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PREPARATION OF POLYETHYLENEIMINE-COATED SILICA GEL FOR ADSORPTION OF FORMALDEHYDE IN WATER

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โสภิดา ศรีวิริยกุล : การเตรียมซิลิกาเจลที่เคลือบด้วยพอลิเอทิลีนอิมีนสำหรับการดูดซับฟอร์แมลดีไฮด์ในน้ำ (PREPARATION OF POLYETHYLENEIMINE-COATED SILICA GEL FOR ADSORPTION OF FORMALDEHYDE IN WATER) อ.ที่ปรึกษาวิทยานิพนธ์หลัก : ผศ.ดร.อภิชาติ อิ่มยิ้ม, อ.ที่ปรึกษาวิทยานิพนธ์ร่วม : ผศ.ดร.เฟื่องฟ้า อุ่นอบ, 61 หน้า.

การเตรียมตัวดูดซับเพื่อใช้ในการดูดซับฟอร์แมลดีไฮด์ในน้ำ สามารถเตรียมได้จากอนุภาคซิลิกาเจลที่เคลือบด้วยพอลิเอทิลีนอิมีน โดยในงานวิจัยนี้ได้ทำการดัดแปรผิวของซิลิกาเจลด้วยไตรเอทอกซีออกทิลไซเลนก่อนเคลือบด้วยพอลิเอทิลีนอิมีนเพื่อเพิ่มประสิทธิภาพในการสกัดและความจำเพาะต่อฟอร์แมลดีไฮด์ จากนั้นหาลักษณะเฉพาะของตัวดูดซับที่เตรียมได้ด้วยวิธีการวิเคราะห์เชิงความร้อน ฟูเรียร์ทรานสฟอร์มอินฟาเรดสเปกโทรเมตรี และการวิเคราะห์ธาตุมูลฐาน พบว่าสามารถเคลือบพอลิเอทิลีนอิมีนบนพื้นผิวของซิลิกาเจลได้ ภาวะที่เหมาะสมในการเคลือบคือใช้ซิลิกาเจลที่ดัดแปรผิวแล้ว 0.10 กรัม สารละลายพอลิเอทิลีนอิมีนเข้มข้น ร้อยละ 2 โดยมวลต่อปริมาตร ปริมาตร 5 มิลลิลิตร และในขั้นตอนการเชื่อมขวางใช้สารละลายอิพิคลอโรไฮดรินเข้มข้น 1.0×10^{-7} โมลาร์ ปริมาตร 3 มิลลิลิตร จากนั้นศึกษาประสิทธิภาพของตัวดูดซับในการสกัดฟอร์แมลดีไฮด์ด้วยระบบแบทช์ ทำการศึกษาปัจจัยที่มีผลต่อการดูดซับฟอร์แมลดีไฮด์ในน้ำ พบว่า พีเอชในช่วง 4-9 เป็นภาวะเหมาะสมที่สุดต่อการดูดซับฟอร์แมลดีไฮด์ เมื่อใช้เวลาในการสกัด 120 นาที ไอโซเทอร์มของการดูดซับเป็นแบบแลงเมียร์และมีค่าความจุดูดซับสูงสุดสำหรับฟอร์แมลดีไฮด์เท่ากับ 25.9 มิลลิกรัมต่อกรัม สามารถชะฟอร์แมลดีไฮด์ออกจากตัวดูดซับที่ใช้แล้วได้โดยใช้กรดไฮโดรคลอริกเข้มข้น 0.1 โมลาร์ ภายในระยะเวลา 5 นาที

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SOPIDA SRIVIRIYAKUL : PREPARATION OF POLYETHYLENEIMINE-COATED SILICA GEL FOR ADSORPTION OF FORMALDEHYDE IN WATER. ADVISOR: ASST.PROF.APICHAT IMYIM, Ph.D., CO-ADVISOR : ASST.PROF. FUANGFA UNOB, Ph.D., 61 pp.

A new adsorbent for formaldehyde extraction from aqueous solution was prepared using silica gel coated with polyethyleneimine. Silica gel was first modified with triethoxyoctylsilane, then polyethyleneimine was coated on the modified silica gel surface to improve the extraction efficiency and selectivity toward formaldehyde. The obtained adsorbents were characterized with thermogravimetric analysis, Fourier transforms infrared spectrometry and elemental analysis. The results showed that polyethyleneimine could be successfully coated on silica gel surface. In the coating step for 0.10 g of surface-modified silica, the suitable concentration of polyethyleneimine solution was 2% w/v (5 mL). And in the crosslink step, 1.0×10^{-7} M epichlorohydrin (3 mL) was used as crosslinking agent. The efficiency in formaldehyde extraction by the adsorbent was evaluated using batch method. The suitable pH for formaldehyde extraction was 4-9, using the extraction time of 120 minutes. The adsorption isotherm of formaldehyde on the adsorbent followed Langmuir isotherm with the maximum adsorption capacity of 25.9 mg/g. The desorption of formaldehyde from used adsorbent was achieved using 0.1 M hydrochloric acid with elution time of 5 minutes.

Field of Study : Petrochemistry and Polymer Science	Student's Signature Sopida Sriviriyakul
Academic Year : 2010	Advisor's Signature
	Co-advisor's Signature Fuangfa Unob

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LIST OF ABBREVIATIONS

cm^{-1}	Wavenumber
^{o}C	Degree Celcius
FT-IR	Fourier transforms infrared spectroscopy
g	Gram
HCl	Hydrochloric acid
L	Litre
mg	Milligram
M	Molar concentration
min	Minute
mL	Milliliter
μL	Microliter
PEI	Polyethyleneimine
ppm	Part per million
RSD	Relative standard deviation
S/m	Siemens per meter
TGA	Thermogravimetric analysis
UV-Vis	Ultraviolet-Visible spectrophotometer
%w/v	Percentage weight by volume
%v/v	Percentage volume by volume

CHAPTER I

INTRODUCTION

1.1 Statement of purpose

Formaldehyde is one type of aldehyde compound, which can naturally be in gas or aqueous phase. Formaldehyde solution 37-50%w/v is called formalin. Generally, the physical properties are colorless, soluble in water and polar solvents. Many formaldehyde applications have been used for disinfection in medical treatment and in the industrial activities. Formaldehyde is almost used in many industries for plastics, formaldehyde-based resins, textile treatments and consumer products [1]. These industries are important for the economy of the country but they could cause environment problems as the contamination in water resource.

Recently, formaldehyde especially in water resource is harmful to human life even at low concentration because of high toxicity. Low levels of formaldehyde (< 0.1 ppm; < 0.12 mg/m^3) can be adsorbed in the respiratory tracts and metabolism in body [2]. The International Agency for Research on Cancer (IRAC), the United States Environmental Protection Agency (U.S. EPA) and the National Occupational Health and Safety Commission (NOHSC) which are part of the World Health Organization (WHO) classified formaldehyde as a probable human carcinogen [1-6]. At present, the standard value of formaldehyde in water source must not be more than 0.1 ppm [5].

Using the adsorbent for adsorption is extensive method for removal of formaldehyde from wastewater. This process is widely used for recovering formaldehyde because of simplicity and low cost. There are many kinds of adsorbent from natural sources for formaldehyde removal such as coffee residuals [7-8], heat-treated rice husks [9] and karamatsu *(Larix leptolepis)* bark [10]. Activated carbon containing amine groups had been used for adsorption of formaldehyde because amine group was responsible for selective adsorption and reactivity [11], and activated carbon fibers were used as the adsorbent for formaldehyde because of high surface area and porosity [12].

Addition to activated carbons, silica gel is widely used as the adsorbent because of its high surface area, inert substance, and cheapness. There are many reports which present the use of modified silica gel with amine group on its surface area for adsorption of formaldehyde. For example, Yang *et al.* [13] studied an efficiency of formaldehyde and acetaldehyde adsorption by using non-modified silica gel and modified silica gel with aminopropyl group. Se-ung *et al.* [14] studied the adsorption of formaldehyde onto porous silica particles functionalized with three kinds of the silane coupling agents and Jadkar *et al.* [15] used Cu_2C_2-silica gel added metal oxide for increasing of capability of formaldehyde adsorption. Owing to high efficiency of modified surface area of silica gel to amine group, we attempt to combine these advantages of silica gel and amine group for using as adsorbent of formaldehyde.

In this research, silica gel particles were first modified with triethoxyoctylsilane, the polyethyleneimine (PEI) was coated onto silica gel surface and crosslinked with epichlorohydrin. The obtained adsorbents were used in adsorption of formaldehyde in water.

1.2 Objectives

1.2.1 To prepare and characterize the adsorbent, the polyethyleneimine-coated silica gel and the epichlorohydrin crosslinked material.

1.2.2 To study the effect of extraction parameters in order to obtain the optimized condition in formaldehyde extraction.

