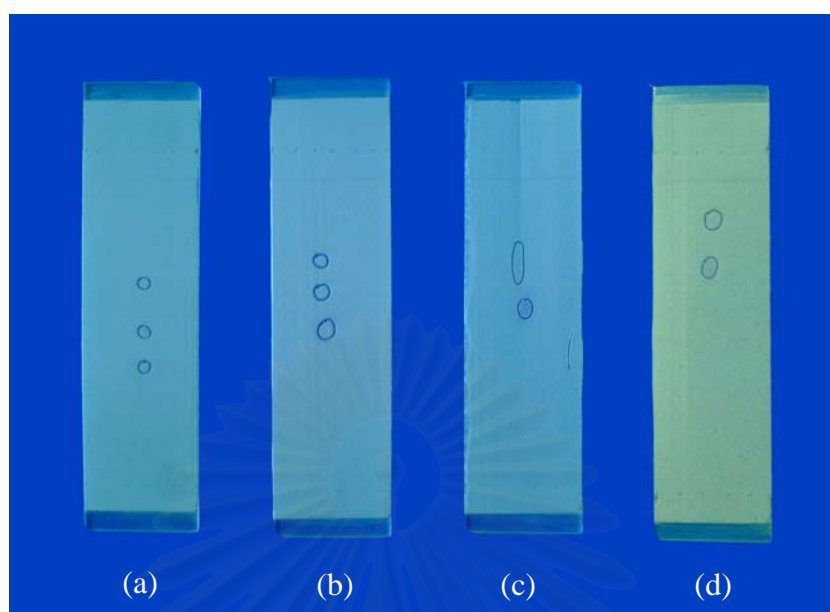


Figure 4.20 TLC testing of various aging pH mixed with 10% BaSO₄; (a) pH 1 (b) pH 3 (c) pH 7 and (d) pH 9.

Table 4.12 R_f values of desired aging pH mixed with BaSO₄ binder

pH	R _f		
	α-naphthol	Diphenylamine	1-naphthylamine
1	0.39	0.63	0.49
3	0.45	0.63	0.55
7	0.53	0.67	
9	0.64	0.77	

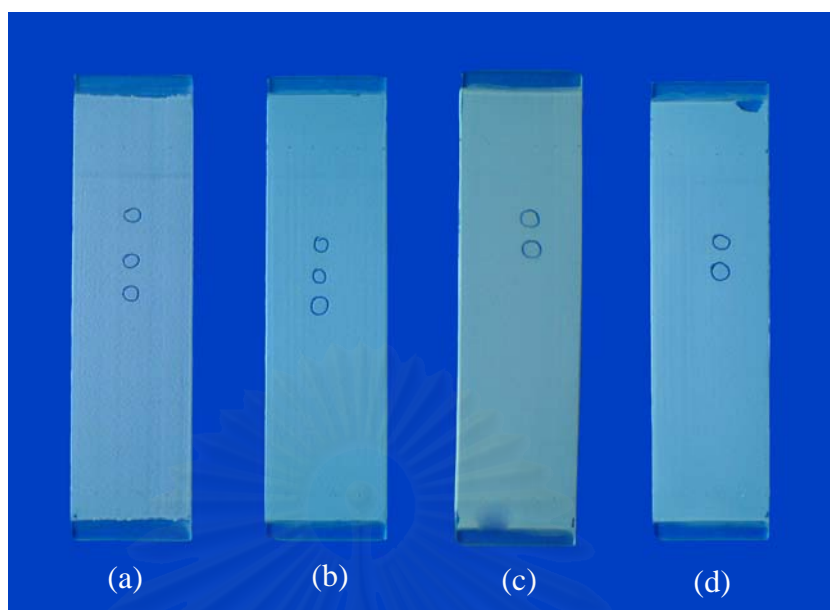


Figure 4.21 TLC testing of various aging pH mixed with 10% MgSO₄; (a) pH 1 (b) pH 3 (c) pH 7 and (d) pH 9.

Table 4.13 R_f values of desired aging pH mixed with MgSO₄ binder

pH	R _f		
	α -naphthol	Diphenylamine	1-naphthylamine
1	0.57	0.80	0.67
3	0.56	0.71	0.63
7	0.72		0.79
9	0.66		0.73

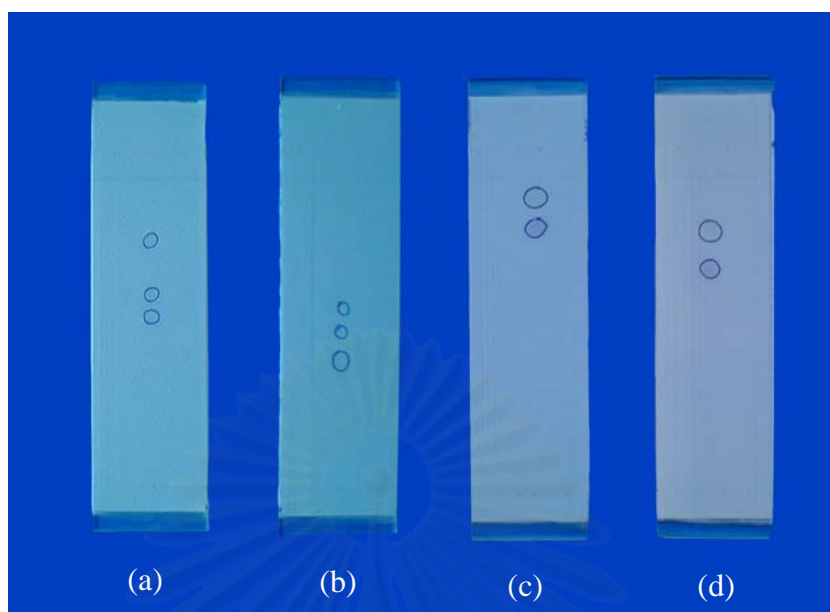


Figure 4.22 TLC testing of various aging pH mixed with 10%Na₂SO₄; (a) pH 1 (b) pH 3 (c) pH 7 and (d) pH 9.

Table 4.14 R_f values of desired aging pH mixed with Na₂SO₄ binder

pH	R _f		
	α-naphthol	Diphenylamine	1-naphthylamine
1	0.51	0.75	0.59
3	0.39	0.55	0.47
7	0.77		0.86
9	0.67		0.75

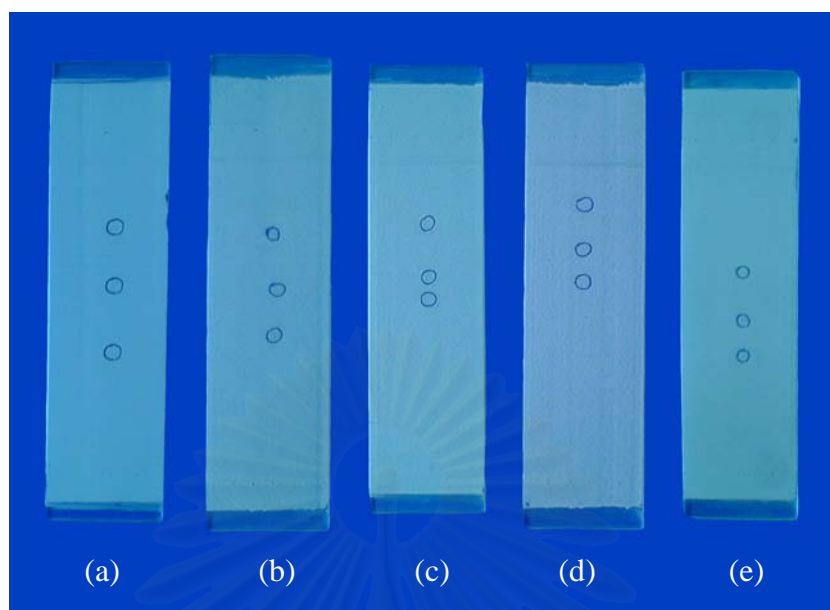


Figure 4.23 TLC testing of silica aging pH 1 mixed with various binders; (a) silica gel 60 G, (b) 10%CaSO₄, (c) 10%BaSO₄, (d) 10%MgSO₄ and (e) 10%Na₂SO₄.

Table 4.15 R_f values of desired aging pH 1 mixed with binders

Samples	R _f		
	α -naphthol	Diphenylamine	1-naphthylamine
Silica gel 60 G	0.36	0.71	0.55
Mixed 10% CaSO ₄	0.46	0.71	0.60
Mixed 10% BaSO ₄	0.39	0.63	0.49
Mixed 10% MgSO ₄	0.57	0.80	0.67
Mixed 10% Na ₂ SO ₄	0.51	0.75	0.59

CHAPTER V

CONCLUSIONS

The objectives of the present thesis are study on preparation high grade silica gel adsorbent from rice husk ash and tested separation efficiency of mixed compounds comparing with two commercially available adsorbents. Because these silica adsorbent are used in a wide range of separation and purification field which its price is very expensive and have to import from foreign countries. In this thesis, rice husk ash has been shown a high potential to be used as starting material for high grade purity silica gel adsorbent.

From research results, synthesized silica at aging pH 3 gave the highest yield of 85.19% and this percent yield decreased when silica gel was prepared at higher aging pH. All synthesized silica samples and two commercially available adsorbents showed type IV isotherm and also presented hysteresis loop at high values of P/P_0 which indicated mesoporous materials. From BET equation, the highest specific surface area was obtained when silica gel sample was aged at pH 1. From XRF results, synthesized silica gel at aging pH 1 also gave the highest purity of 99.962%. Results from XRD technique confirmed that all synthesized silica gel samples showed amorphous nature of silica. IR spectra of all synthesized sample presented a little difference of about 951 cm^{-1} which presented Si-OH bond stretching. This peak showed the strongest when the silica samples were aged at pH 1 which indicated that the surface contained a lot of silanol groups.

For separation efficiency testing by column chromatography, synthesized silica at aging pH 1 gave the highest resolution of 1.69 which can completely separate mixed compounds whereas the samples which prepared at higher aging pH showed poor resolution and cannot separate mixed compounds correspond to the results of specific surface area of silica products. Then synthesized silica at aging pH 1 showed the highest of surface area. Silica gel 60 gave a little higher resolution value (1.96) when compared with silica gel sample which prepared at aging pH 1. For thin-layer chromatography, synthesized silica gel aging at pH 1 showed the best separation when compared to the other samples. Adding CaSO_4 as binder can improve the

separation efficiency more than the other types of binder but it gave a little lower separation efficiency when compared with silica gel 60G. From the results of separation efficiency with two techniques, it was found that commercial adsorbents showed a lower of surface area but gave a better of separation efficiency when compared to the silica product at aging pH 1. It may be due to the effect of pore size distribution. Commercial adsorbents gave a narrow of pore size distribution more than our synthesized adsorbents.

As future work, pore size distribution of synthesized silica should be controlled. Pore size distribution can be improved by adding additives such as water soluble polymer or alcohol.



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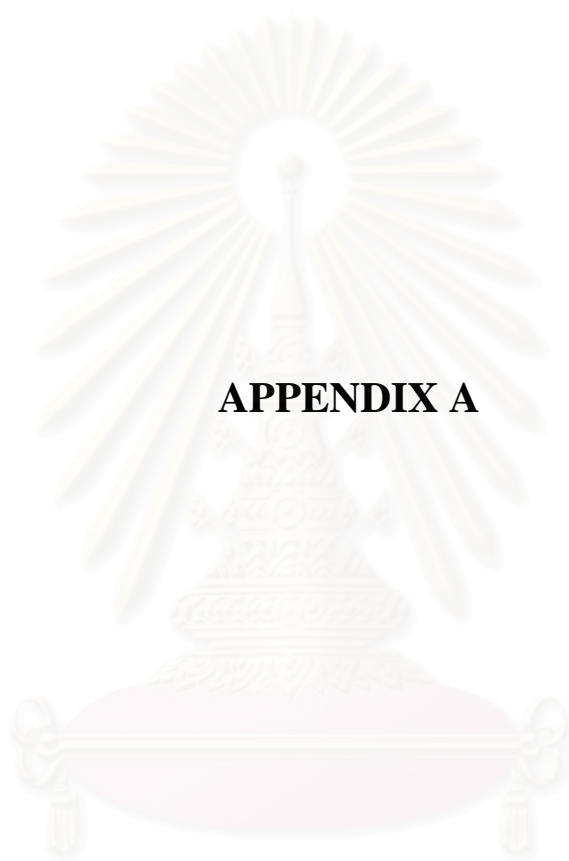
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APPENDICES

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย



APPENDIX A

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

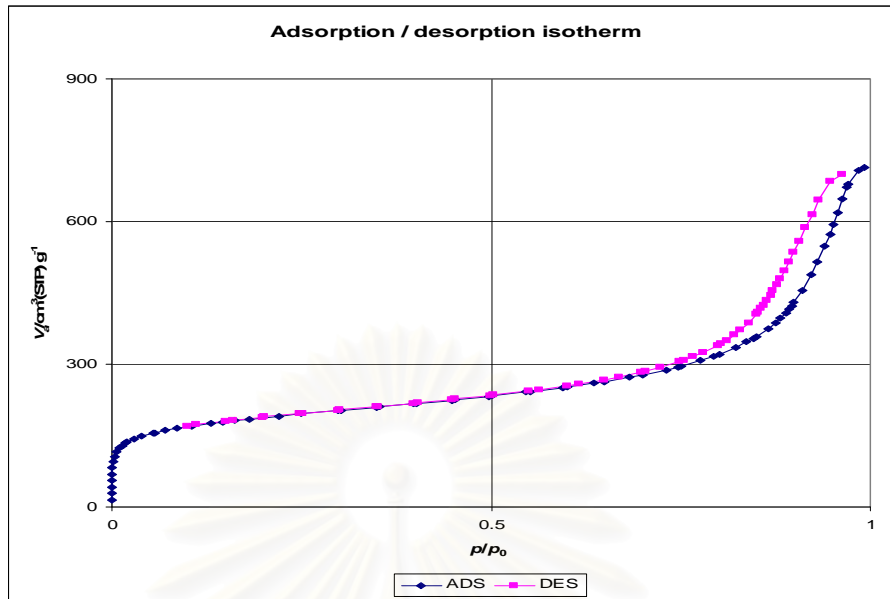


Figure A1 Adsorption isotherm of synthesized silica at aging pH 1.

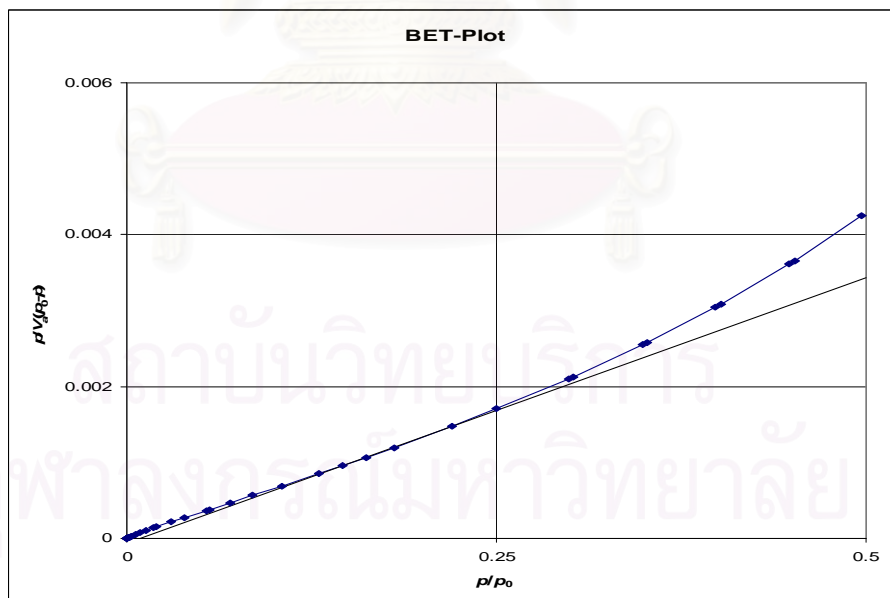


Figure A2 BET plot of synthesized silica at aging pH 1.

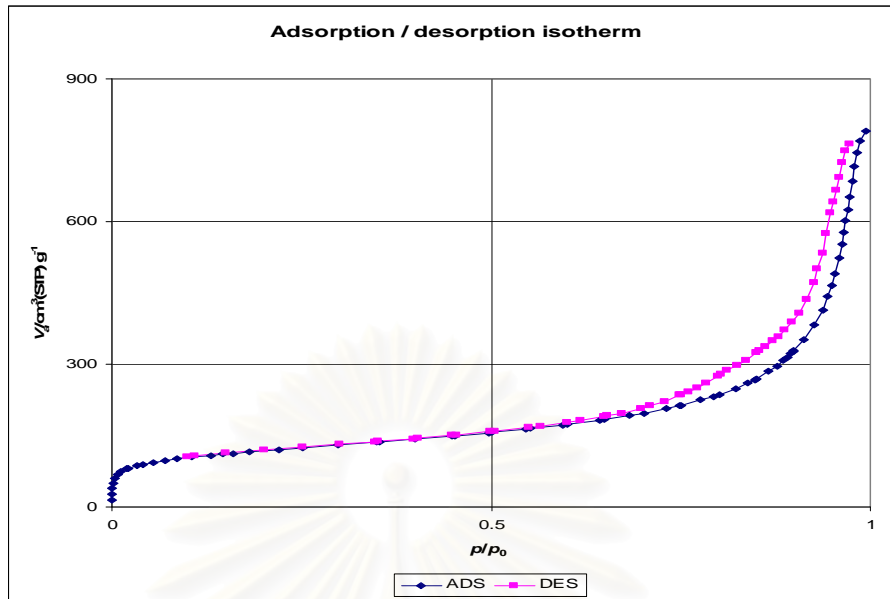


Figure A3 Adsorption isotherm of synthesized silica at aging pH 3.