1.2.3 To apply the prepared adsorbent to extract formaldehyde in real water sample.

1.3 Scopes of this research

Silica gel particles are first modified with triethoxyoctylsilane. Then, the polyethyleneimine (PEI) is coated on silica gel surface and crosslinked with epichlorohydrin. The obtained adsorbents are characterized by Fourier transform infrared (FT-IR) spectroscopy, thermogravimetric analysis (TGA), and elemental analysis. Finally, the polyethyleneimine-coated silica gels are used as adsorbent in the extraction of formaldehyde in aqueous solution using batch method.

In formaldehyde extraction, effect of pH of formaldehyde solution, extraction time, adsorption isotherm, eluent agent, and elution time are studied. The adsorbent is applied to extract formaldehyde in real water sample. The efficiency of formaldehyde adsorption and elution were studied by determination of formaldehyde with standard method of ASTM and UV-visible spectrophotometry.

1.4 The benefit of this research

The adsorbent based on polyethyleneimine coated onto silica gel surface and crosslinked with epichlorohydrin was obtained and used in the extraction of formaldehyde containing wastewater.

CHAPTER II

THEORY

2.1 Silica gel

2.1.1. Chemistry of silica gel

Silica gel is an inorganic polymer consisting of inter-linked SiO_4 with the ratio of Si:O of 1:2. Silica gel is a porous and granular material. The major component is the silicon atoms linked by oxygen atoms, so called siloxane bond (≡Si-O-Si≡). The surface of silica is terminated by silanol group (≡Si-OH). Ong *et al*. [16] investigated the dissociation of the hydroxyl group and found that the pK_a values of the silanol group were 4.9 and 8.5 at the silica/water interfaces. Other type of silanols with higher pK_a value (8.5) is believed to be those connected to each other through hydrogen bonding or via the bridging water molecule. Silica gel is a great resistance material to organic solvents [17]. Silica gel has high mass exchange characteristics and no swelling [18]. Due to its high surface area and good thermal and chemical resistance, silica gel is widely used as solid support for catalyst and adsorbents. Moreover, the presence of surface silanol groups allows the modification of silica gel surface with different functionalities.

2.1.2 Surface modification of silica gel

In general, the modification of silica surface is the process that the chemical composition on the surface can be changed without damage or change in original silica gel structure. The modification of silica surface involves many processes that affect to change in chemical properties of the silica surface. Physical treatment (thermal or hydrothermal) is a method which can change ratio of silanol and siloxane concentration of silica surface. Meanwhile, chemical treatment is a process which leads to the change in chemical characteristics of silica surface. The most convenient method for chemical modification of silica surface is simple immobilization or fixing the functional group on surface by electrostatic interaction, hydrogen bond formation or other interactions.

2.1.2.1 Modification through impregnation

Impregnation of modifier solutions on silica is a simple method for functionalization of silica surface with physical interaction between the modifier and silica solid support, for example, the modification of silica gel through impregnation with 8-hydroxyquinoline (8-HQ) [19], ECB-T [20], Lucigenin (bis-N-methyllacridinium nitrate) [21] for metal ions extraction. 2,4-Dinitrophenylhydrazine (2,4-DNPH) was also impregnated on silica gel surface for adsorption of formaldehyde in air as hydrazone complex [22].

2.1.2.2 Modification through grafting

Grafting of organic functional groups on silica surface has been widely manipulated for production of many different types of modified silica. Due to the inert property of silica gel, the activation of the silanol surface is required. In the activation step, organic molecule containing the desired organic functional group is directly attached to the support. Then the activated silica surface can be further reacted with other molecules to enhance the specific adsorption, for example, copper(II), nickel(II), zinc(II) and cadmium(II) ions adsorption and the treatment of chloropropyl silica surface with diethylenetriamine (DETA) [23] for iron(III), nickel(II), copper(II), zinc(II),cadmium(II) and lead(II) ions adsorption. The silylization process is the most usefulness method for activating the silica surface. This reaction is employed to generate products of coupling agents to permit the fixation of a reagent that is able to fulfill predetermined specific applications. A silanol group on the silica surface reacts with the silane compound to yield a covalent bond on the silica surface [17], for example, functionalization of acidic surface of silica with 3-aminopropyltrimethoxysilane (APTS), followed by 2,4-dichlorophenoxyacetic acid (2,4-D) [24].

2.2 Polyethyleneimine

Polyethyleneimine (PEI) is a polymer that is soluble in water, methanol, ethanol or chloroform. The branched polyethyleneimine is in liquid form at all molecular weights at room temperature. It was shown that the behavior of polyethyleneimine was accounted for (a) the branched structure of the polymer containing three different types of amine group (primary, secondary and tertiary amine groups); (b) strong inter and intra molecular electrostatic and hydrogen bonding interactions between polyethyleneimine and proton donors and (c) the pH dependent structure of the polymer in aqueous solution [25]. The majority of amine groups on the polymer chains is protonated in aqueous solution of pH lower than 10 [26]; therefore polyethyleneimine is a cationic polyelectrolyte and it can interact with negatively charged particles like silica gel. Polyethyleneimine has been used in separation and purification of biomacromolecules [27], in drug releasing system [28] and so on.

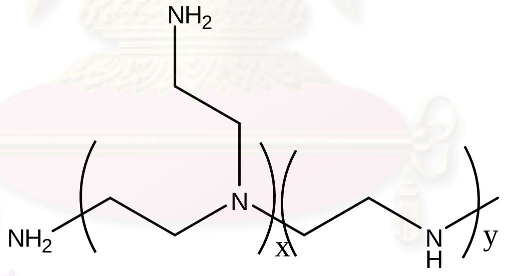


Figure 2.1 The structure of polyethyleneimine.

Amine groups can react easily with various compounds. The silica gel adsorbent modified with amine groups can extract formaldehyde [13-14, 29] via the schiff base compound formation. Primary amines can react with formaldehyde to form imine ($-N=CH_2$) functional groups as shown in the following Equation (2.1).

$$HCHO + R\text{-}NH_2 \longrightarrow R\text{-}N=CH_2 + H_2O \quad ; \; R\text{-}NH_2 = \text{poly(allylamine)} \qquad (2.1)$$

The PEI coated silica gel is an alternative for improving the efficiency of adsorbent [26, 30-32]. The large amount of amine groups on PEI in combination with a high surface area and good mechanical strength of silica gel will give a stable adsorbent that have good performance in the extraction. As polyethyleneimine dissolves readily in water, it may be detached from the silica gel surface when use in the water. Therefore, PEI must be crosslinked with suitable crosslinking agents such as ethylenedibromide, ethylenedichloride, glutaraldehyde, epichlorohydrin, etc. before use [31].

2.3 Crosslinker

The mechanism is to link the polymer chains together through ionic or covalent bonds to form a network. There are two categories of crosslinking [33]:

1) Crosslinking during polymerization by polyfunctional monomer.
2) Crosslinking in a separate processing step after the polymer is formed.

The crosslinker molecules may contain the same structural as the main polymer chains, or they may have an entirely different structure. A number of extreme changes in polymer properties may accompany the crosslinking. For water soluble polymer, it would no longer dissolve after being crosslinked. In the presence of a solvent, a crosslinked polymer swells as solvent molecules penetrate the network. For polyethyleneimine, the polymer will be insoluble in water after undergone the crosslink reaction when suitable agents. A number of crosslinking agents have been used, such as epichlorohydrin and glutaraldehyde [31]. We have adopted this method of crosslinking to maintain polyethyleneimine on silica gel surface.

2.4 Adsorption

The adsorption is a phenomenon of the sorption that occurs between the liquid or gas phase and solid phase. The species in the liquid or gas phase move to the solid surface and can be further adhered on the surface of solid phase, which is called mass transfer. The solid phase and the target species in the liquid or gas phase are called adsorbent and adsorbate, respectively.

2.4.1 Types of adsorption

Adsorption process is generally classified as physisorption and chemisorptions.

2.4.1.1 Physisorption

Physisorption is a physical separation process that the adsorbed substance does not chemically react to the solid phase and adsorbs on the surface through van der Waals forces. This phenomenon can occur in any solid/liquid system depending on geometrical or electronic properties of both the adsorbent and adsorbate. Molecules of adsorbate can excessively adsorb on surface as multilayer adsorption or filling in micro or mesopores. The reaction of this adsorption is called outer-sphere surface reaction, which the analytes adsorb independently on the adsorbent surface and the adsorption is a reversible process.

2.4.1.2 Chemisorption

Chemisorption is a chemical separation process that occurs at the surface and characterized by chemical specificity. The interaction between the adsorbate and adsorbent surface involves chemical bonds formation such as ionic or covalent bond that is irreversible reaction. The adsorbate molecules usually occupy certain specific adsorption sites on the surface and can form only one adsorption layer on adsorbent (monolayer adsorption). The chemical adsorption is also called inner-sphere surface reaction.

2.4.2 Adsorption isotherm models

The adsorption process that refers to the partition of adsorbates between liquid or gas phase and solid phase at equilibrium and constant temperature is called adsorption isotherm. Adsorption isotherm plot is the relation between the quantity of adsorbate adsorbed and the adsorbate in the bulk liquid phase or the partial pressure in the gas phase. There are the several isotherm equations describing the adsorption equilibrium and the most common of them are Langmuir and Freundlich isotherm.

2.4.2.1 Langmuir isotherm

The most important model assuming monolayer adsorption is Langmuir isotherm. The assumptions of the Langmuir isotherm are: (1) adsorption energy is constant over all sites, (2) The adsorption takes place at specific sites of the adsorbents and no further adsorption occurs at that site, (3) there is no interaction between adsorbates and (4) the adsorption phenomena is the monolayer coverage on adsorbents surface. This isotherm equation is given as,

$$q = \frac{q_m bC}{1+bC} \tag{2.2}$$

$$\frac{C}{q} = \frac{1}{bq_m} + \frac{C}{q_m} \tag{2.3}$$

where C = the residual concentration in solution at equilibrium (mol L^{-1})

q = the amount of adsorbed per gram of sorbent (mol g^{-1})

q_m = the maximum sorption capacity of the sorbent (mol g^{-1})

b = Langmuir constant related to energy of adsorption (L mol^{-1})

Experimental data are plotted as shown either in Figure 2.2 or in one of the two alternate linear forms shown in Figure 2.3. The model is described by equation 2.3 and the plot of $\frac{C}{q}$ against C yields a straight line with a slope of $\frac{1}{q_m}$ and intercept of $\frac{1}{bq_m}$ (Figure 2.3(b)).

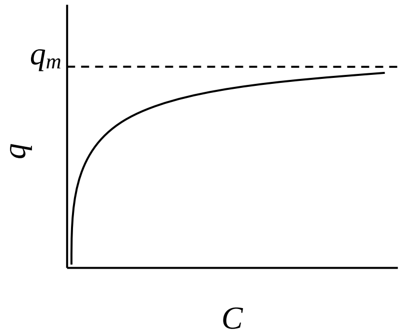


Figure 2.2 Form of Langmuir adsorption isotherm [34].

The plot of Langmuir isotherm will demonstrate whether the model is applicable and also will allow the determination of the values of q_m and *b*. In many cases, a single model will not be satisfactory for a wide range of concentrations but will serve in narrow regions.

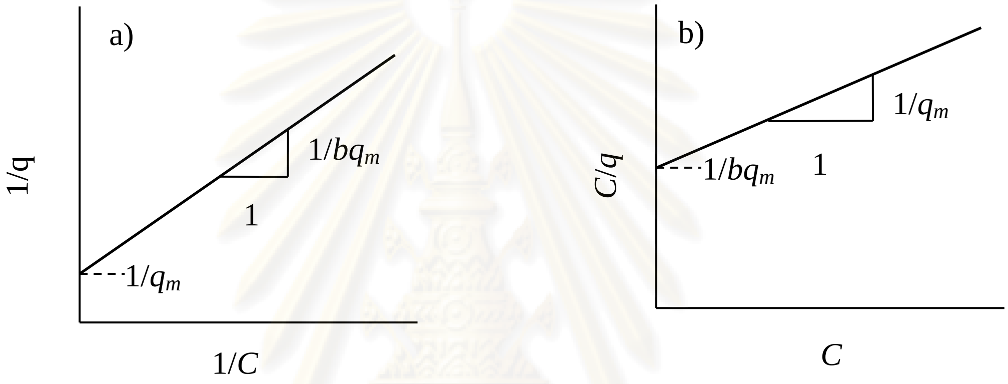


Figure 2.3 Conventional linear form of Langmuir adsorption isotherm (a) and modified form of Langmuir adsorption isotherm emphasizing higher concentration data (b).

2.4.2.2Freundlich isotherm

The Freundlich isotherm is used to describe multilayer adsorption on heterogeneous surface or surface containing active sites of varied affinities. The common form of the Freundlich is expressed by the following Equation 2.4,

$$q = K_f C^{1/n} \tag{2.4}$$

where K_f is the Freundlich adsorption coefficient and *n* is the numerical value of Freundlich constant. A plot of *q* versus *C* results in a curve of the form shown in Figure 2.4. Equation 2.5 is generally used in the linear form, represented by:

$$\log q = \log K_f + \left(\frac{1}{n}\right)\log C \tag{2.5}$$

A linear plot of log q versus log C gives a slope of $\frac{1}{n}$ and intercept of log K_f as presented in Figure 2.5. The equation 2.3 is common and simple and has been used to fit experimental data. Usually the Freundlich isotherm is plotted on log-log scale (Figure 2.5) to facilitate determination of the model’s validity and the values of the coefficients K_f and n.

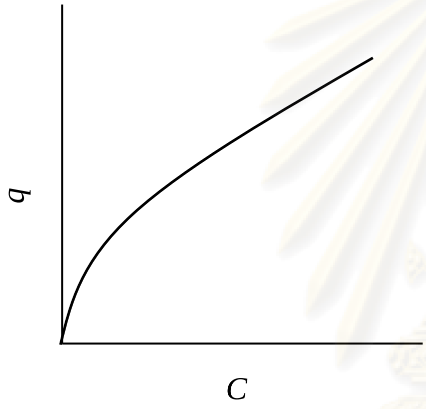


Figure 2.4 Form of Freundlich adsorption isotherm [34].

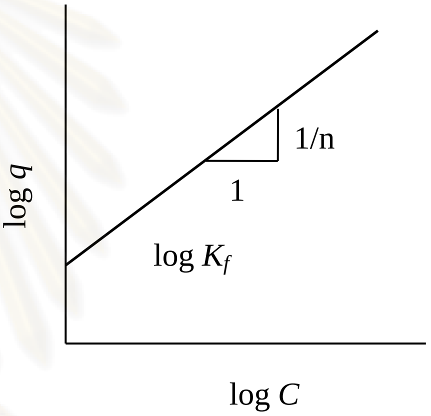


Figure 2.5 Linear form of Freundlich adsorption isotherm [34].

2.5 Characterization of adsorbent

2.5.1 Fourier transforms infrared (FT-IR) spectroscopy

The FT-IR spectroscopy is a technique that provides identification information about the structure of samples either organic or inorganic material in term of functional groups or chemical bonds. Samples can be either solids, liquids or gaseous. Most FT-IR spectrometers work in the mid-infrared region from 4000 cm^{-1} to 400 cm^{-1} and offer high sensitivity and accuracy as well as improve data collection speed compared to dispersive instruments because the whole spectra is measured at the same time and hence multiple scanning of the sample is possible [35].

The basic principle of IR-spectroscopy is based on the absorption of IR radiation of the material, resulting in molecular bond vibration when compounds are excited by radiation of a suitable frequency. FT-IR spectrum is recorded in term of the correlation between the percentage transmittance and the wavenumbers, which is the direct proportion to the frequency of the absorbed radiation responsible for the molecular vibration or the absorption process. FT-IR is a beneficial instrument to detect functional groups in a sample but it cannot be used to clarify the complete structure of an unknown molecule. KBr pellet is commonly used in the analysis of solid sample. Solid samples are grounded and milled with potassium bromide (KBr) to obtain a homogeneous powder. This powder is compressed into a thin pellet and then analyzed [36].

In this research, FT-IR was used to identify the functional groups on the silica gel surface before and after coating with polyethyleneimine and being crosslinked with epichlorohydrin.

2.5.2 Thermogravimetric analysis (TGA)

TGA is a thermal analysis technique that measures the weight loss or weight change of materials as a function of temperature. The measurement can be carried out in air or nitrogen atmosphere. During the measurement, the decrease of sample weight is observed due to the loss of volatile components and moisture. This technique is usually used to determine the thermal stability and composition of both organic and inorganic materials, especially polymer [37].

TGA gives qualitative and quantitative information about the sample. The onset temperature is the temperature at which a mass loss occurs and can be used for quanlitative analysis, because it can be compared to the temperature values where standards are lost from the surface under identical measurement conditions. Quantitative analysis is done by measuring the weight loss obtained when a known molecular weight component is vaporized from the sample [38].

2.6 Literature review

Many past researches reported about silica gels adsorbents modified with polyethyleneimine. For example, Gao *et al*. synthesized adsorbent by grafting polyethyleneimine on the surface of silica gel for extraction of uric acids and Zn(II), Cu(II) and Cd(II) ions in water [26, 30]. The results showed that the physical adsorption of uric acid occurred through hydrogen bonding between polyethyleneimine and 2,6,8-trihydroxypurine which is an uric acid's tautomer. The chemical adsorption of uric acid could occur via schiff base compounds formation.

Chanda *et al*. prepared silica gels coated with polyethyleneimine by adding Cu (II) on the surface of silica gel for acting as host ion to keep polymers together on the silica surface [31]. Then the coated polymer was crosslinked with glutaraldehyde. It was found that $-NH_2$ functional groups on polyethyleneimine had been changed to $-N(CH_2)-CH(OH)-(CH_2)_3-$ with the crosslinking reaction and the adsorbents were used in adsorption of uranium and iron.