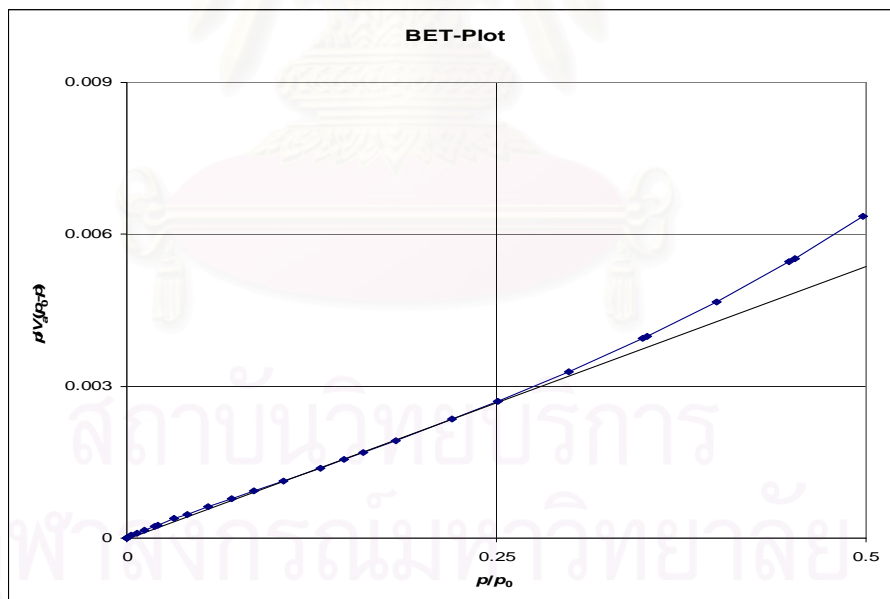


Figure A4 BET plot of synthesized silica at aging pH 3.

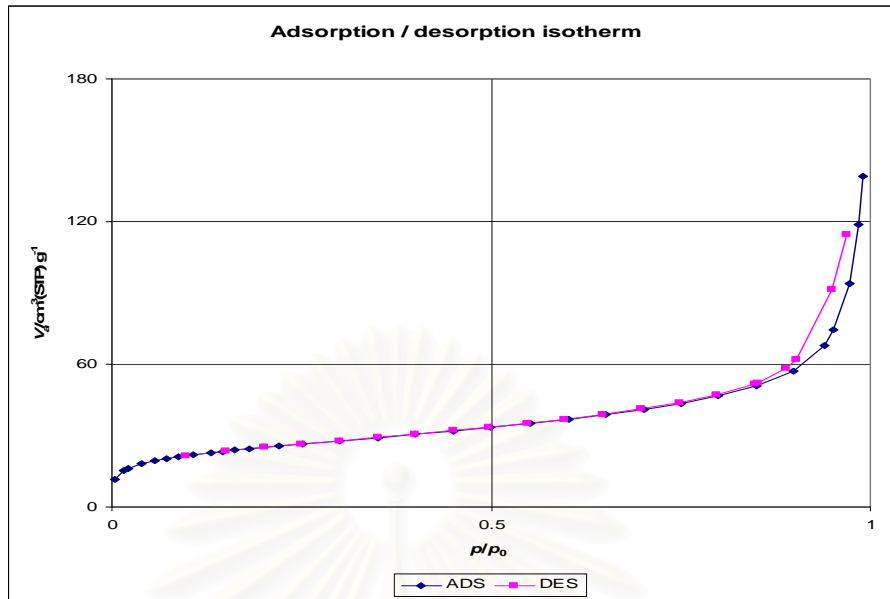


Figure A5 Adsorption isotherm of synthesized silica at aging pH 7.

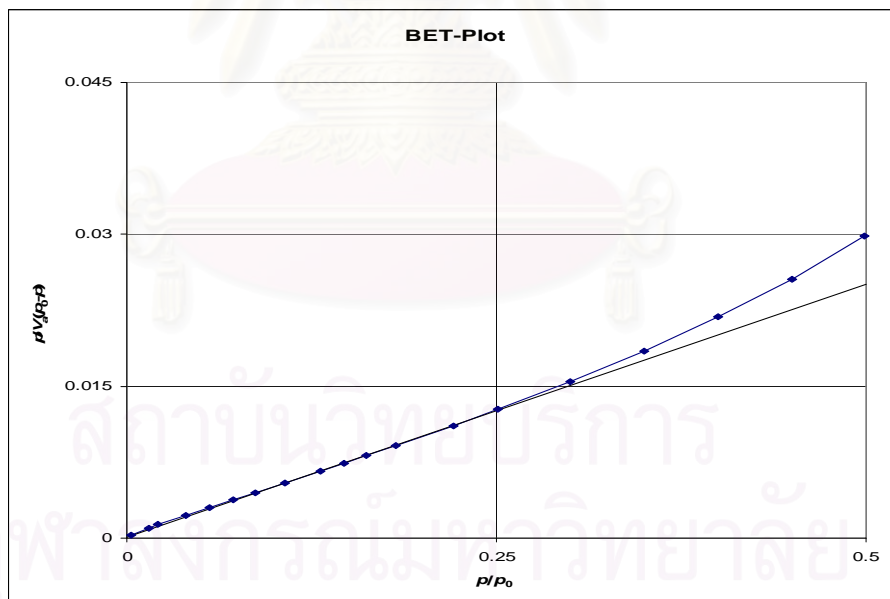


Figure A6 BET plot of synthesized silica at aging pH 7.

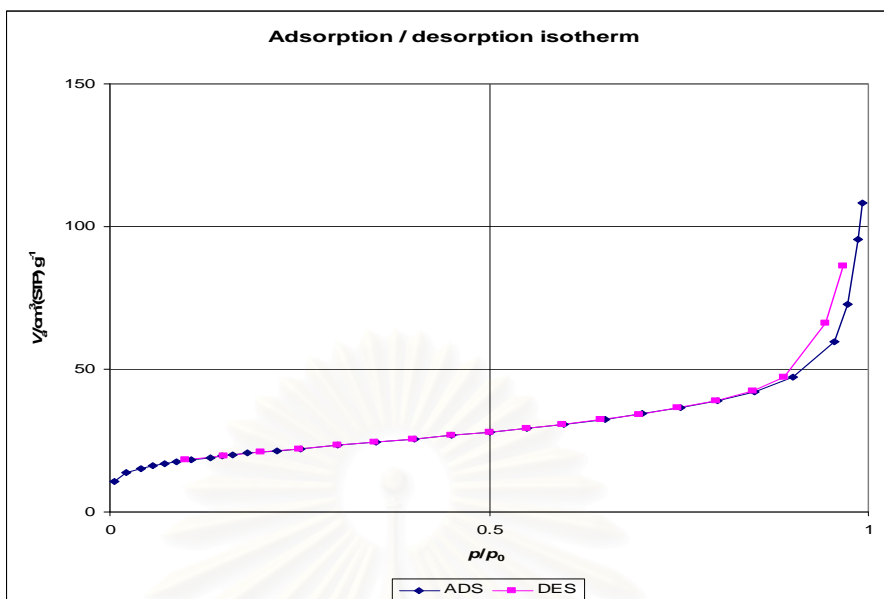


Figure A7 Adsorption isotherm of synthesized silica at aging pH 9.

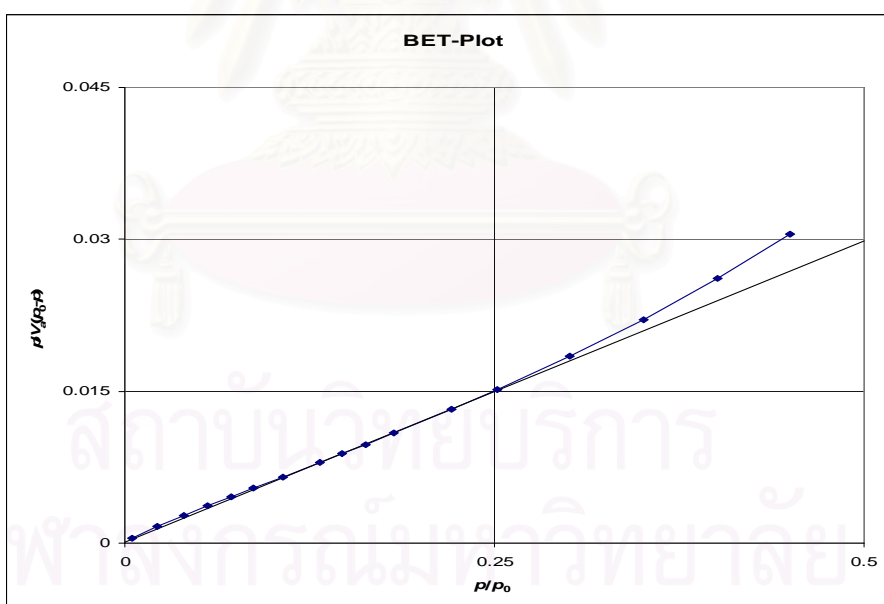


Figure A8 BET plot of synthesized silica at aging pH 9.

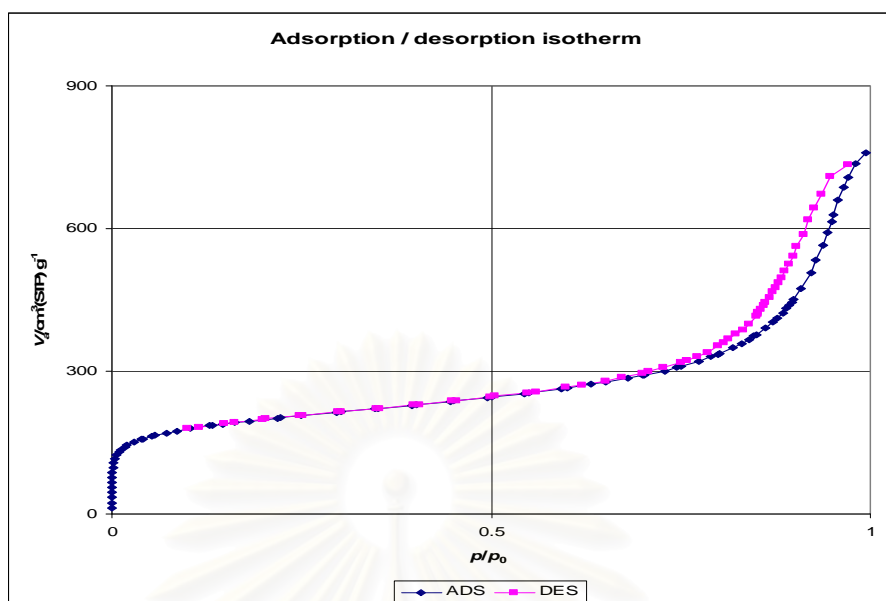


Figure A9 Adsorption isotherm of synthesized silica at aging pH 1 which was sieved through 325 mesh.

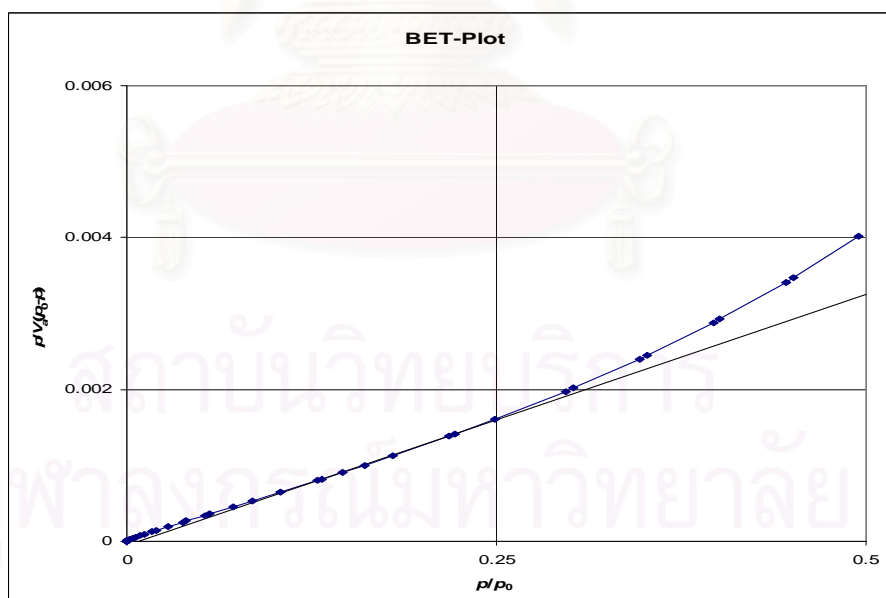


Figure A10 BET plot of synthesized silica at aging pH 1 which was sieved through 325 mesh.

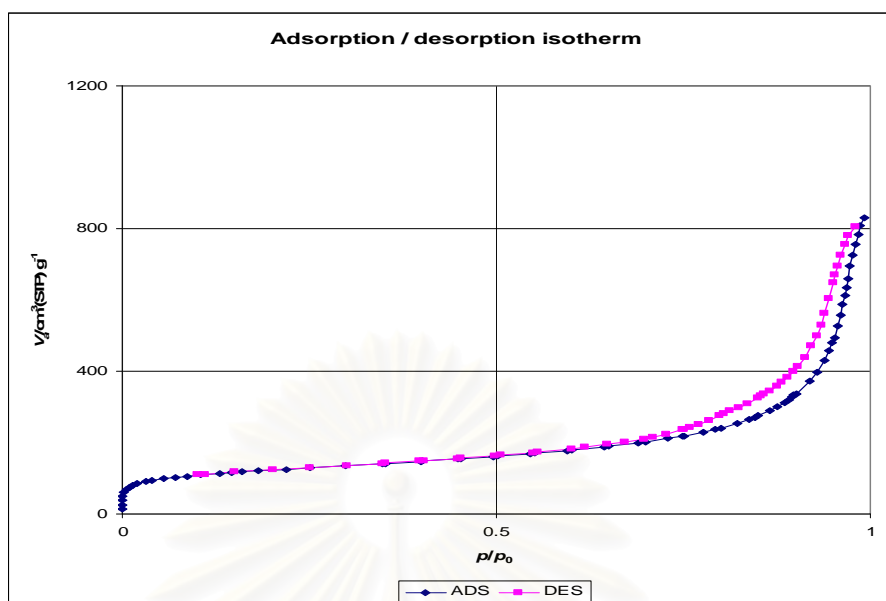


Figure A11 Adsorption isotherm of synthesized silica at aging pH 3 which was sieved through 325 mesh.

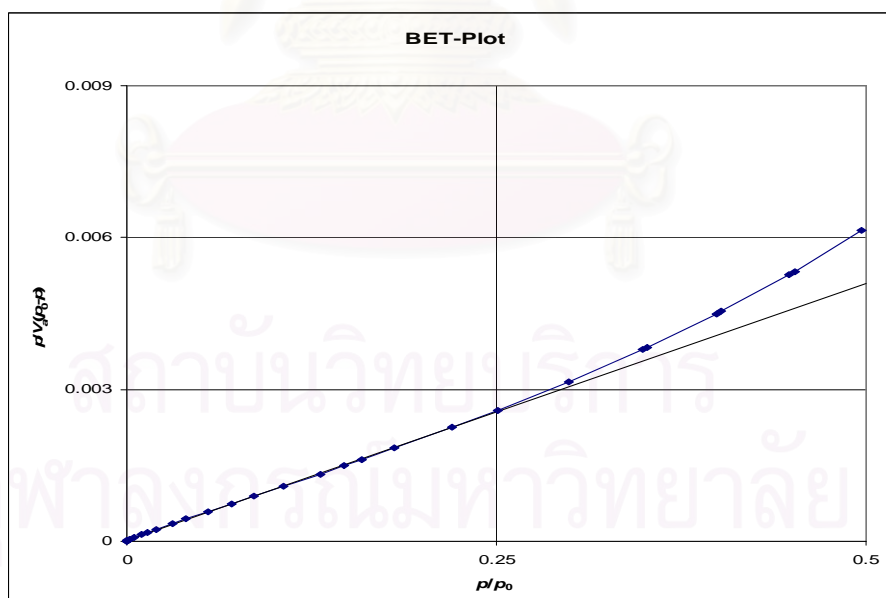


Figure A12 BET plot of synthesized silica at aging pH 3 which was sieved through 325 mesh.