Ghoul *et al*. prepared silica gels coated with polyethyleneimine and crosslinked with glutaraldehyde for extraction of Pb(II), Zn(II), Cd(II) and Ni(II) in water [32]. By comparing the performance with adsorbent prepared without crosslinking, the results indicated that the crosslinked adsorbents had lower adsorption capacity than non-crosslinked adsorbents. And adsorbents can be reused after regeneration with acid.

From these researches, they prepared silica gel modified with polyethyleneimine in many ways. In this study, we are interested in the preparation of silica gel coated with polyethyleneimine by environmental friendly process for the use as an adsorbent for formaldehyde adsorption. As polyethyleneimine is soluble in water, then the adsorbents preparation and surface coating could be performed in aqueous media to reduce the use of organic solvent. Firstly, the silica surface will be grafted with the triethoxyoctylsilane through the silylated reaction. The presence of octyl moiety on surface improved the surface hydrophobicity and enhanced the efficiency in further surface coating with polyethyleneimine. When the silica gel surface is more hydrophobic, polyethyleneimine can adsorb on the silica gel surface via Van der Waals force more efficiently than the direct coating of polyethyleneimine on hydrophilic surface of raw silica gel. Compared to the other grafting process, the silica coated polyethyleneimine can be prepared easily and the organic solvents were not used.

There are many reports which present the use of modified silica gel containing amine groups for adsorption of formaldehyde. For example, Yang *et al.* studied the adsorption of formaldehyde and acetaldehyde by non-modified silica gel and silica gel modified with aminopropyl group [13]. The results indicated that the efficiency of aminopropylsilylated silica gel in formaldehyde adsorption was higher than non-modified silica. The silica gel containing aminopropyl extracted formaldehyde through the schiff base compound formation resulting in imine groups.

Se-ung *et al.* studied the adsorption of formaldehyde onto porous silica particles functionalized with three silane coupling agents including 3-aminopropyl-triethoxysilane (APTES), *n*-(2-aminoethyl)-3-aminopropyl-trimethoxysilane (AEAP) and 3-(2-(2-aminoethylamino) ethylamino) propyltrimethoxysilane (AEEA) [14]. Silica gel with amine groups could adsorb formaldehyde more effectively than non-modified silica gel. APTES was the most suitable coupling agent for functionalization on silica gel for formaldehyde adsorption. The adsorbent could adsorbed formaldehyde gas via the schiff base compound or imine formation. The maximum adsorption capacity was 1208 mg/g of adsorbent.

In this research, we attempted to combine the advantages of silica gel and amine group for using as one type of the adsorbent of formaldehyde. The silica gel particles were first modified with triethoxyoctylsilane, then the polyethyleneimine (PEI) was coated onto silica gel surface and crosslinked with epichlorohydrin solution. The obtained adsorbents were used in adsorption of formaldehyde in water.

CHAPTER III

EXPERIMENTAL

3.1 Instruments

The instruments used for measurements and characterization in this thesis are shown in Table 3.1.

Table 3.1 List of instruments

Instruments	Manufacture: Model	Purpose
1. Fourier transforms infrared spectrometer (FT-IR)	Nicolet: 6700	Functional group identification
2. Thermogravimetric analyzer (TGA)	Perkin Elmer: Pyris1	Thermal stability of the adsorbents
3. CHN analyzer	Perkin Elmer: 2400 SeriesII	Determination of carbon, nitrogen, and hydrogen content on the adsorbents
4. UV-Visible spectrometer	Hewllet Packard: 8453	Determination of formaldehyde
5. pH meter	Hanna instruments: pH 211	pH measurement
6. Stirrer	Gem: MS 101	Agitation of solution in adsorbents preparation and extraction experiments

3.2 Chemicals

All chemicals used in this thesis are listed in Table 3.2.

Table 3.2 List of chemicals

Chemicals	Suppliers/Grade
Silica gel	Merck/ AR Grade
Triethoxyoctylsilane	Merck/ for synthesis
Polyethyleneimine	Aldrich/ for synthesis
Epichlorohydrin	Merck/ for synthesis
Formaldehyde solution, 37%	Merck/for analysis
Ninhydrin	Aldrich/ for analysis
Sodium carbonate	J.T.BaKer/ AR Grade
Iodine resublimed	CARLO ERBA/ for analysis
Sodium thiosulphate	Ajax Finechem/ AR Grade
Potassium iodate	Ajax Finechem/ AR Grade
Concentrated hydrochloric acid, 36.5-38%	Merck/ for analysis
Concentrated sulfuric acid, 98%	Merck/ for analysis
Sodium hydroxide	Merck/ for analysis
2,4-Pentane dione (Acetyl acetone)	CARLO ERBA/ for analysis
Ammonium acetate	Scharlau/ AR Grade
Glacial acetic acid	Merck/ for analysis
Ethanol	Merck/ for analysis
Potassium bromide	Merck/ for IR spectroscopy

3.3 Experimental procedures

3.3.1 Preparation of chemicals and reagents

Formaldehyde solutions

Formaldehyde stock solution (1000 mg/L) was prepared from concentrated formaldehyde solution (37%) and standardized before use. Formaldehyde stock solution (1000 mg/L) was used to prepare the formaldehyde solutions of desired concentrations by dilution with de-ionized water. Formaldehyde solution (10 mg/L) was used as a working standard solution for the determination based on the ASTM standard method.

Polyethyleneimine solutions

Polyethyleneimine or PEI solution (50% w/v) with the average molecular weight of 750,000 was used to prepare the polyethyleneimine solutions of desired concentrations by dilution with de-ionized water and used for adsorbents preparation.

Epichlorohydrin solutions

Epichlorohydrin stock solution (1.25×10^{-4} M) was prepared by dilution of the concentrated epichlorohydrin solution with de-ionized water and used to prepare the epichlorohydrin solutions of desired concentrations as a crosslinking agent in the range of 1.04×10^{-7} to 4.18×10^{-6} M.

Acetyl acetone reagent

Acetyl acetone reagent was prepared by adding acetylacetone (2 mL) and glacial acetic acid (3 mL) to ammonium acetate solution (154 g of CH_3COONH_4 in de-ionized water). The final volume was adjusted to 1000 mL using de-ionized water and used in formaldehyde analysis by a UV-Visible spectrometer.

Hydrochloric acid solutions

Hydrochloric acid solutions (1 and 5% v/v) were prepared by dilution of the concentrated hydrochloric acid solution with de-ionized water and used for desorption study and pH adjustment.

Sodium hydroxide solutions

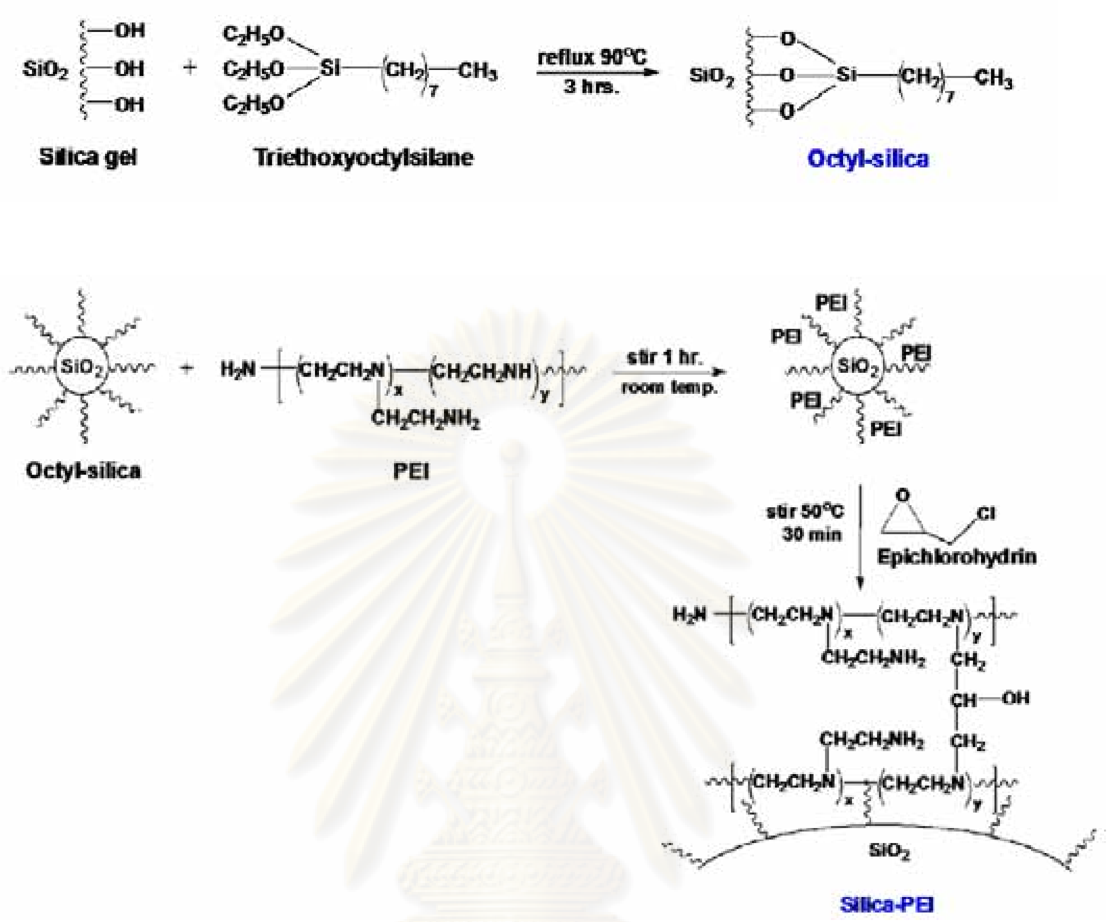
Sodium hydroxide solutions (1 and 5% w/v) were prepared by dissolving the appropriate amount of NaOH in de-ionized water and used for pH adjustment.