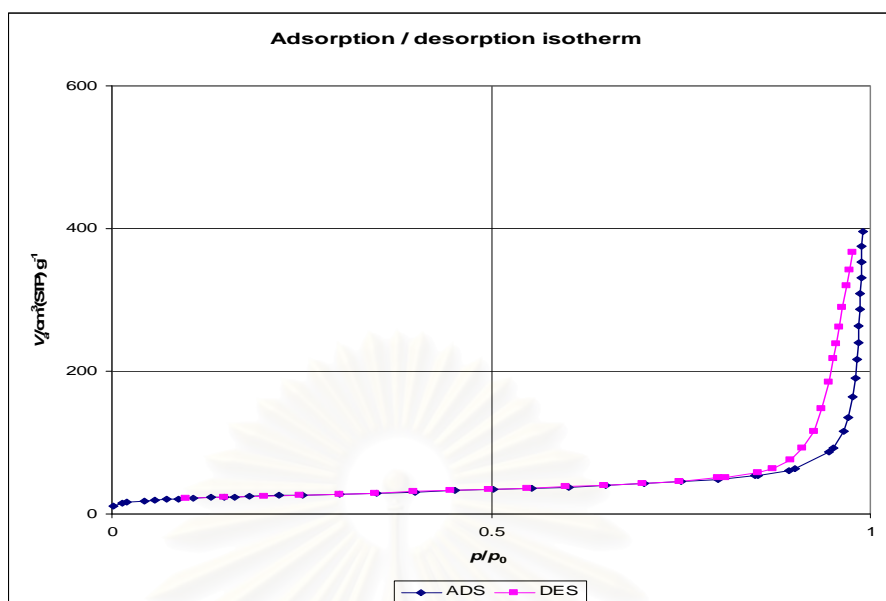


Figure A13 Adsorption isotherm of synthesized silica at aging pH 7 which was sieved through 325 mesh.

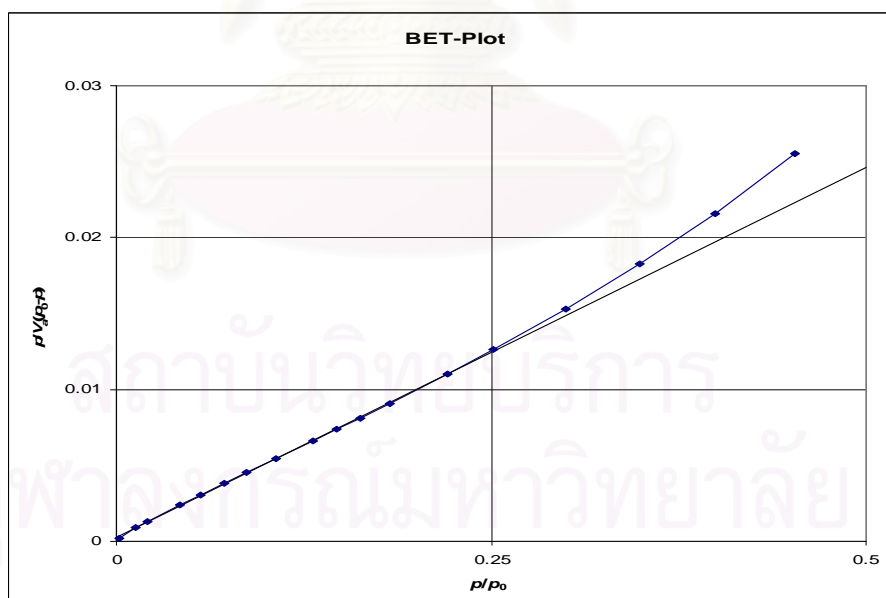


Figure A14 BET plot of synthesized silica at aging pH 7 which was sieved through 325 mesh.

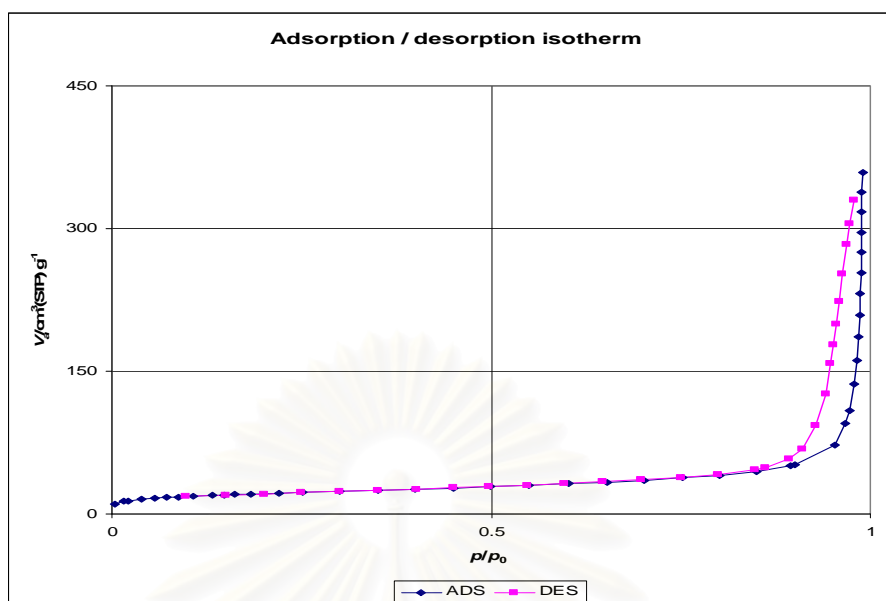


Figure A15 Adsorption isotherm of synthesized silica at aging pH 9 which was sieved through 325 mesh.

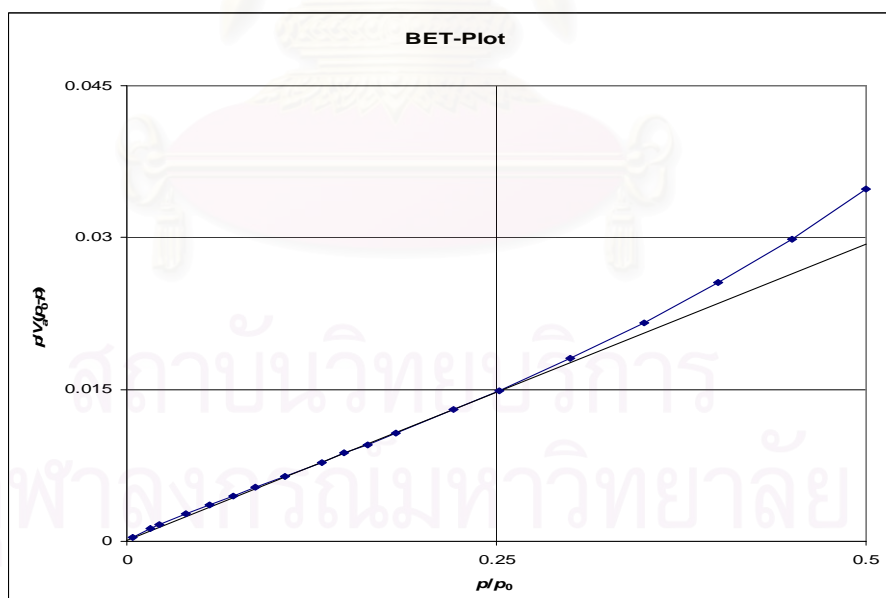


Figure A16 BET plot of synthesized silica at aging pH 9 which was sieved through 325 mesh.

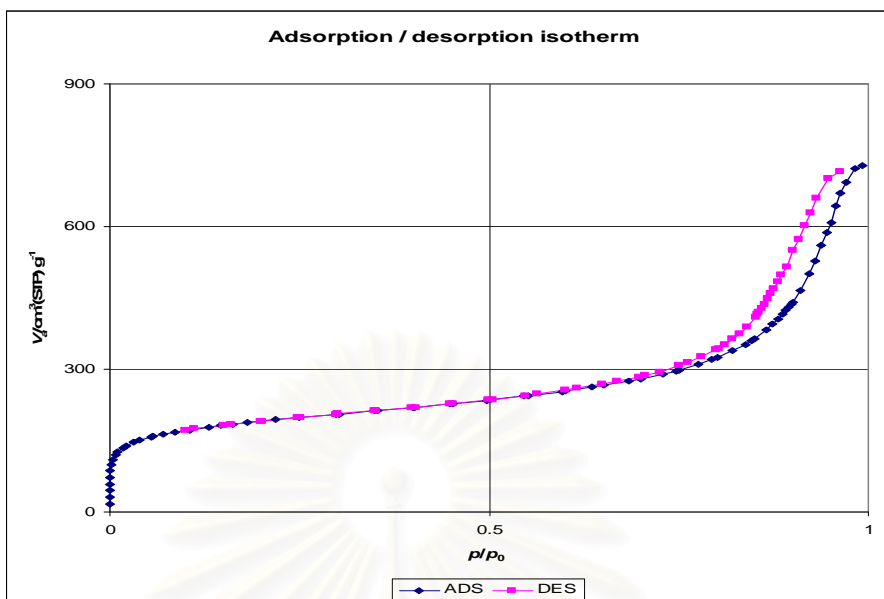


Figure A17 Adsorption isotherm of synthesized silica at aging pH 1 which was sieved through 200 mesh.

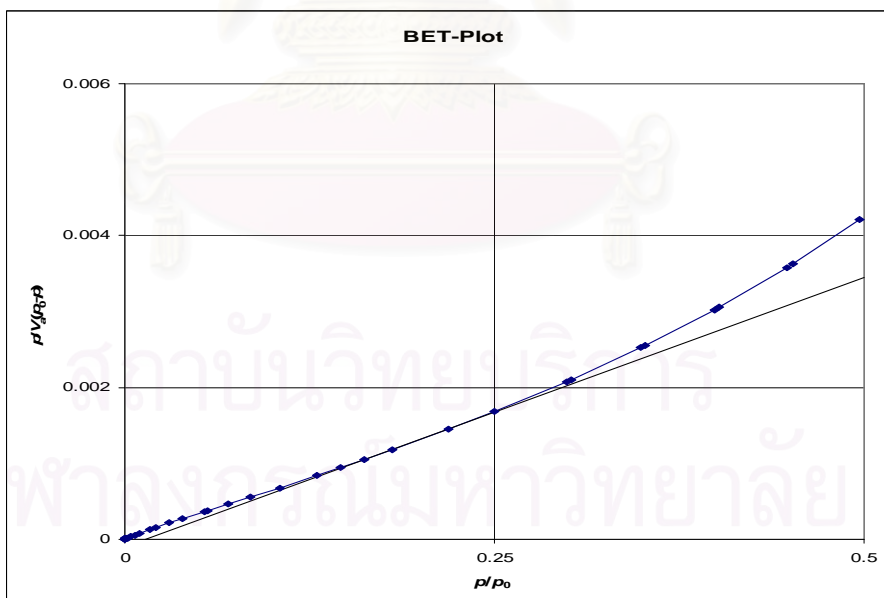


Figure A18 BET plot of synthesized silica at aging pH 1 which was sieved through 200 mesh.

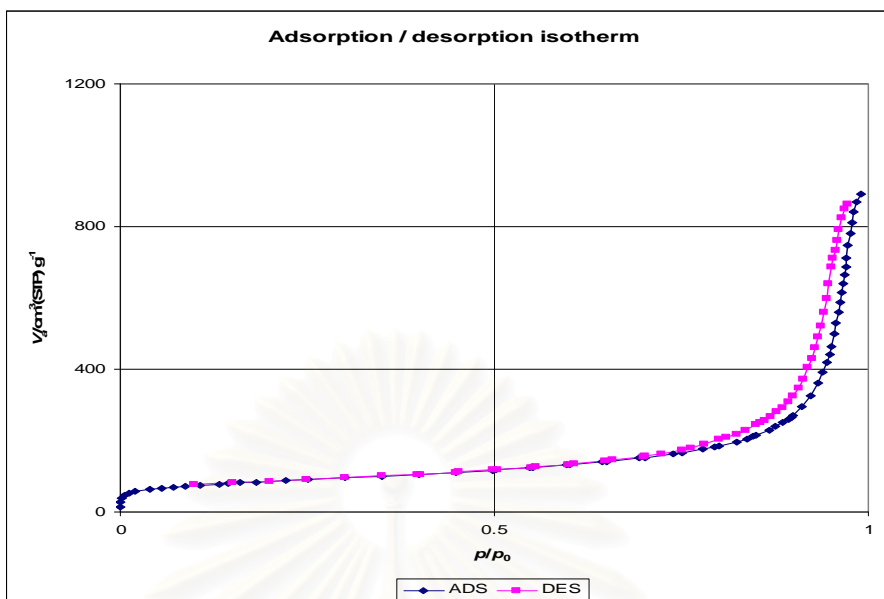


Figure A19 Adsorption isotherm of synthesized silica at aging pH 3 which was sieved through 200 mesh.

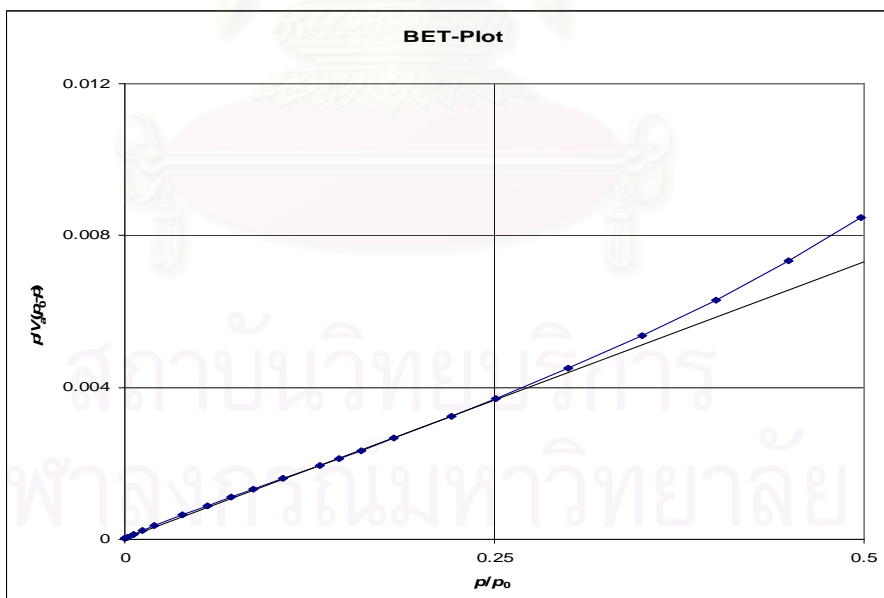


Figure A20 BET plot of synthesized silica at aging pH 3 which was sieved through 200 mesh.

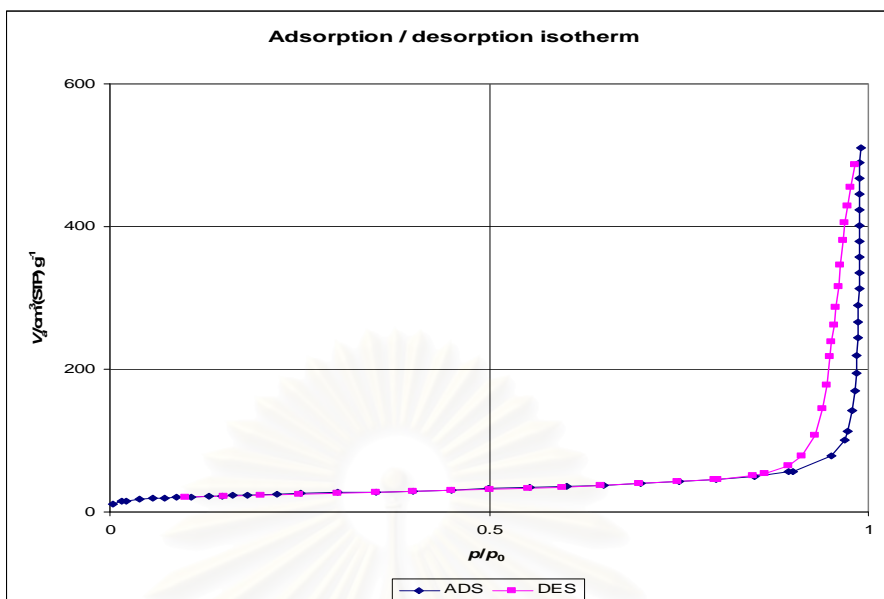


Figure A21 Adsorption isotherm of synthesized silica at aging pH 7 which was sieved through 200 mesh.

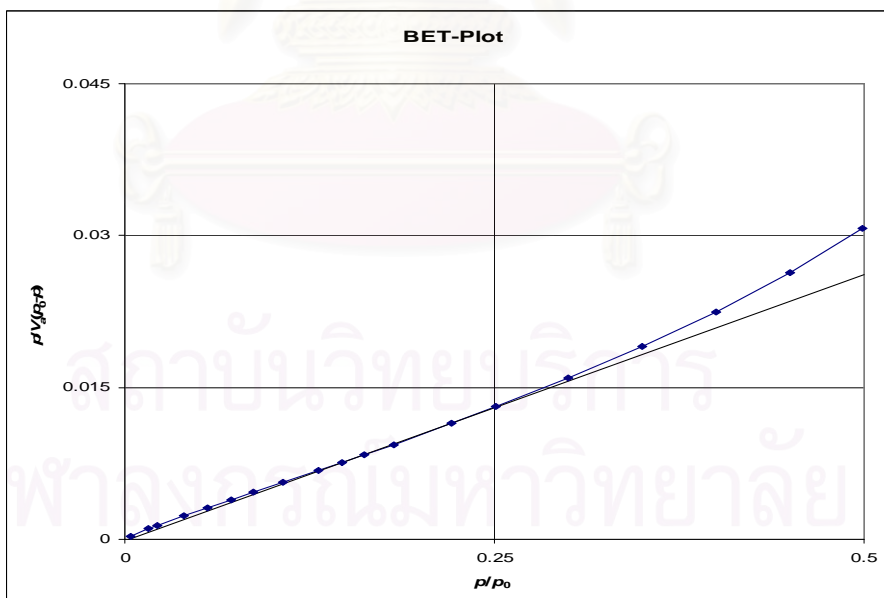


Figure A22 BET plot of synthesized silica at aging pH 7 which was sieved through 200 mesh.