Ninhydrin solution

Ninhydrin solution was prepared by dissolving 500 mg of ninhydrin in 10 mL of ethanol. The yellow color appeared after dissolving. This solution was used to confirm the presence of amine groups of PEI on the adsorbent surface.

3.3.2 Preparation of silica coated with PEI sorbent (Silica-PEI)

Before coating PEI onto the silica support, the silica was first modified with triethoxyoctylsilane by refluxing silica gel (2.0 g) with triethoxyoctylsilane (2 mmol) in de-ionized water (30 mL) for 3 hours under N_2 atmosphere. The resulting solid was filtered and then washed with de-ionized water until pH of the filtrate was neutral. The product was dried overnight under vacuum at 100°C until the weight of sorbent remained constant. The obtained sorbent (0.100 g) was added into PEI aqueous solution 2%w/v (5 mL). Then, the reaction mixture was stirred for 1 hour at room temperature. The product was first washed with de-ionized water and then crosslinked with epichlorohydrin 1.04×10^{-7} M (3 mL) at 50°C for 30 minutes. The sorbent was filtered and washed with de-ionized water prior to vacuum drying overnight at 60°C. The obtained product (silica-PEI) was kept in a dessicator until used. The preparation of silica-PEI was shown in Scheme 3.1.



Scheme 3.1 Preparation of Silica-PEI.

3.3.2.1 Effect of the concentration of PEI solution

A 5 mL aliquot of PEI solution containing PEI in the range of 50-1000 mg was stirred with 0.100 g of triethoxyoctylsilane modified silica (or Octyl-silica) for 60 minutes. The solid was separated and washed with de-ionized water three times, then the attached PEI were crosslinked with a 3 mL aliquot of epichlorohydrin solution (4.18×10^{-7} M) and heated 30 minutes at 50 °C. The sorbent was filtered and washed with de-ionized water prior to vacuum drying overnight at 60°C. The efficiency in formaldehyde adsorption by the resulting adsorbents was evaluated.

3.3.2.2 Effect of the amount of epichlorohydrin

A 5 mL aliquot containing 100 mg of PEI was stirred with 0.100 g of triethoxyoctylsilane modified silica for 60 minutes. The sorbent was separated and washed with de-ionized water three times, then the attached PEI were crosslinked with a 3 mL aliquot of epichlorohydrin solution having concentration in the range of 1.04×10^{-7} - 4.18×10^{-6} M and heated 30 minutes at 50 °C. The sorbent was filtered and washed with de-ionized water prior to vacuum drying overnight at 60°C. The efficiency in formaldehyde adsorption by the resulting adsorbents was evaluated.

3.4 Characterization

The adsorbents were characterized by FT-IR, TGA and Ninhydrin test to confirm the success of the surface modification.

3.4.1 Fourier-transform infrared spectrometry (FT-IR)

Functional groups of functionalized and non-functionalized adsorbents were identified with FT-IR (Nicolet 6700) by KBr pellet method within the wavenumber range of 40-4000 cm^{-1} and 16 scans with resolution of wavenumber of ± 4 cm^{-1} in transmittance mode.

3.4.2 Thermogravimetric analysis (TGA)

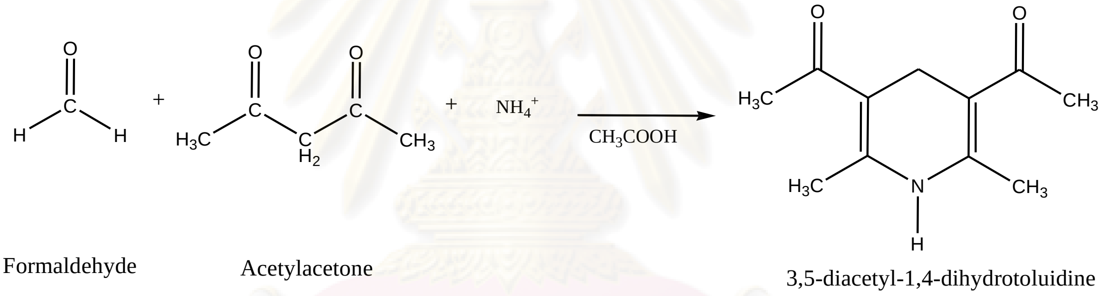
The modified adsorbent (silica-PEI) was examined and compared with non-modified one using thermogravimetric analyzer providing the measurement of weight loss of material associated with transition and thermal degradation of the sample. A sample weight for analysis was about 2-3 grams. Silica-PEI was heated in the range of 30-900°C at a heating rate of 10°C/min. TGA thermogram showed the weight loss on silica sample as the percentages compared with the initial weight of sample.

3.5 Ninhydrin test

Ninhydrin test is the method for analysis of amino acids. In this research, ninhydrin test was used to detect free terminal-amine groups of polyethyleneimine modified on adsorbent. A small amount of adsorbents (Silica-PEI) was transferred into a test tube and 1 mL of ninhydrin solution was added. The color of adsorbent will change from yellow to purple or blue when amine groups are present. However, the color of adsorbent will not change when there is no amine groups on the adsorbent.

3.6 Detection of formaldehyde by ASTM method [D6303-98]

Quantities of formaldehyde solution after adsorption or elution were detected as absorbance value at a maximum wavelength of 412 nm by UV-visible spectrophotometer. Prior to detection based on Hantzsch reaction, formaldehyde solution needed to be derivatized by acetyl acetone reagent consisted of 154 g ammonium acetate, 200 µL acetyl acetone and 300 µL glacial acetic acid in 100 mL of de-ionized water. And then the resultant yellow solutions were heated at 60°C for 10 minutes. When the solutions were cooled down to room temperature, these were ready to detect with the above mention technique. The reaction is shown in scheme 3.2.



Scheme 3.2 Derivatization of formaldehyde to form 3,5-diacetyl-1,4-dihydrotoluidine.

Eight standard formaldehyde solutions including concentrations of 0.0, 0.5, 1.5, 2.5, 3.5, 4.5, 6.0, and 7.5 mg/L were prepared for calibration curve by dilution of 10 mg/L formaldehyde solution that was prepared from 1000 mg/L formaldehyde stock solution. And formaldehyde samples which obtained from adsorption and elution for detection with the spectrometer must be diluted until the concentrations were in the linear range of calibration curve.

3.7 Adsorption of formaldehyde solution

The batch method was used for adsorption study in this work. The adsorption of formaldehyde in aqueous solution by Silica-PEI was studied. Silica-PEI was weighed about 0.025 g and immersed into 5.00 mL of formaldehyde solution (100 mg/L) in a closed glass vial. The mixture was stirred at room temperature before the adsorbents were separated by filtration. The concentration of formaldehyde in the solution was determined based on Hantzsch reaction described in the ASTM standard method. The derivatized product was analysed by UV-Visible spectrometer at 412 nm. The effect of formaldehyde solution pH and extraction time were studied. The adsorption isotherms were also investigated.

3.7.1 Effect of formaldehyde solution pH

The effect of pH on extraction efficiency was studied by varying the pH in the range of 4.0-9.0. The initial concentration of formaldehyde in solution was 100 mg/L. The pH of solution was adjusted to the desired value using NaOH (1 and 5% w/v) and HCl (1 and 5% v/v). Silica-PEI (0.025 g) were immersed into 5.00 mL of formaldehyde solution (100 mg/L) and stirred for 2 hours before separating the adsorbents by filtration. Then, the amount of formaldehyde in the solution before and after adsorption was determined spectrophotometriccaly.

3.7.2 Effect of extraction time

The effect of extraction time on extraction efficiency was studied using contact times from 5 to 480 minutes. The initial concentration of formaldehyde in solution was fixed at 100 mg/L. The experiment was performed using 0.025 g of Silica-PEI in 5.00 mL of formaldehyde solution at pH 6. Then, the adsorbent was separated and the amount of formaldehyde in the solution before and after adsorption was determined.

3.7.3 Adsorption isotherms

The experiment was performed when the initial concentration of formaldehyde solution was varied in the range of 100 to 900 mg/L at fixed adsorbent amount, under optimum pH and extraction time. The temperature was controlled at 25 ± 0.5 °C. The equilibrium concentration of formaldehyde was determined.

3.8 Desorption of formaldehyde

Hydrochloric acid solution was used as eluent in this study. The adsorbent containing adsorbed formaldehyde (0.025 g) was added in 5.00 mL of hydrochloric acid solution. The mixture was stirred for one hour and the solid was separated from the eluent. The amount of formaldehyde in the solution before and after desorption was determined.

3.8.1 Effect of the concentration of hydrochloric acid

The HCl concentration was varied in the range of 0.1 to 2.0 M. The used adsorbent was obtained from the adsorption experiment using 100 mg/L of formaldehyde solution. The used adsorbent (0.025 g) was added in 5.00 mL of various concentrations of HCl and stirred for an hour before separating the adsorbents by filtration. Then, the adsorbent was separated. The concentration of formaldehyde in eluent after desorption was determined.

3.8.2 Effect of desorption time

The suitable concentration of hydrochloric acid was selected from the results from experiment 3.8.1. The effect of desorption time was studied by varying the contact time from 5 to 120 minutes. Then, the concentration of formaldehyde in eluent after desorption was determined.

3.8.3 Reusability of the adsorbent

The repeated adsorption/desorption cycles were performed 2 cycles for extraction of formaldehyde. The suitable eluent and desorption time from the experiment 3.8.1and 3.8.2 were used. Then, the formaldehyde concentrations after both adsorption and desorption were determined.

CHAPTER IV

RESULTS AND DISCUSSION

This chapter is divided into three sections. Firstly, the surface of silica gel was modified with PEI and characterized. The characterization results of non-coated silica gel, triethoxyoctylsilane modified silica gel and silica gel coated with PEI (silica-PEI) are shown. Then, the efficiency of silica-PEI in adsorption of formaldehyde in water was studied. Finally, the elution of adsorbed formaldehyde from silica-PEI with acids was examined.

4.1 Preparation and characterization of polyethyleneimine-coated silica gel (silica-PEI)

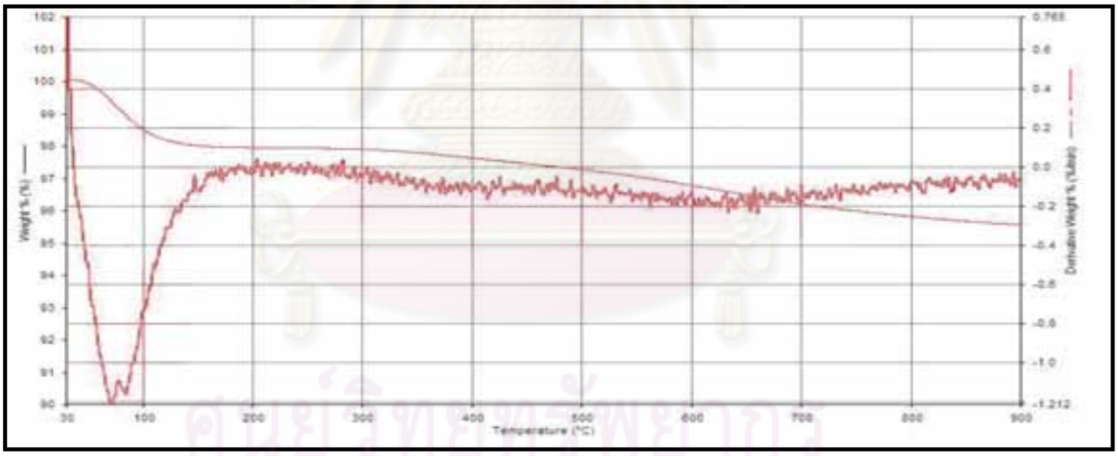
The preparation of silica-PEI is shown in Scheme 3.1. The preparation of silica-PEI started with the modification of silica gel surface with triethoxyoctylsilane. The silylation reaction between silanol groups on silica surface and triethoxyoctylsilane yielded silica gel containing octyl moiety and ethanol as by-products. After surface modification with triethoxyoctylsilane, the surface of silica gel would have more hydrophobic property and the further adsorption of polyethyleneimine onto the surface could occur via Van der Waals force. To prevent the desorption of polyethyleneimine from the surface, the crosslink of the attached polyethyleneimine was performed using epichlorohydrin solution to create the network between chains of polyethyleneimine. The obtained crosslinked polyethyleneimine was insoluble; therefore the polymer could be retained and coated onto octylsilane-modified silica gel surface. Epichlorohydrin was chosen as crosslinking agent because it was reactive with polyethyleneimine and soluble in water. However, white color of silica gel, silica-triethoxyoctylesilane and silica-PEI observed by naked eyes was not different.

4.1.1 Characterization

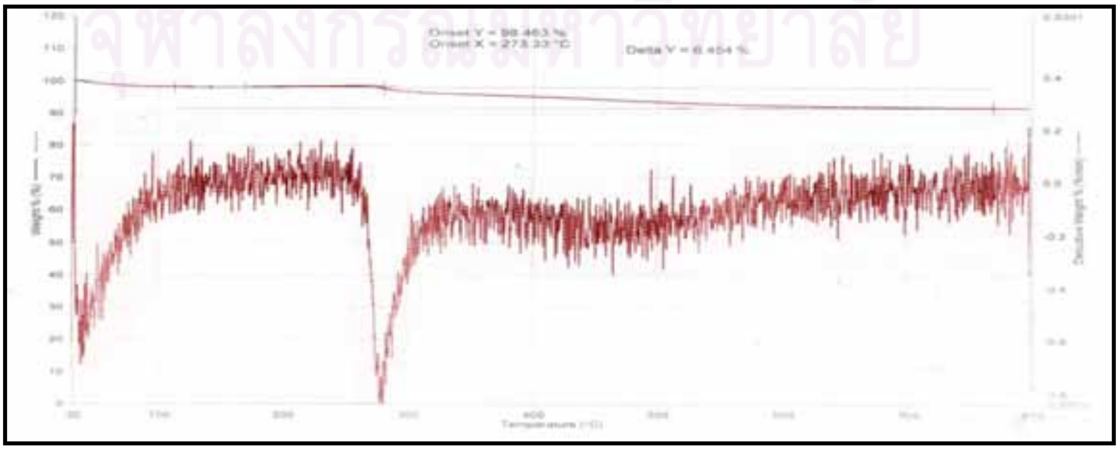
4.1.1.1 Thermogravimetric analysis (TGA)

The thermal stability of the prepared silica-PEI was investigated to confirm the success of the preparation. The TGA results are shown in Figure 4.1. All TGA curves show the weight loss at the temperature below 200 °C due to the vaporization of water. The decomposition of the organic compounds modified on the surface of silica gel was observed in the temperature range of 200 to 350 °C as shown in Figure 4.1(b-c). When compared the TGA profile of non-coated silica and coated silica, the non-coated silica curve did not show any change in weight after heating above 200 °C. The TGA curve of octyl-silica shows the weight loss of 6.45% while that of silica-PEI shows the weight loss of 11.50% at the temperature range of 200 to 350 °C. The increasing trend of weight loss from the materials indicates that the surface was successfully coated with different molecules.

(a)



(b)



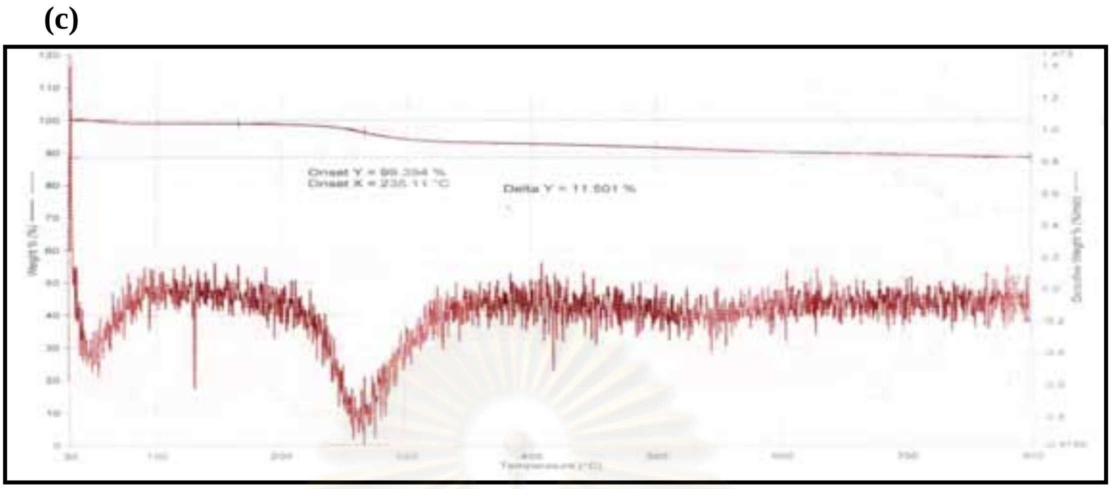


Figure 4.1 TGA curves of (a) silica gel, (b) silica-triethoxyoctylesilane and (c) silica-PEI.