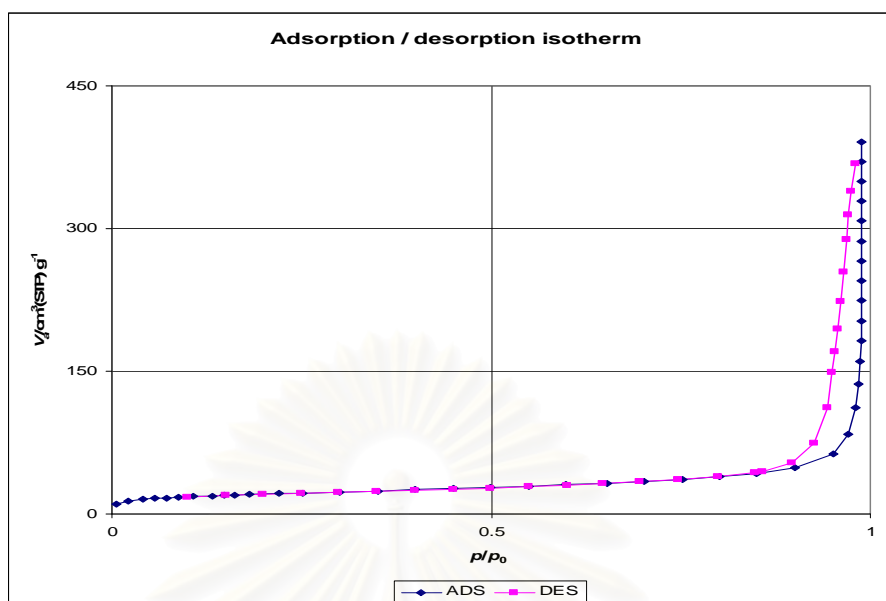


Figure A23 Adsorption isotherm of synthesized silica at aging pH 9 which was sieved through 200 mesh.

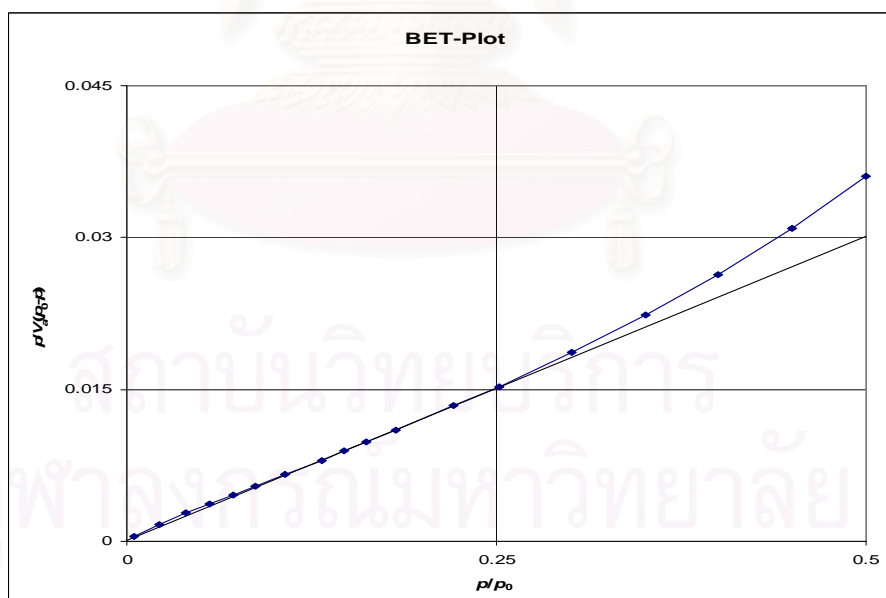


Figure A24 BET plot of synthesized silica at aging pH 9 which was sieved through 200 mesh.

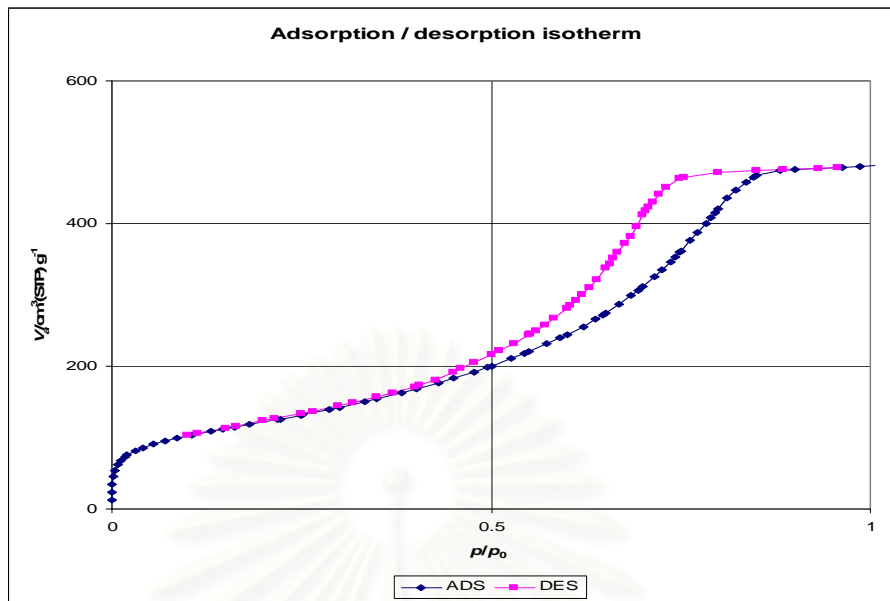


Figure A25 Adsorption isotherm of silica gel 60 from Merck Company.

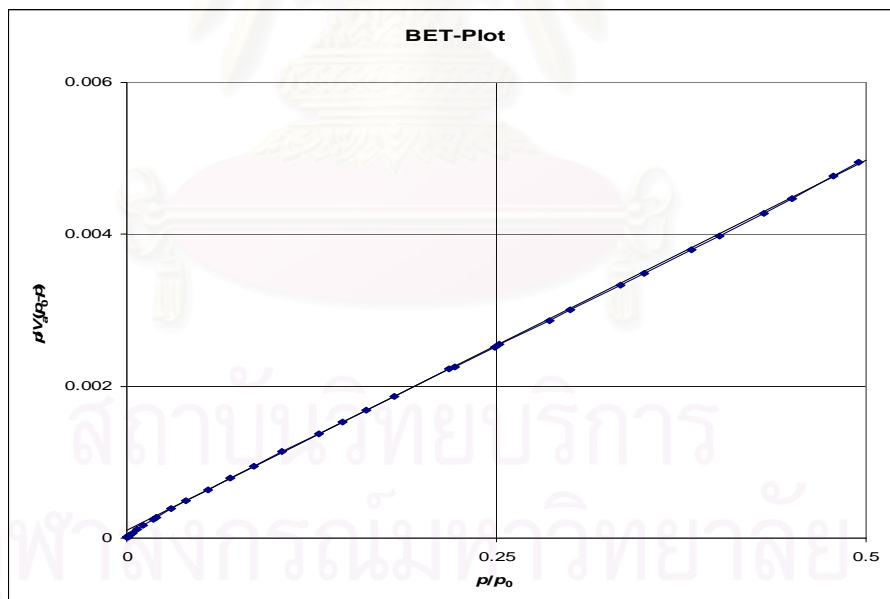


Figure A26 BET plot of silica gel 60 from Merck Company.

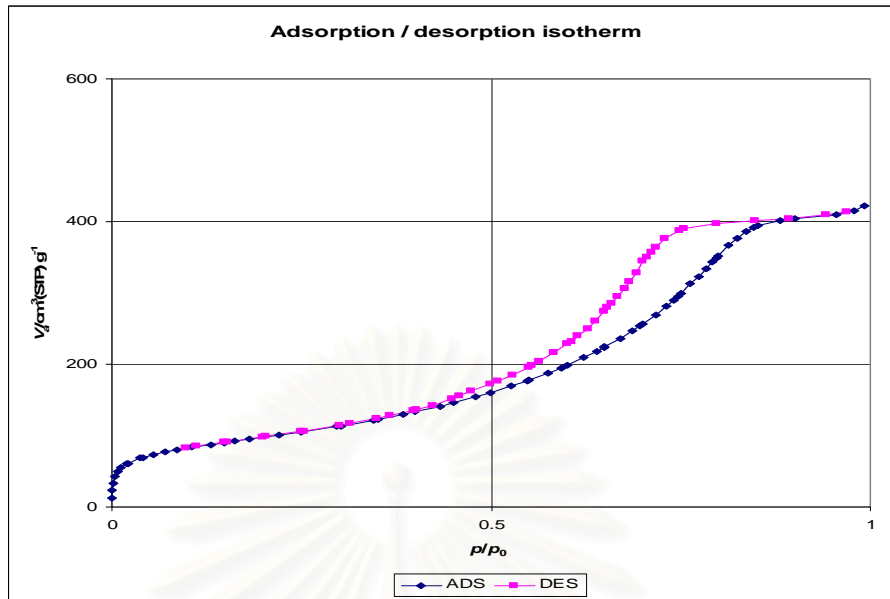


Figure A27 Adsorption isotherm of silica gel 60G from Merck Company.

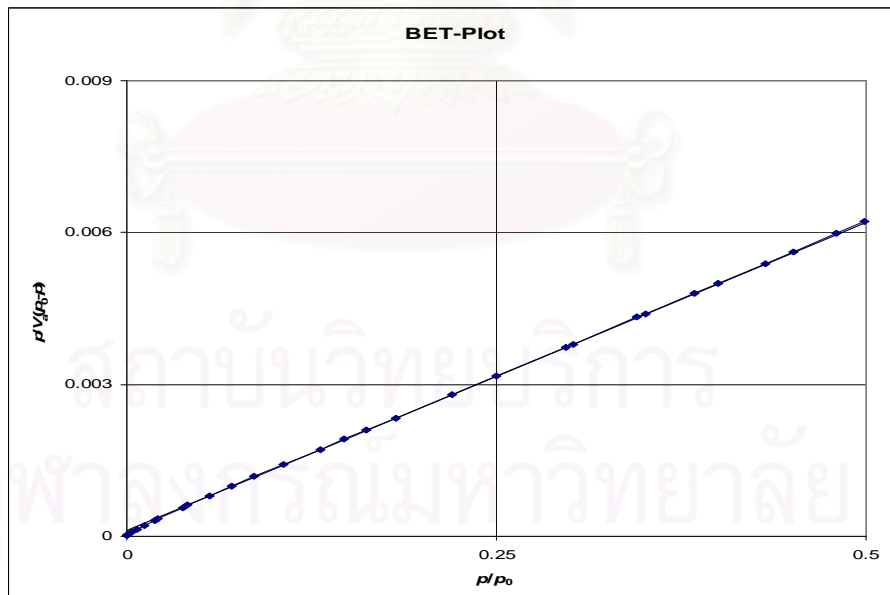
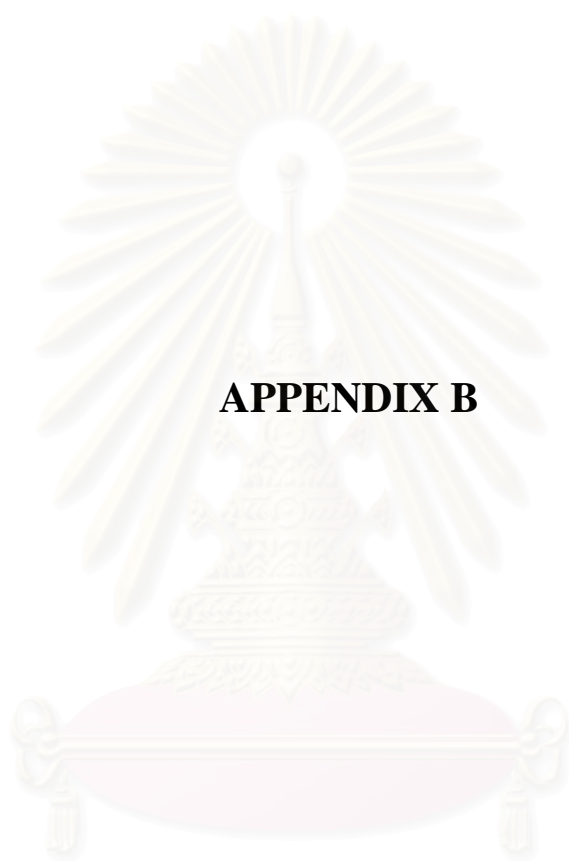


Figure A28 BET plot of silica gel 60 G from Merck Company.



APPENDIX B

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

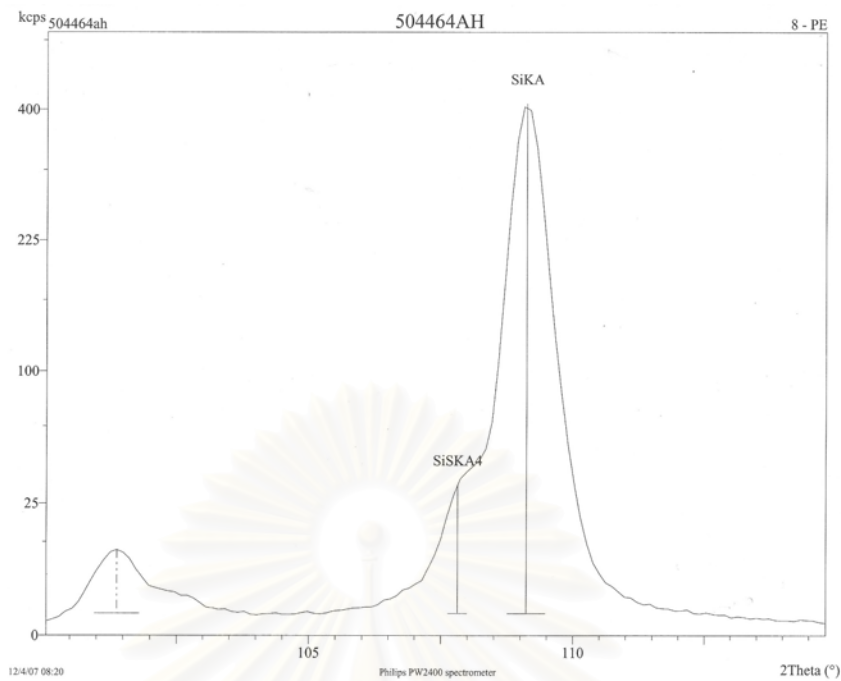


Figure B1 XRF spectrum of rice husk ash sample.

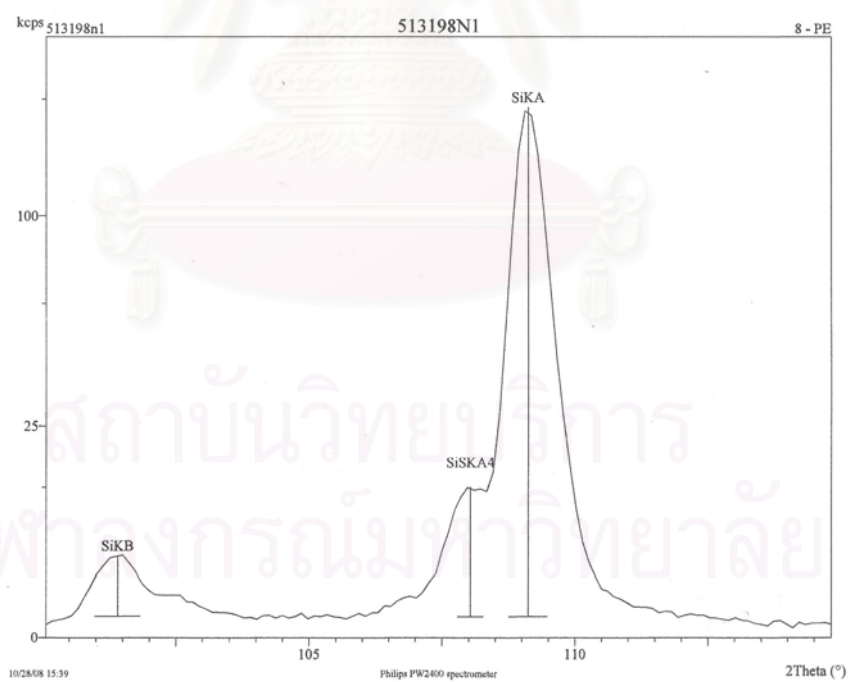


Figure B2 XRF spectrum of synthesized silica gel at aging pH 1.

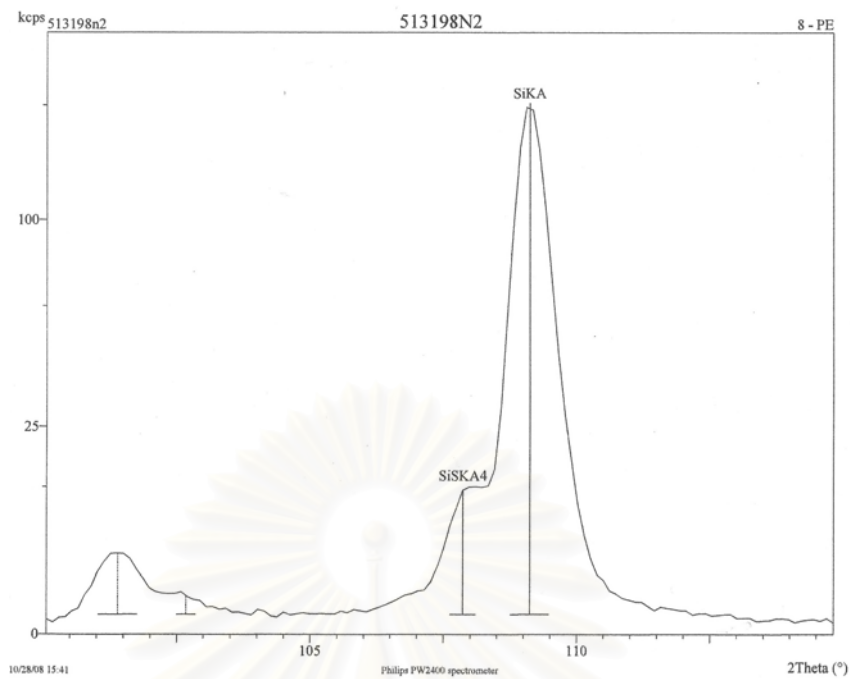


Figure B3 XRF spectrum of synthesized silica gel at aging pH 3.

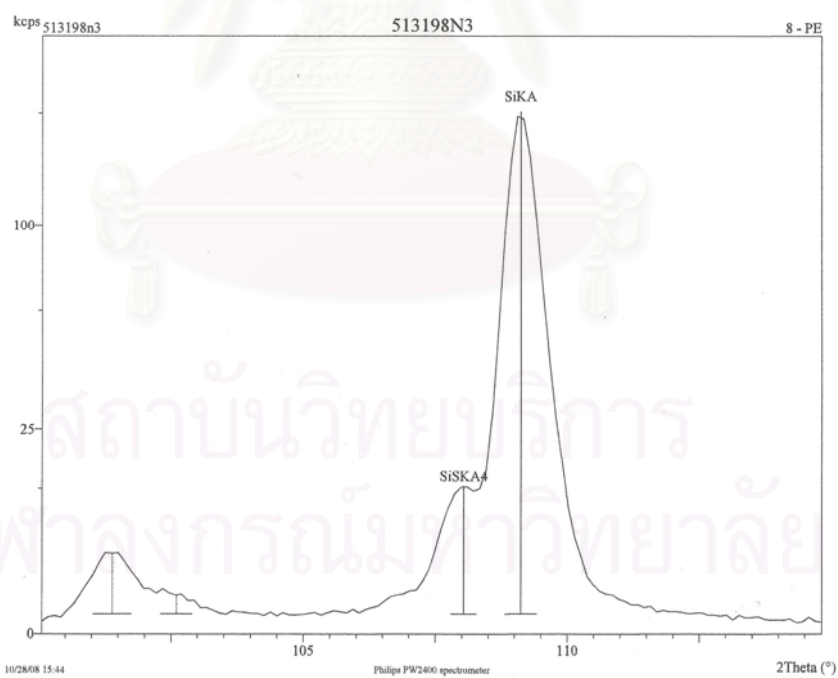


Figure B4 XRF spectrum of synthesized silica gel at aging pH 7.

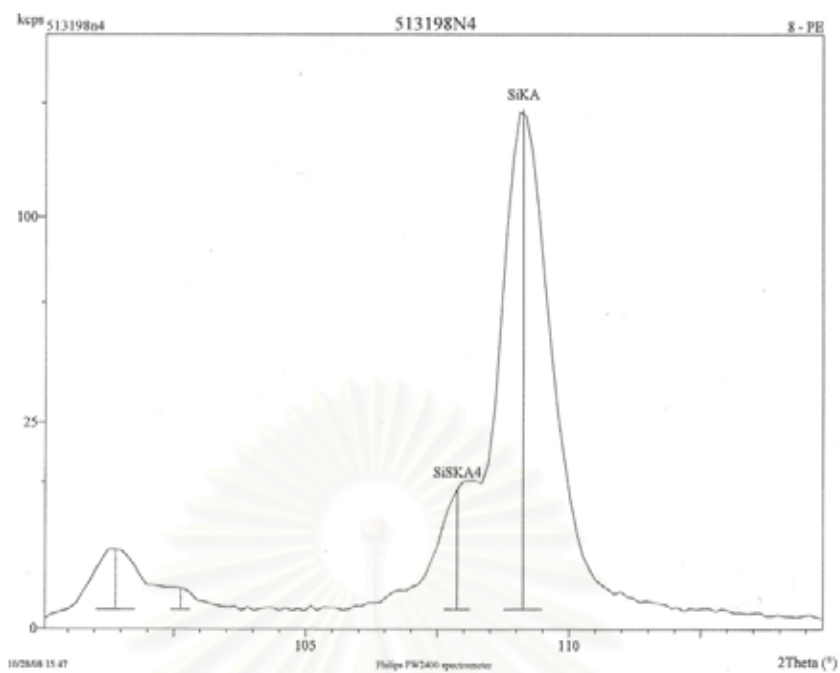


Figure B5 XRF spectrum of synthesized silica gel at aging pH 9.

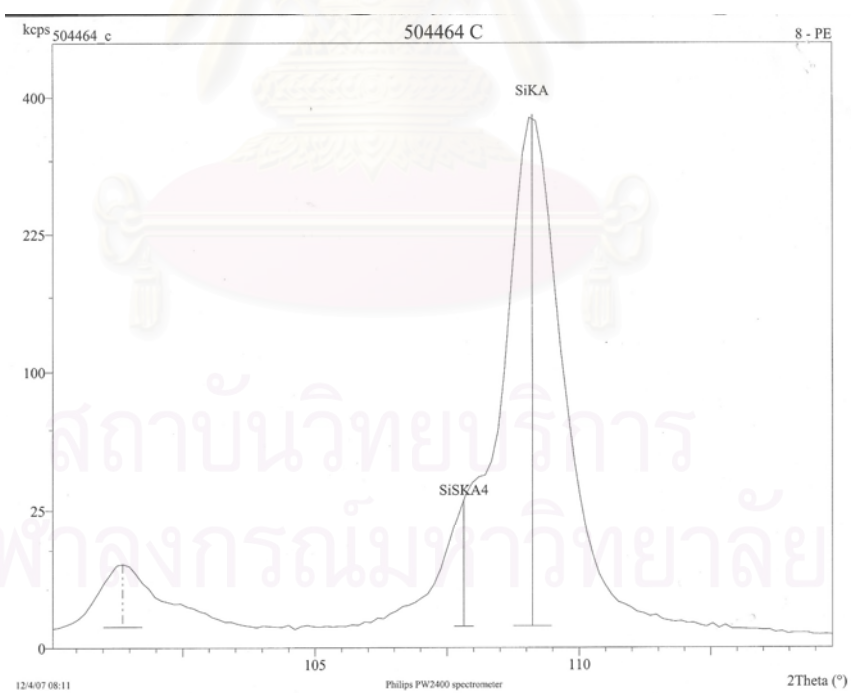


Figure B6 XRF spectrum of silica gel 60 G from Merck Company.

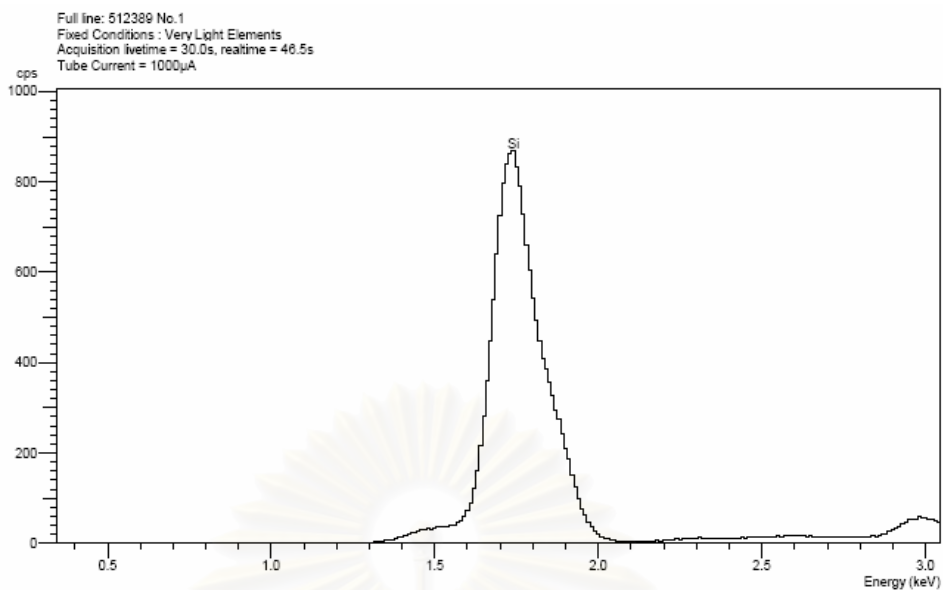


Figure B7 XRF spectrum of silica gel 60 from Merck Company.

สถาบันวิทยบริการ
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APPENDIX C

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

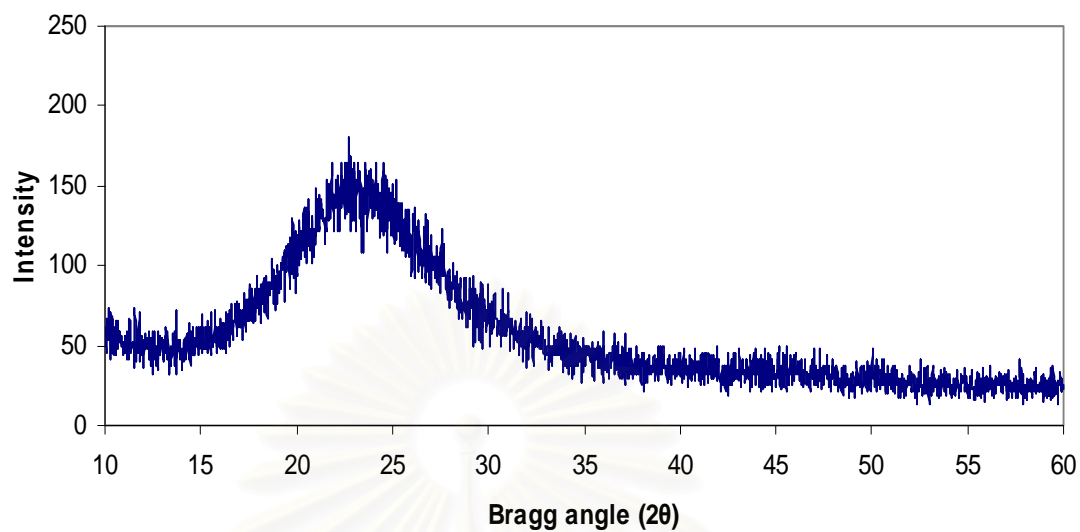


Figure C1 X-ray diffraction pattern of synthesized silica gel aging at pH 1.

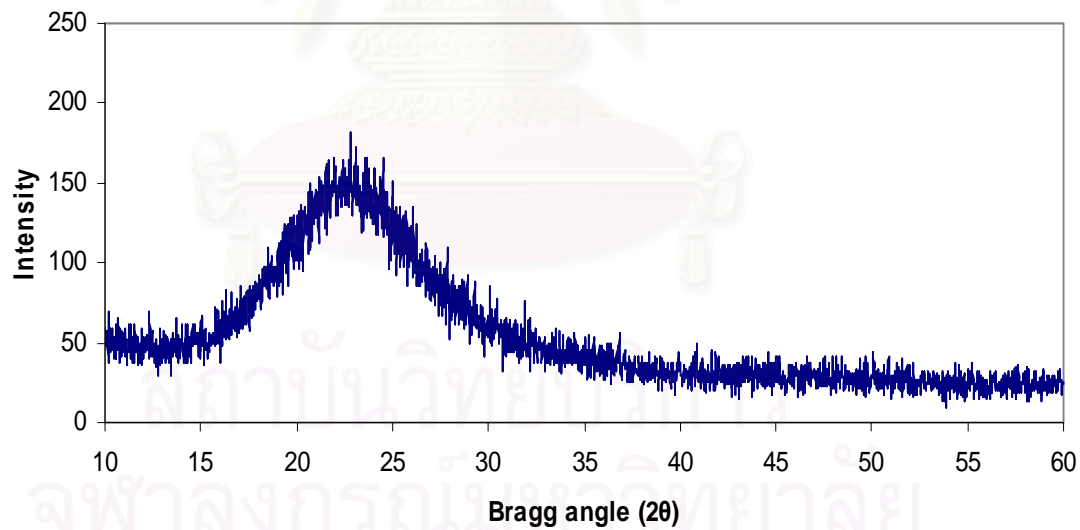


Figure C2 X-ray diffraction pattern of synthesized silica gel aging at pH 3.

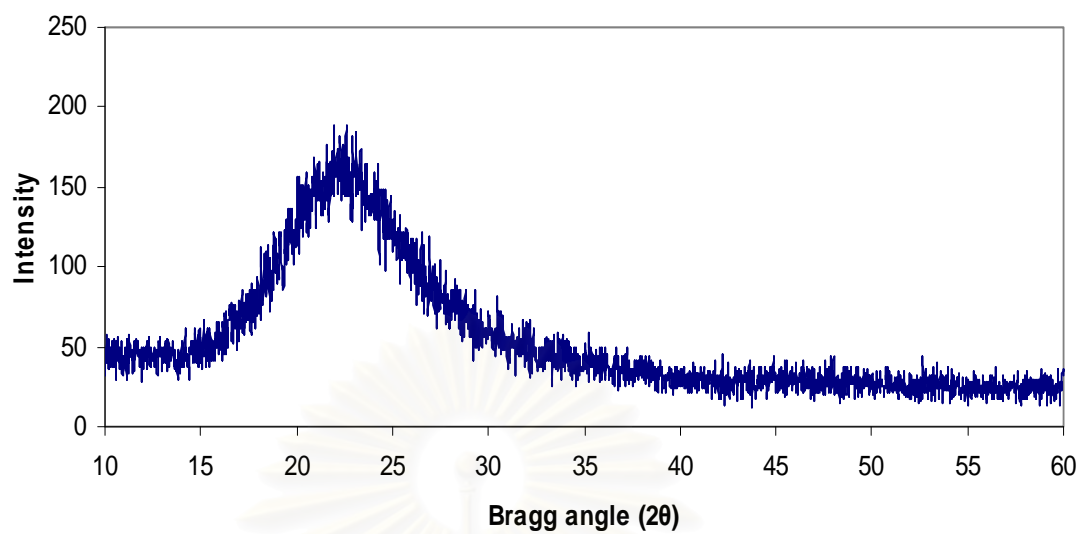


Figure C3 X-ray diffraction pattern of synthesized silica gel aging at pH 7.

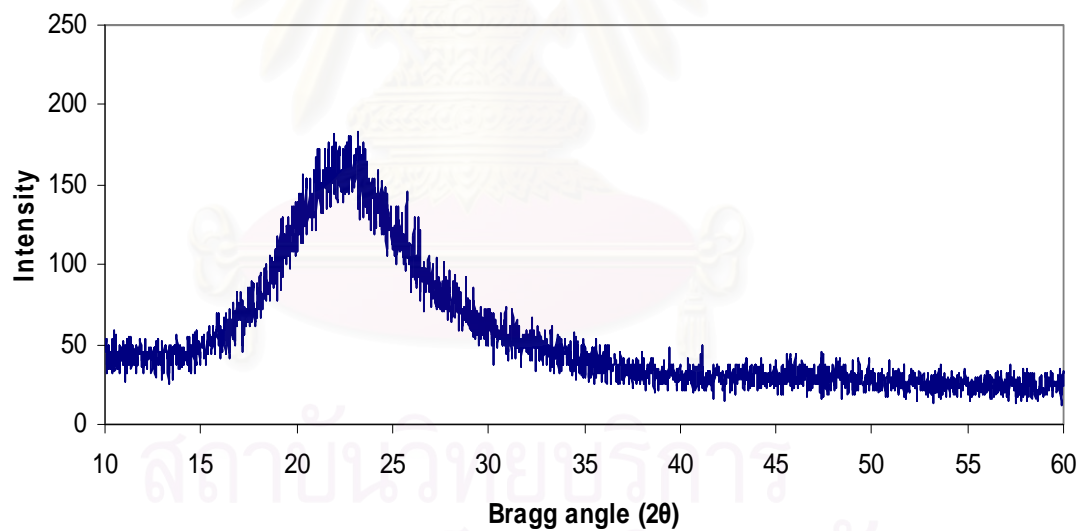


Figure C4 X-ray diffraction pattern of synthesized silica gel aging at pH 9.