4.1.1.2 Fourier transforms infrared spectroscopy

The signal of functional groups of the silica gel, silica-triethoxyoctylsilane and silica-PEI are shown in Figure 4.2. The FT-IR bands of the bare silica gel and the new bands after modification with triethoxyoctylsilane and coating with PEI are interpreted as following.

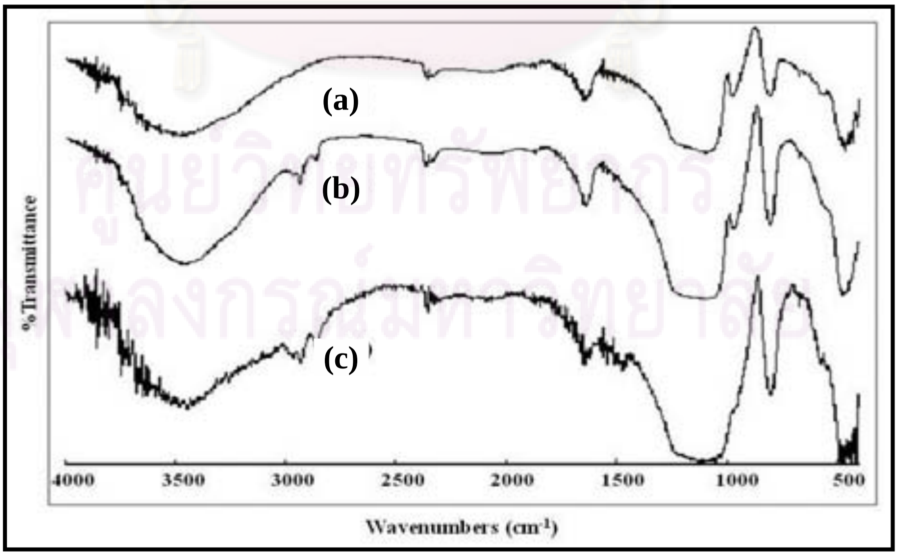


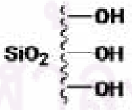
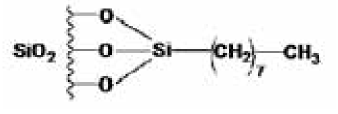
Figure 4.2 FT-IR spectra of (a) silica gel, (b) silica-triethoxyoctylsilane and (c) silica-PEI.

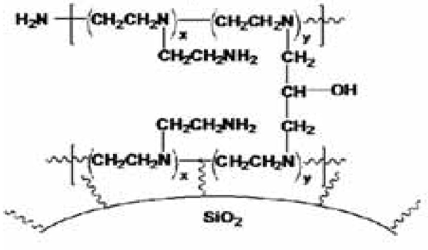
Figure 4.2(a) shows the FT-IR spectrum of bare silica gel. The characteristic peak at 1090 cm^{-1} corresponds to the Si-O-Si vibration. After modification of silica gel particles with triethoxyoctylsilane (Figure 4.2(b)), the stretching vibration of C-H bond at 2958 and 2848 cm^{-1} appeared. The results indicate that $–CH_2$ and $–CH_3$ groups were present on the surface of silica gel after the modification. Comparing the spectra of silica-triethoxyoctylsilane to that of silica-PEI (Figure 4.2(c)), there was a difference between the bands of both IR spectra at around 1400-1600 cm^{-1} which were assigned to the symmetric bending vibration of $-NH_2$ at 1558 and 1470 cm^{-1} [39]. Besides, the produced bands at 1560 cm^{-1} are ascribed to the stretching vibration of C-N bond. The peak assigned for $Si-CH_2$ stretching bands around 1150 cm^{-1} could not be clearly identified because it may overlap with the strong peak attributed to vibration of Si-O-Si band at 1090 cm^{-1}. The appearance of these bands revealed that the chains of PEI were coated onto the surface of silica gel particles and the silica-PEI was successfully prepared.

4.1.1.3 Elemental analysis

The elemental analysis of the materials was carried out after each step of the synthesis pathway as reported in Table 4.1.

Table 4.1 Elemental composition of the functionalized silica

Sample	%C	%H	%N
 Silica gel	0.05±0.01	1.64±0.04	0.01±0.01
 Silica-triethoxyoctylsilane	1.93±0.04	1.96±0.08	0.06±0.03

 Silica-PEI	7.34±0.06	2.34±0.07	3.43±0.02

The elemental analysis was used to monitor change in the percentages of C, H and N of the adsorbents obtained from each step of the preparation. There was trace amount of carbon and nitrogen present on silica gel, which was probably due to the surface contamination with organic compounds. The percentage of carbon of silica-PEI was higher than that of silica-triethoxyoctylsilane and silica gel, respectively. This confirmed the success of phase preparation in these steps. The percentage of C in silica-triethoxyoctylsilane increased when compared to bare silica gel, due to the addition of triethoxyoctylsilane. As the reaction proceeded, the percentage of C and N become significantly higher due to the loading of polyethyleneimine onto the silica gel surface.

4.1.1.4 Ninhydrin test

Ninhydrin method was used to detect free terminal amine groups of the PEI on the surface of adsorbent. The color of ninhydrin solution will change from yellow to purple if the amine groups are present. The experimental results of ninhydrin test are shown in Table 4.2. The color of ninhydrin solution was yellow when tested with silica gel and silica-triethoxyoctylsilane. These results agreed with their structure which did not contain any amine group. On the other hand, when tested with silica-PEI, the color of ninhydrin solution changed from yellow to purple as shown in Figure 4.3. The expected color change indicates that there were free terminal amine groups of PEI on the adsorbent.

Moreover, for checking the PEI detachment from silica-PEI adsorbent when used in formaldehyde extraction, the extracted formaldehyde solution was tested with ninhydrin solution. The ninhydrin solution remained yellow, indicating that the PEI was not detached from the adsorbent during the extraction process.

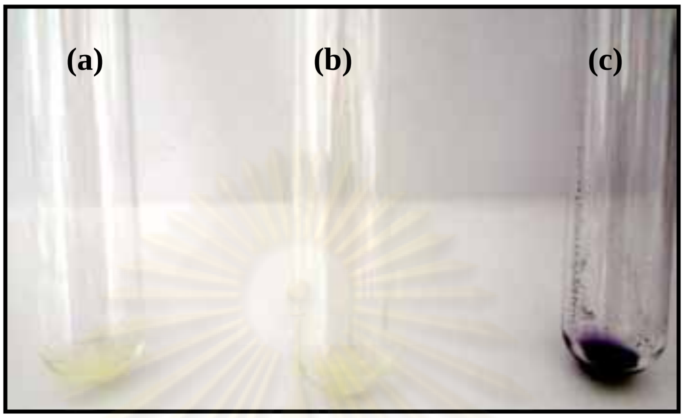


Figure 4.3 Ninhydrin test of (a) silica gel, (b) silica-triethoxyoctylesilane and (c) silica-PEI.

Table 4.2 Ninhydrin test results

Sample	Color of sorbent	Color of ninhydrin solution
Ninhydrin solution	-	yellow
Silica-triethoxyoctylsilane	yellow	yellow
Silica-PEI	purple	purple
Extracted formaldehyde solutoin[a]	-	yellow

[a] Formaldehyde solution after extraction with silica-PEI.

4.1.2 Effect of PEI amount on the silica gel coating

In the preparation of silica-PEI, the effect of the PEI amount used for coating the silica gel was investigated by varying the amount of PEI in the range of 0.050 to 1.000 g in 5.0 mL solution for coating 0.1 g of silica-triethoxyoctylsilane. The polymer was afterwards crosslinked with 1.04×10^{-7} M epichlorohydrin solution.

The thermal stability of silica-PEI prepared using different PEI amount was investigated. The TGA profiles are shown in Appendices. The decomposition of the

PEI coated on the surface of silica gel was observed in the temperature range of 200 to 350° C. The TGA result of silica-PEI shows the average weight loss of 12.20%, 11.50%, 10.46%, 11.89%, 13.42% and 4.97% when used the PEI amount of 0.050, 0.100, 0.025, 0.500, 0.750 and 1.000 g, respectively. The calculated amounts of PEI coated on silica gel are shown in Table 4.3. The amount of coated PEI on silica gel (mg/g silica) should increase proportionally to the initially used PEI amount. However, due to the possible random errors in TGA resulting to invalid results, the expected tendency of the amount of coated PEI on silica gel could not be observed. We have decided to take into account the efficiency in formaldehyde adsorption which was more valid in analytical point of view to select the optimized coating conditions.