APPENDIX D

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

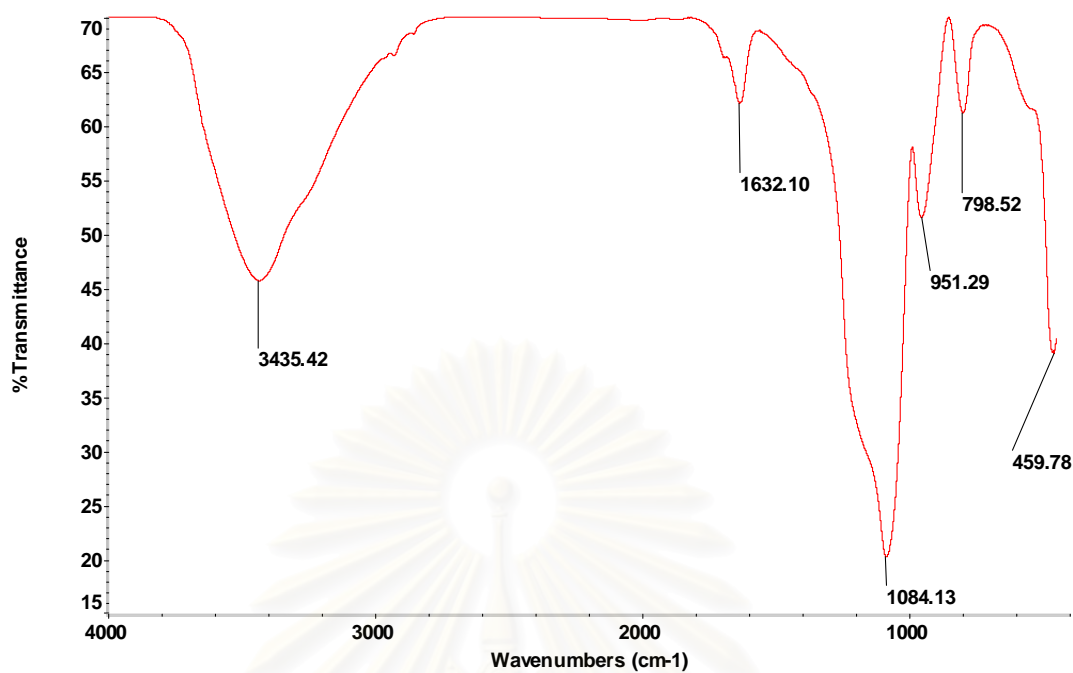


Figure D1 Fourier transform infrared spectra of silica as aging at pH 1.

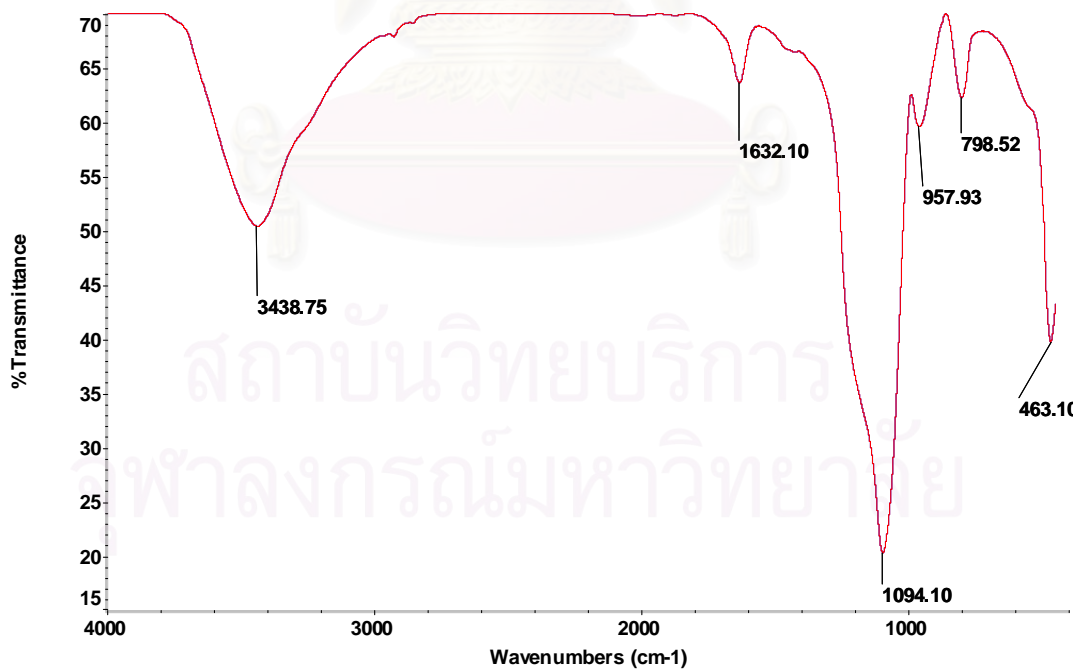


Figure D2 Fourier transform infrared spectra of silica as aging at pH 3.

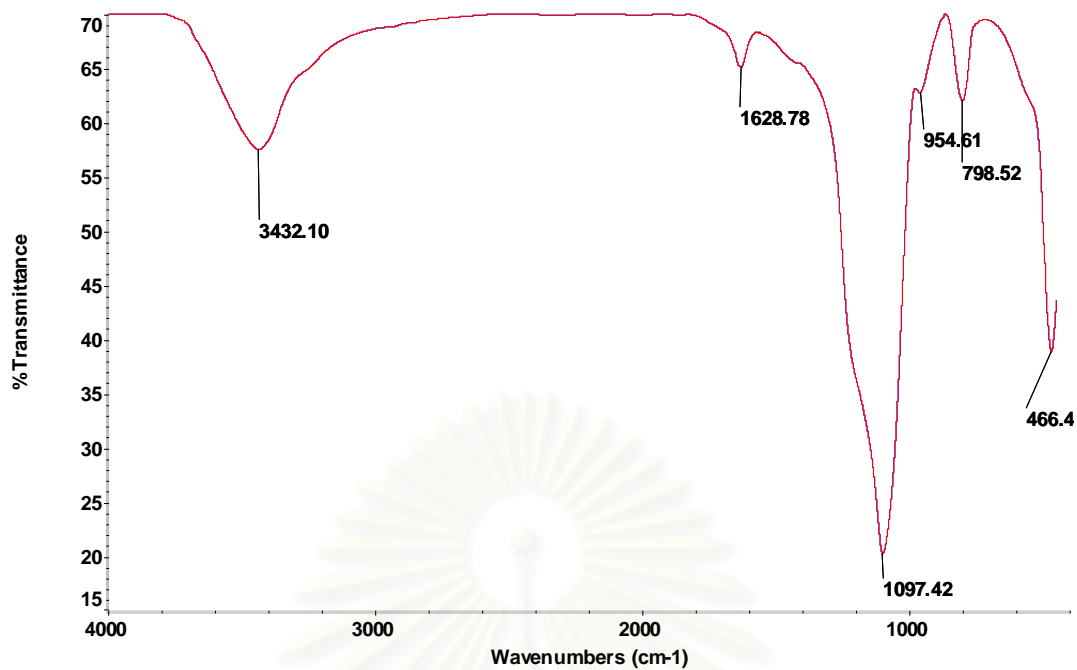


Figure D3 Fourier transform infrared spectra of silica as aging at pH 7.

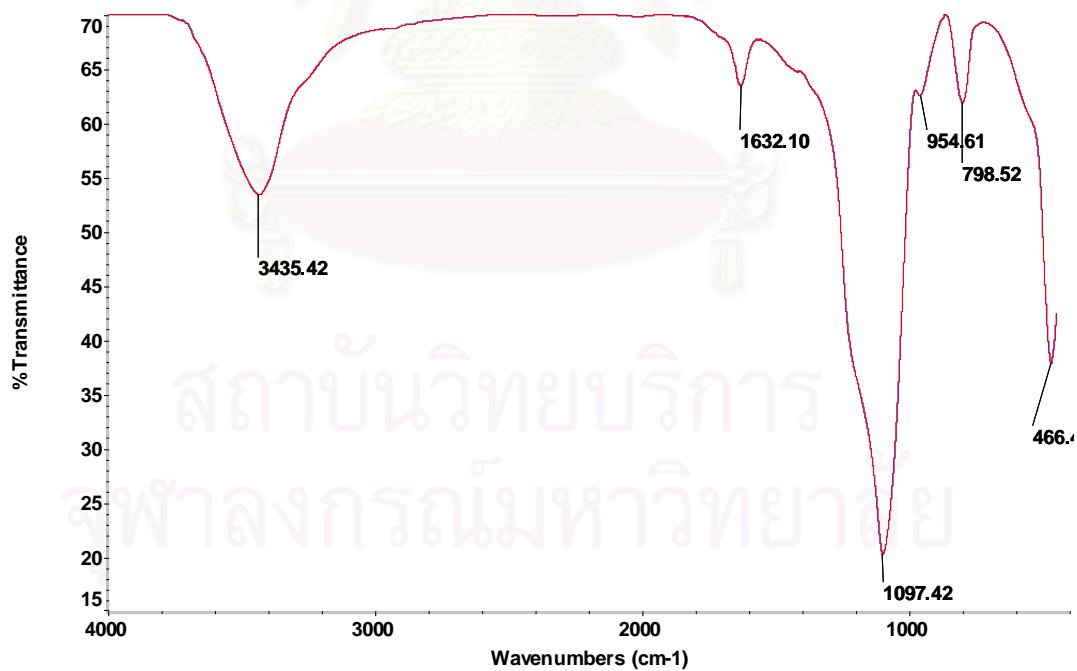
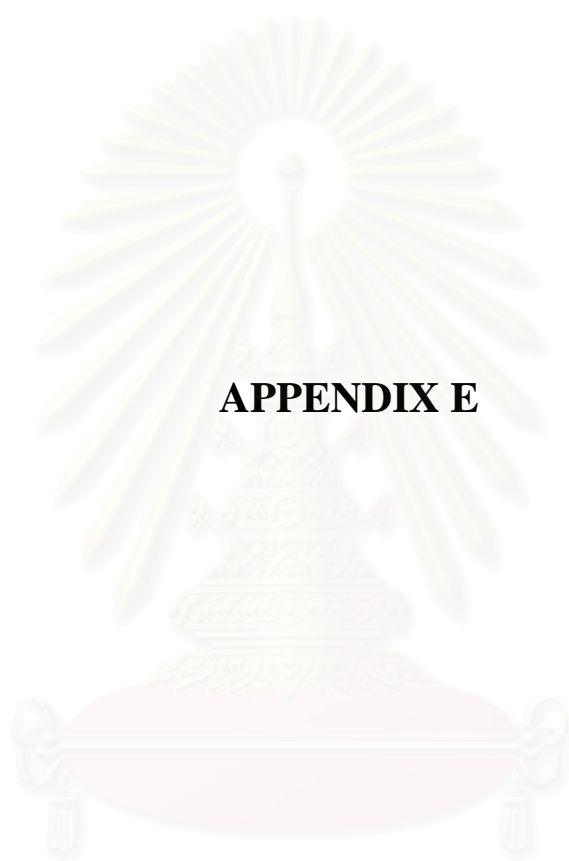


Figure D4 Fourier transform infrared spectra of silica as aging at pH 9.



APPENDIX E

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

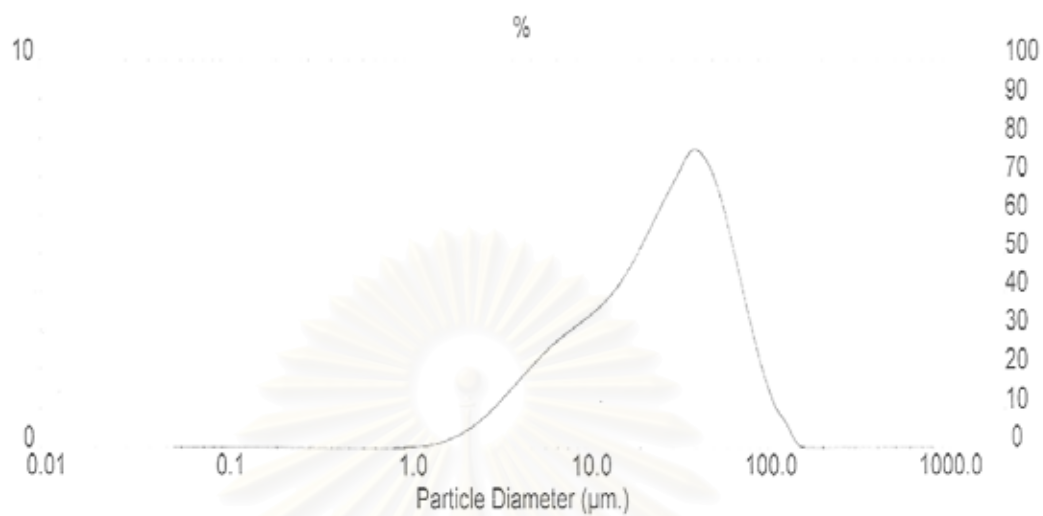


Figure E1 Particle size distribution of synthesized silica gel passed through 325 mesh.

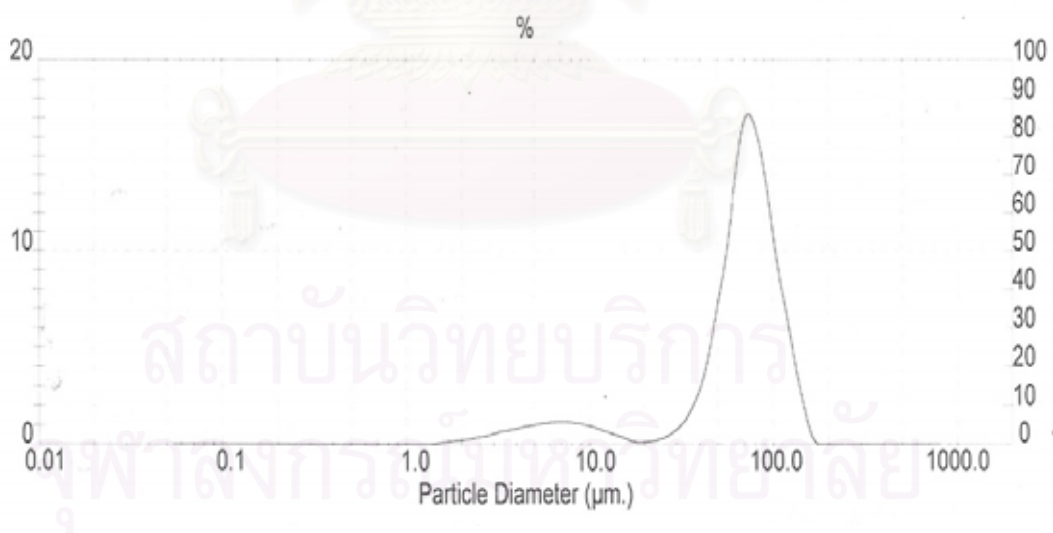


Figure E2 Particle size distribution of synthesized silica gel passed through 200 mesh.

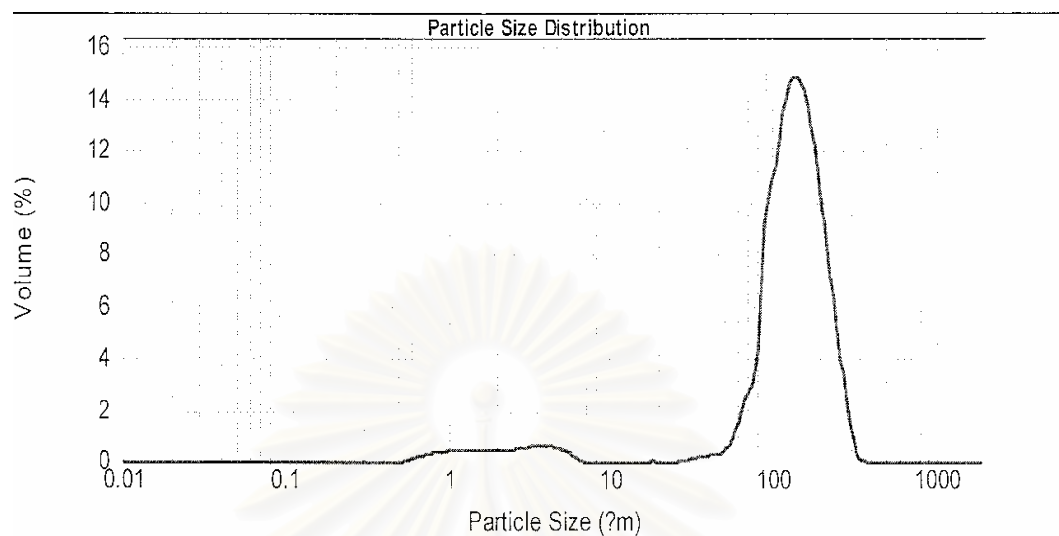


Figure E3 Particle size distribution of synthesized silica gel passed through 80 mesh.

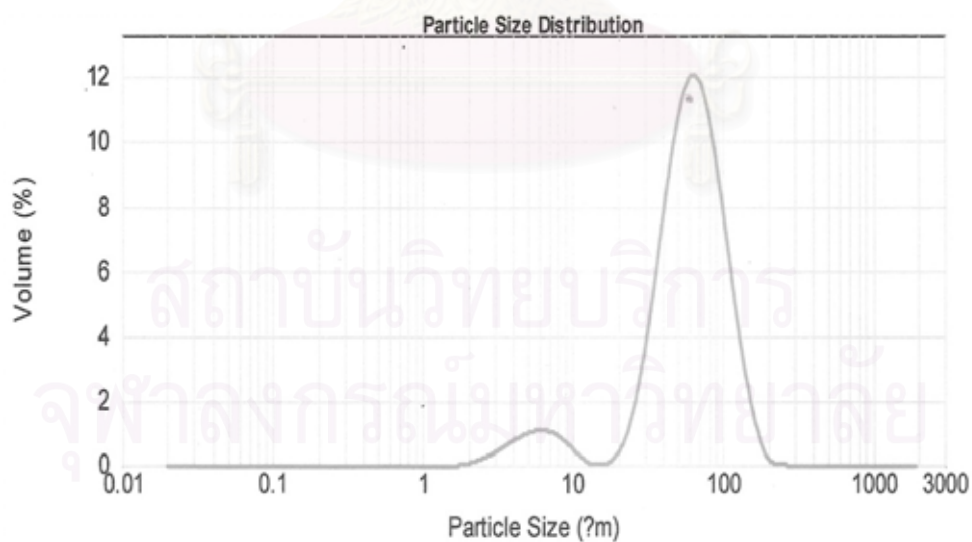


Figure E4 Particle size distribution of silica gel 60 from Merck Company.

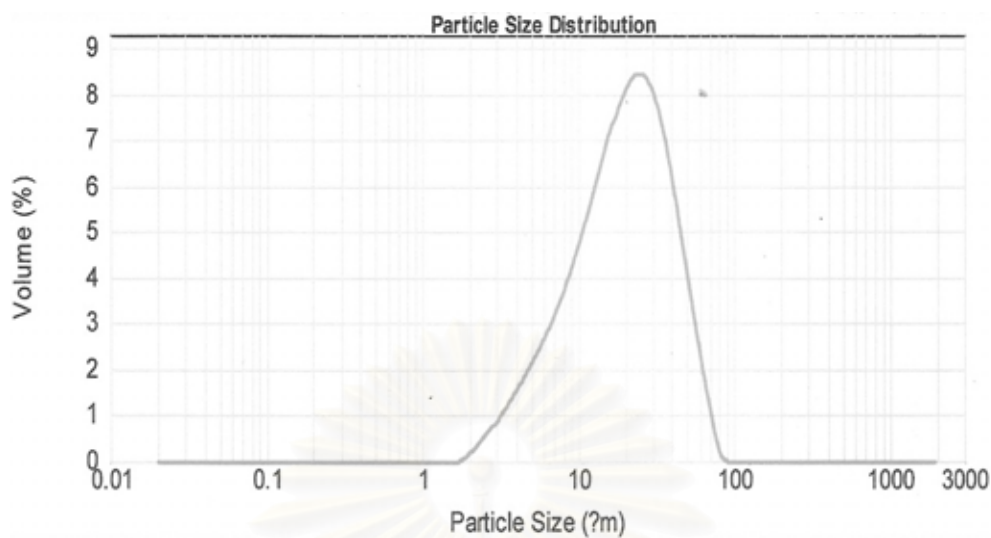
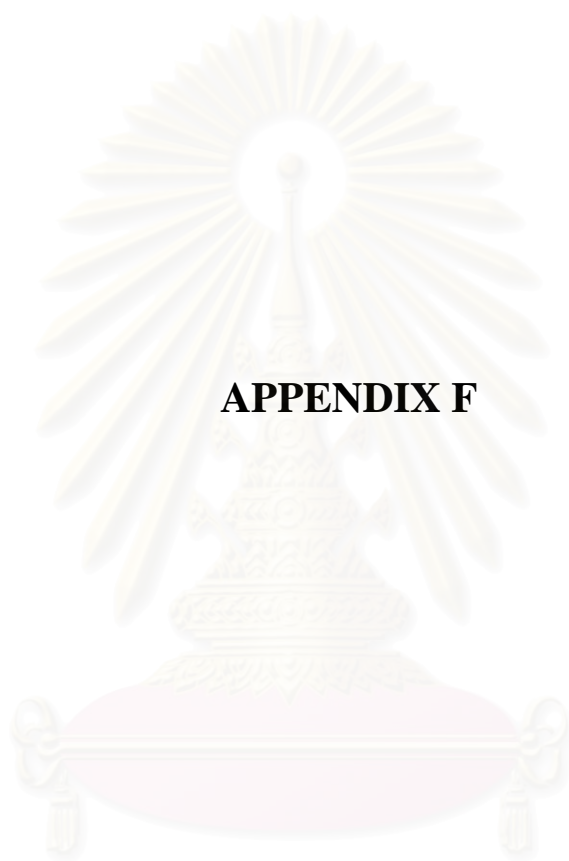


Figure E5 Particle size distribution of silica gel 60 G from Merck Company.

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APPENDIX F

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

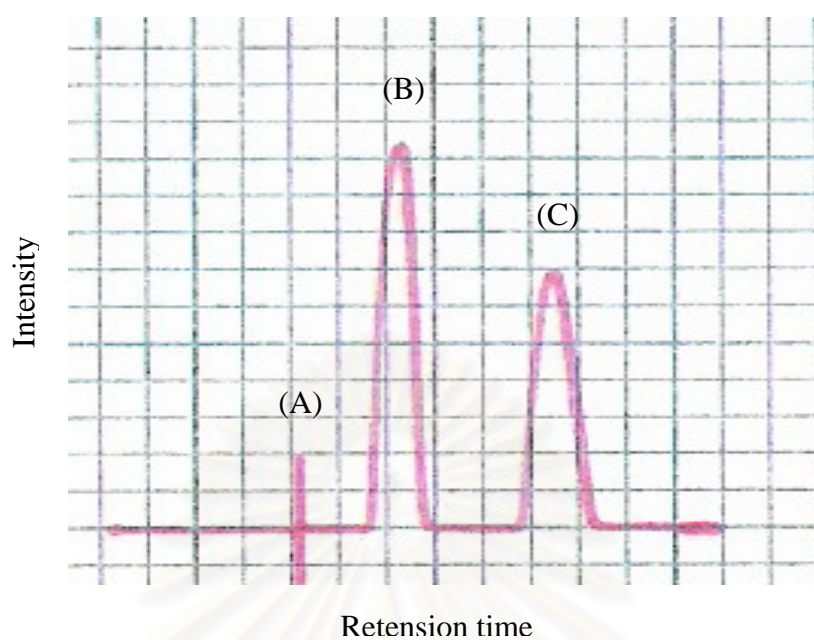


Figure F1 Chromatogram of silica gel 60 from Merck (A) injection point, (B) naphthalene, and (C) α -naphthol.

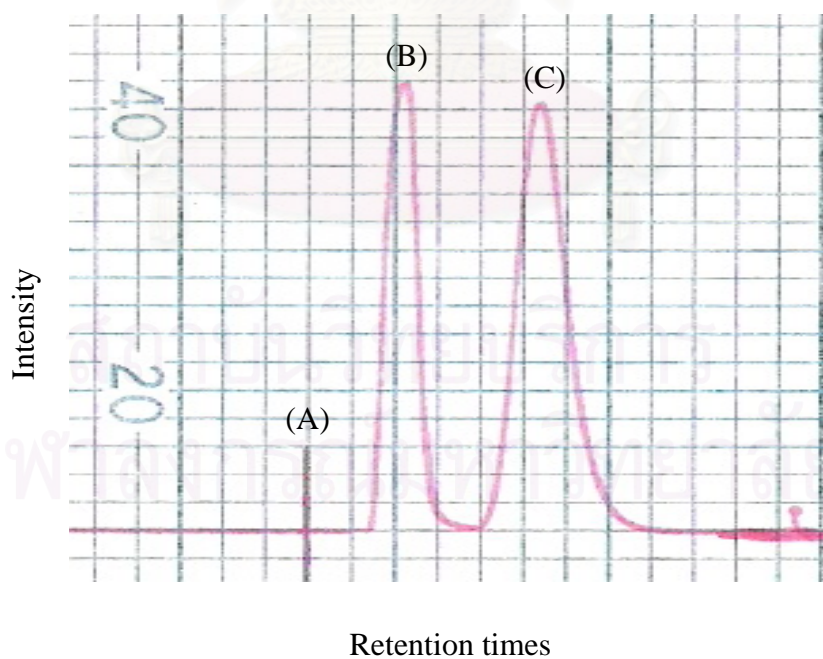


Figure F2 Chromatogram of silica gel which was prepared at aging at pH 1 (A) injection point, (B) naphthalene, and (C) α -naphthol.

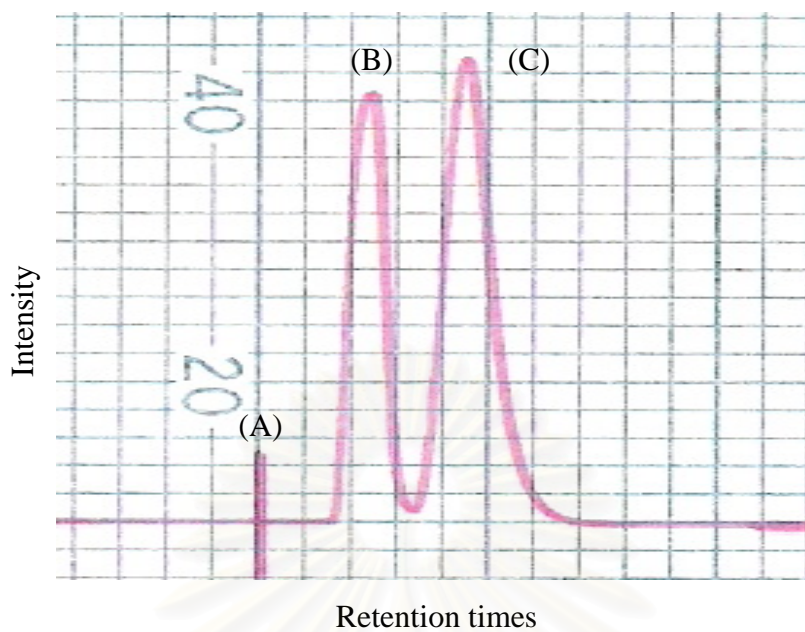


Figure F3 Chromatogram of silica gel which was prepared at aging at pH 3, (A) injection point, (B) naphthalene, and (C) α -naphthol.

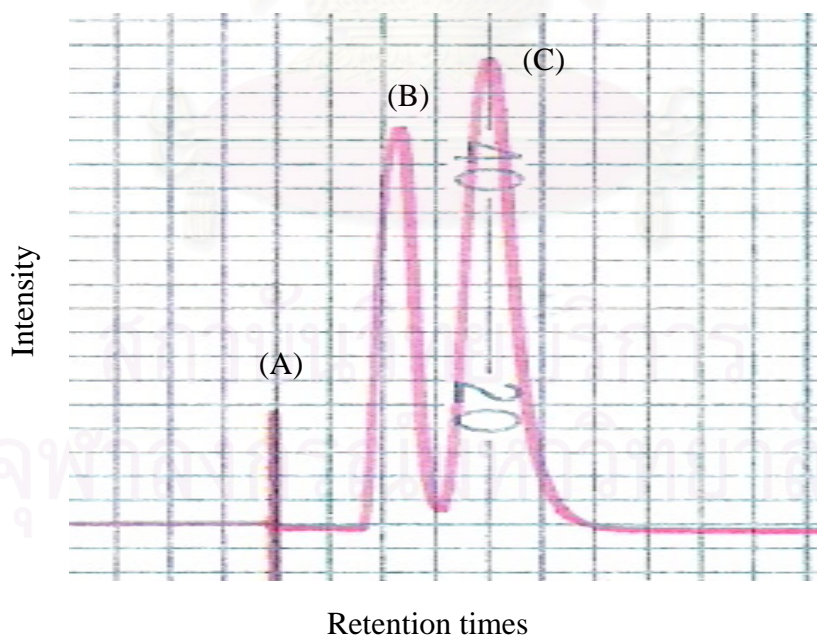


Figure F4 Chromatogram of silica gel which was prepared at aging at pH 7, (A) injection point, (B) naphthalene, and (C) α -naphthol.

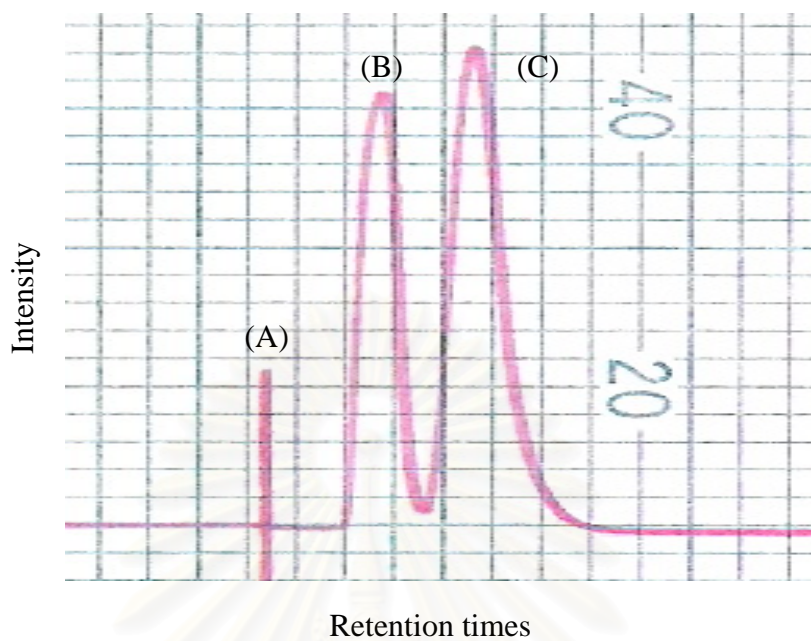


Figure F5 Chromatogram of silica gel which was prepared at aging at pH 9 (A) injection point, (B) naphthalene, and (C) α -naphthol.

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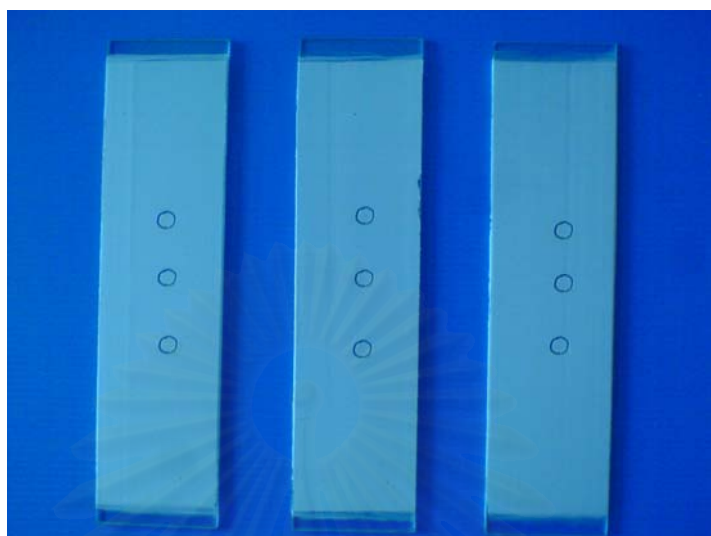


Figure F6 TLC testing of silica gel 60 G from Merck Company.



Figure F7 TLC testing of synthesized silica gel at aging pH 1.

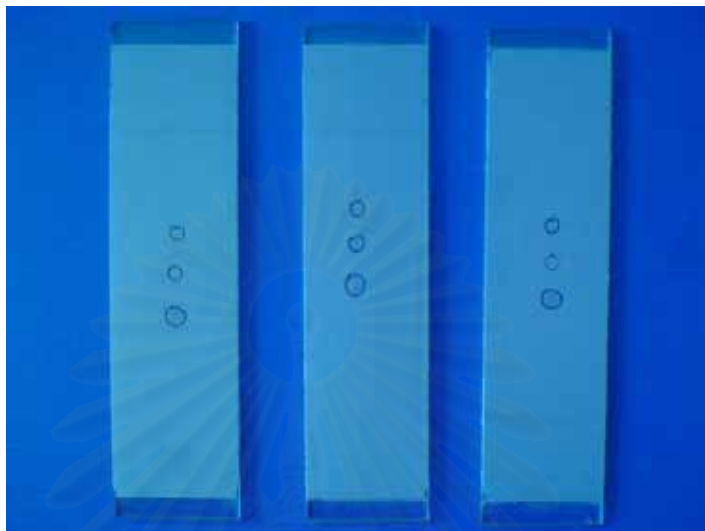


Figure F8 TLC testing of synthesized silica gel at aging pH 3.

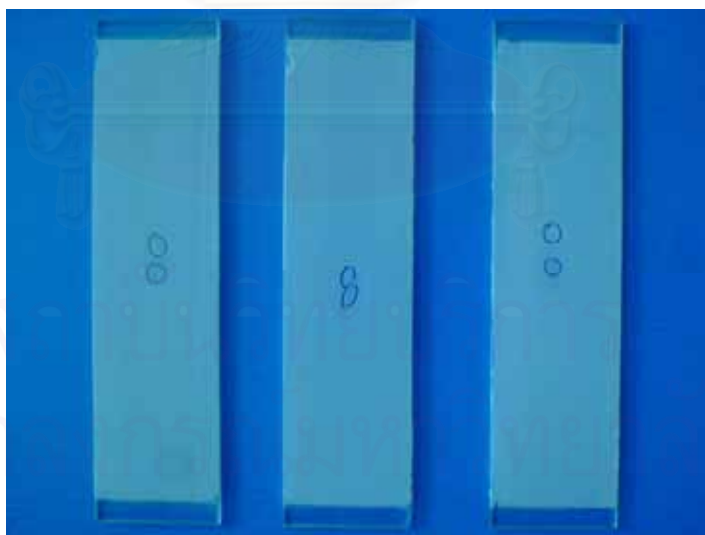


Figure F9 TLC testing of synthesized silica gel at aging pH 7.

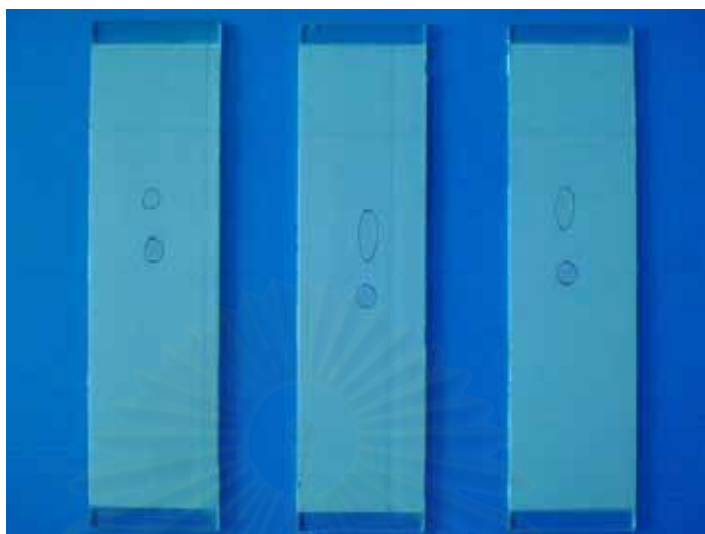


Figure F10 TLC testing of synthesized silica gel at aging pH 9.

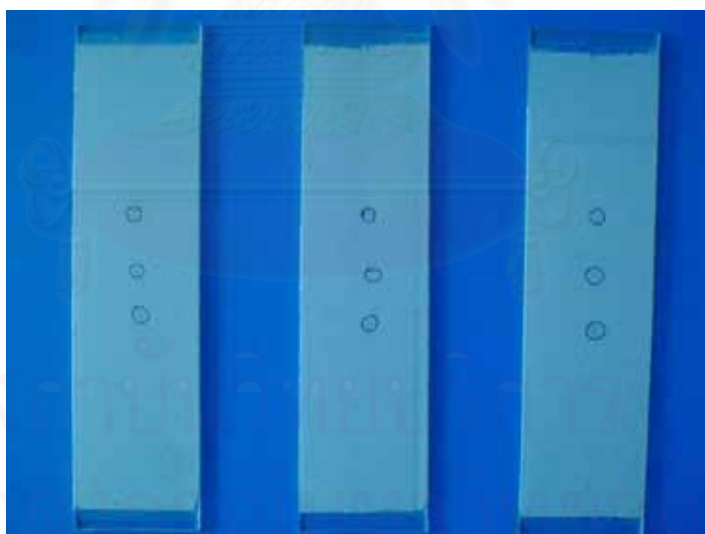


Figure F11 TLC testing of synthesized silica gel at aging pH 1 mixed with 10% CaSO_4 .

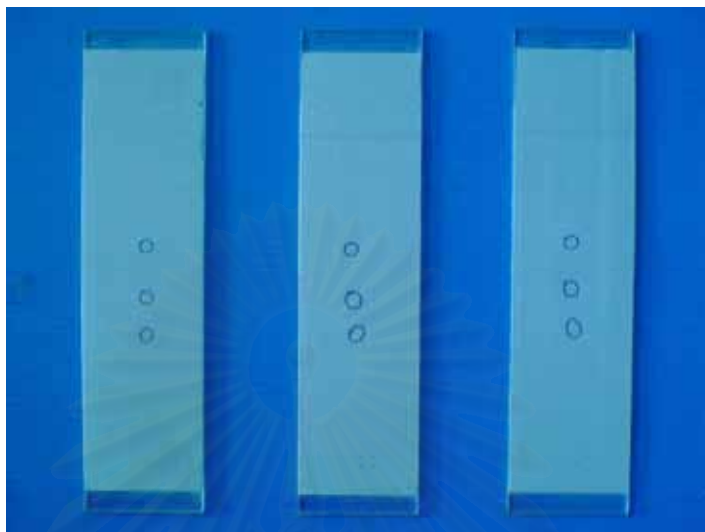


Figure F12 TLC testing of synthesized silica gel at aging pH 1 mixed with 10% BaSO₄.

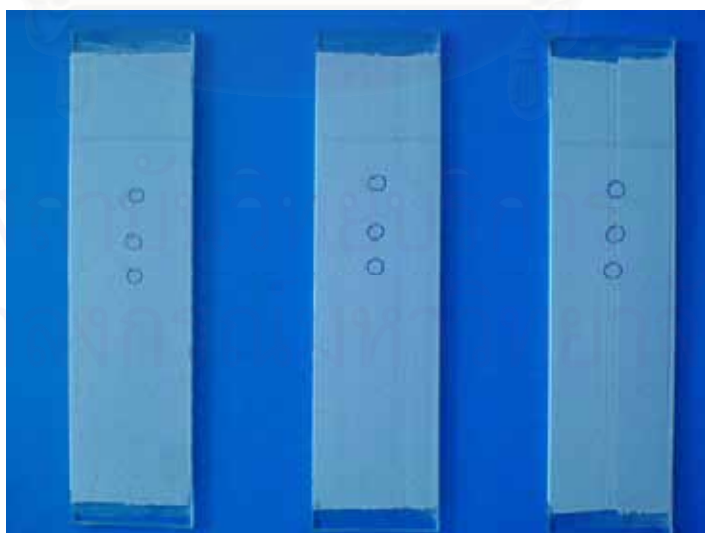


Figure F13 TLC testing of synthesized silica gel at aging pH 1 mixed with 10% MgSO₄.

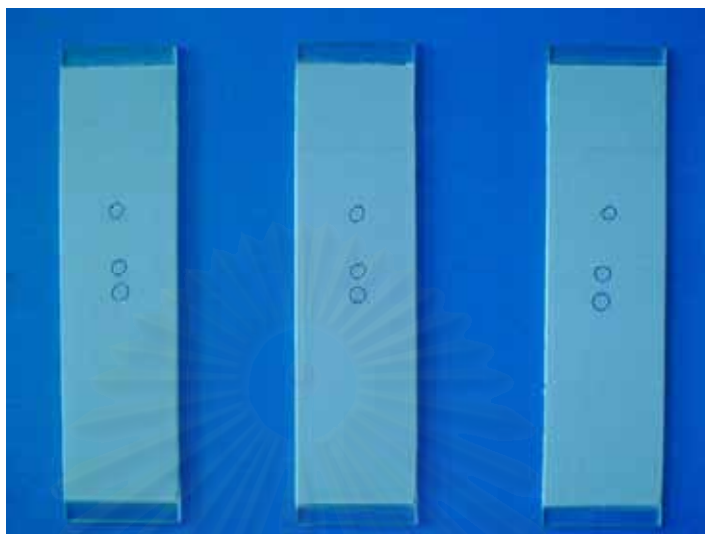


Figure F14 TLC testing of synthesized silica gel at aging pH 1 mixed with 10% Na₂SO₄



Figure F15 TLC testing of synthesized silica gel at aging pH 3 mixed with 10% CaSO₄.



Figure F16 TLC testing of synthesized silica gel at aging pH 3 mixed with 10% BaSO₄.

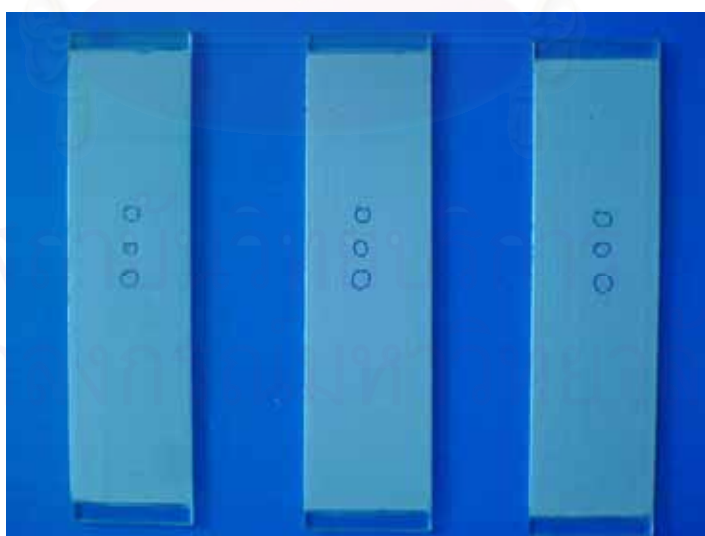


Figure F17 TLC testing of synthesized silica gel at aging pH 3 mixed with 10% MgSO₄.



Figure F18 TLC testing of synthesized silica gel at aging pH 3 mixed with 10% Na_2SO_4 .



Figure F19 TLC testing of synthesized silica gel at aging pH 7 mixed with 10% CaSO_4 .



Figure F20 TLC testing of synthesized silica gel at aging pH 7 mixed with 10% BaSO₄.

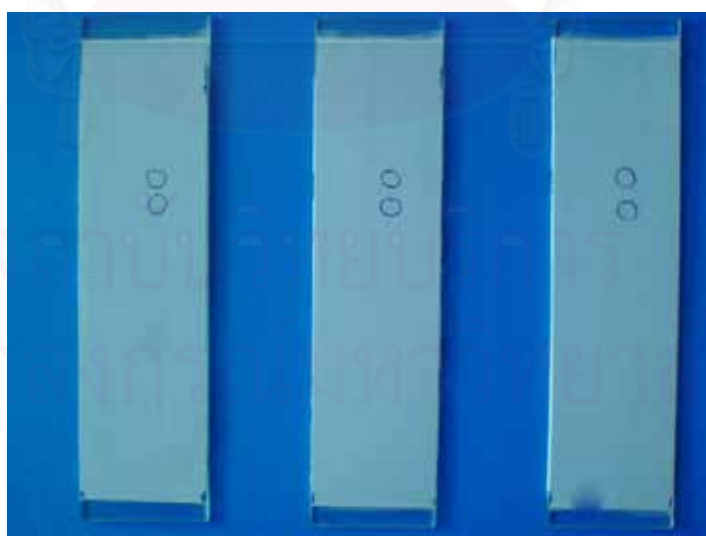


Figure F21 TLC testing of synthesized silica gel at aging pH 7 mixed with 10% MgSO₄.



Figure F22 TLC testing of synthesized silica gel at aging pH 7 mixed with 10% Na_2SO_4 .

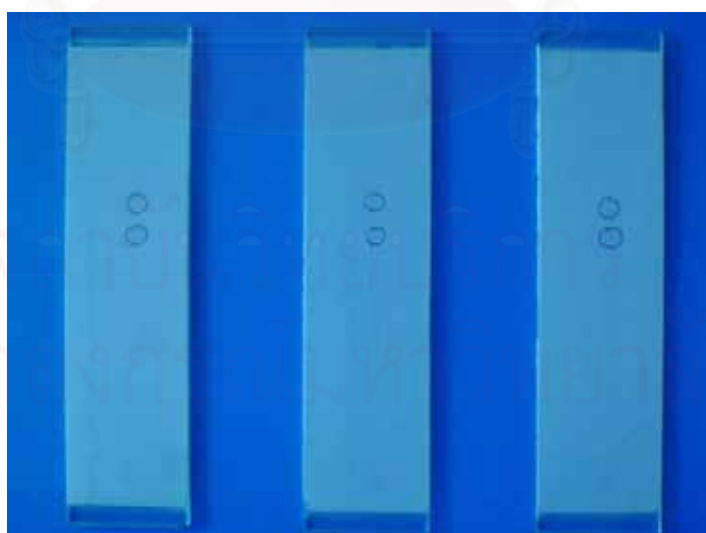


Figure F23 TLC testing of synthesized silica gel at aging pH 9 mixed with 10% CaSO_4 .

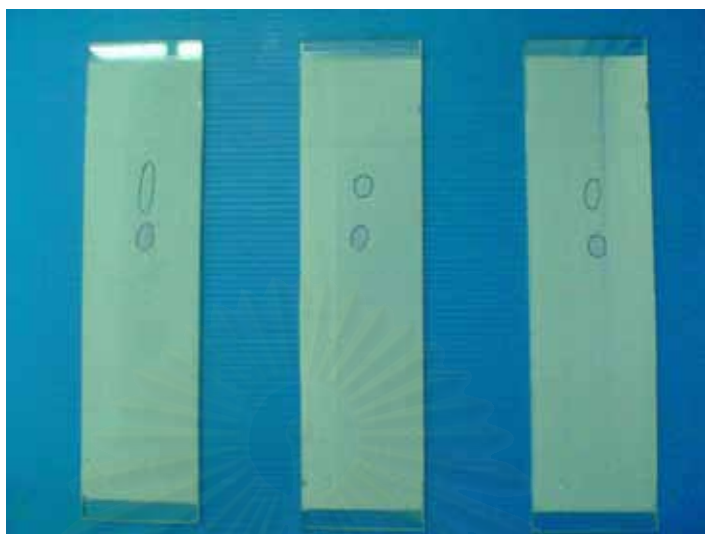


Figure F24 TLC testing of synthesized silica gel at aging pH 9 mixed with 10% BaSO₄.

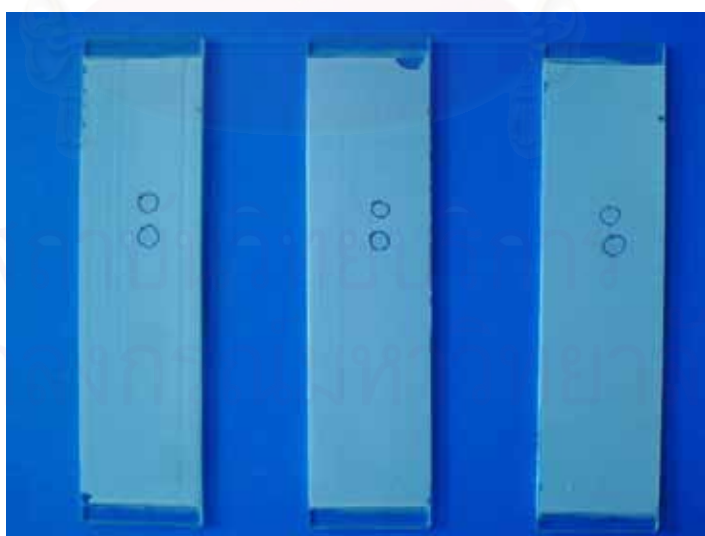


Figure F25 TLC testing of synthesized silica gel at aging pH 9 mixed with 10% MgSO₄.

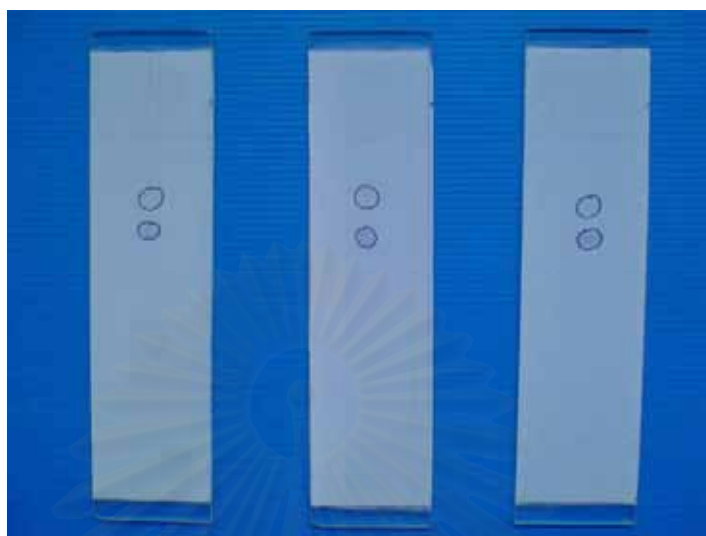


Figure F26 TLC testing of synthesized silica gel at aging pH 9 mixed with 10%Na₂SO₄.

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VITA

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