The efficiency in formaldehyde adsorption by obtained silica-PEI (0.025 g) was evaluated using 100 mg/L formaldehyde solution (5.00 mL) (Table 4.3). The results from batch adsorption experiments show that the efficiency in formaldehyde adsorption by the final product increased when the added PEI amount increased from 0.050 g to 0.100 g due to the increase in active sites number. Comparing the adsorption efficiency of adsorbents coated with 0.100 to 1.000 g PEI, the calculation from ANOVA statistics showed that the efficiency in formaldehyde adsorption is not different significantly despite of the different amount of polymer coating observed by TGA. It is possibly because an increase amount of polymer on surface in the range of 60 – 140 mg/g did not lead to dramatically change in accessible active site numbers. The polymer chain folding may also reduce the available active sites for adsorption. The PEI amount of 0.100 g was chosen to prepare the silica-PEI afterwards.

Table 4.3 The amount of PEI coated on silica gel calculated from TGA results and adsorbed amount of formaldehyde results

Added PEI amount (g)	Amount of coated PEI (mg/g silica) [a]	Adsorbed amount of formaldehyde (mg/g)
Silica gel	-	0.45 ± 0.3
Silica-triethoxyoctylsilane	-	1.44 ± 0.7
0.050	39.9±0.04	8.12 ± 0.3

0.100	94.0±0.02	10.75 ± 0.9
0.250	113.2±0.15	10.92 ± 1.8
0.500	95.2±0.10	10.97 ± 0.6
0.750	140.2±0.05	12.85 ± 1.2
1.000	60.4±0.05	11.30 ± 0.4

[a] Mean ± S.D.(n=3)

4.1.3 Effect of concentration of epichlorohydrin solution

The results in formaldehyde adsorption by adsorbents prepared by using various epichlorohydrin concentrations are shown in Figure 4.4. The octyl-silica (0.100 g) was coated with solution (5.00 mL) containing 0.100 g PEI before the crosslink step. The obtained silica-PEI was evaluated for adsorption efficiency in formaldehyde solution (100 mg/L).

From the results in Figure 4.4, increasing the concentration of epichlorohydrin from 1.04×10^{-7} M to 4.18×10^{-6} M did not affect the efficiency in formaldehyde extraction by the obtained silica-PEI because epichlorohydrin crosslinked PEI molecular chains at the position of secondary amine groups, while the adsorption of formaldehyde probably occurred at primary amine groups through imine formation. Thus, the increasing of epichlorohydrin concentration may not change the number of primary amine on the PEI chains; therefore, the extraction efficiency did not change. The calculation from ANOVA statistics showed that the amounts of formaldehyde adsorbed by silica-PEI are not significantly different when used the epichlorohydrin concentrations higher than 1.04×10^{-7} M in the crosslink reaction. Ninhydrin test of the extracted formaldehyde solutions was negative when used adsorbents prepared using various epichlorohydrin concentrations, indicating that there was no PEI detached from the adsorbents. Therefore, the epichlorohydrin concentration of 1.04×10^{-7} M was enough to fix the polymer on the silica surface and this concentration was chosen in the crosslink step to prepare the adsorbent.

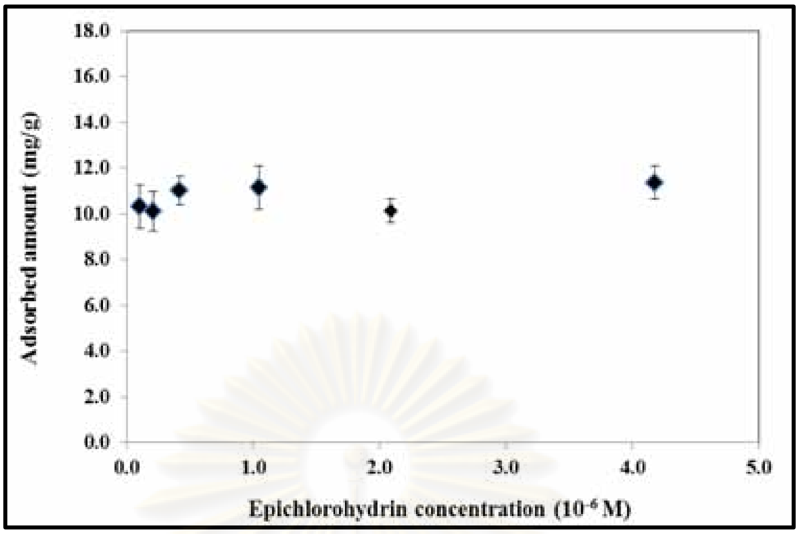


Figure 4.4. Effect of epichlorohydrin concentrations on adsorption efficiency of silica-PEI in formaldehyde extraction. (silica-PEI 0.025 g, concentration of formaldehyde = 100 mg/L).

4.2 Adsorption of formaldehyde in water

The silica-PEI was used as adsorbent in adsorption study of formaldehyde in aqueous solutions using batch method. The effects of pH and contact time were studied and the optimized conditions for formaldehyde extraction were proposed. The adsorption isotherms were also investigated. Moreover, eluent type and elution time were studied after adsorption experiment.

The formaldehyde extraction efficiency is presented in term of percentage of extraction and formaldehyde adsorbed amount on adsorbent, calculated from the change of the formaldehyde concentration in solution using the Equations 4.1 and 4.2, respectively,

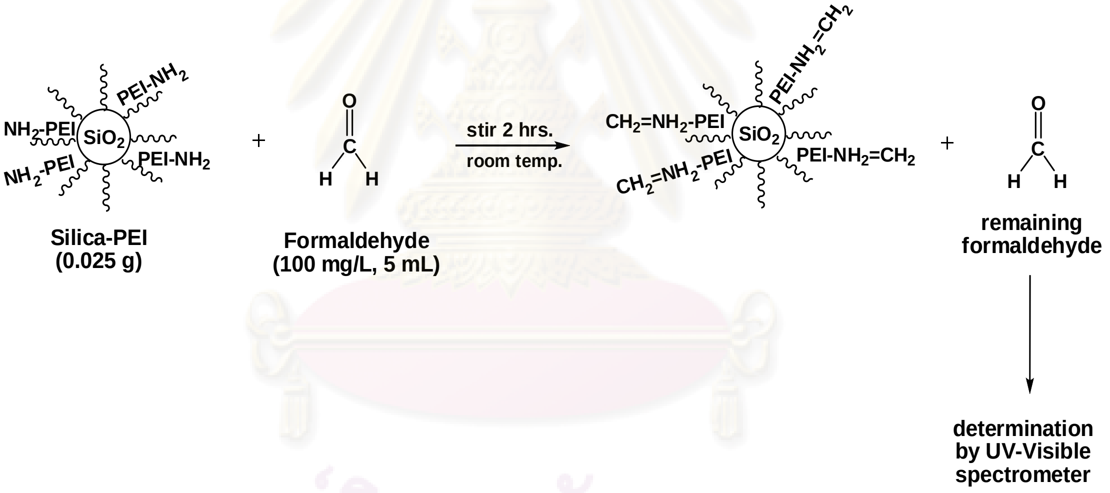
$$\%\text{Extraction} \quad = \quad \frac{C_i - C_e}{C_i} \times 100 \qquad (4.1)$$

$$\text{Adsorbed amount (q)} \quad = \quad \frac{(C_i - C_e)V}{m} \qquad (4.2)$$

where q = formaldehyde amount adsorbed on adsorbent (mg/g)
C_i = initial concentration of formaldehyde (mg/L)
C_e = equilibrium concentration of formaldehyde (mg/L)
V = volume of formaldehyde (L)
m = mass of adsorbent (g)

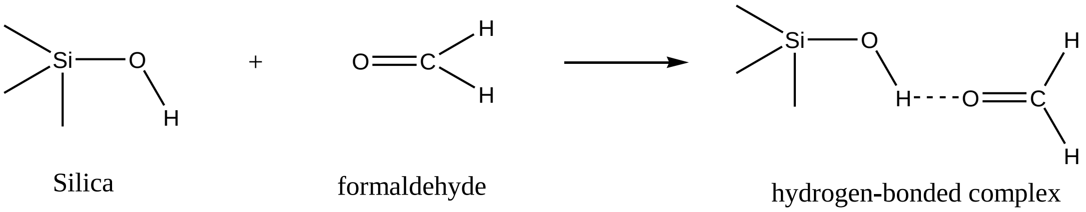
4.2.1 Comparison of efficiency in formaldehyde adsorption by modified and non-modified silica gel

After the modification of silica gel with PEI, the efficiency in formaldehyde extraction by silica-PEI adsorbents prepared at optimum conditions was evaluated. Formaldehyde adsorbed on the adsorbent via chemical bonding formation at an amine group coated on silica surface giving imine (-N=CH_2) as shown in Scheme 4.1.

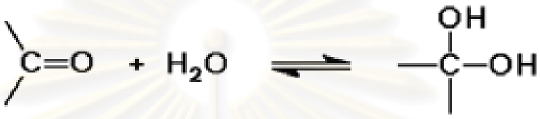


Scheme 4.1 The extraction of formaldehyde by PEI modified silica gel through imine formation.

From the results in Table 4.3, it indicates that silica-PEI is an effective adsorbent. For non-modified silica gel, it could slightly extract formaldehyde in solution and its adsorption efficiency was much lower than the silica-PEI. Yang and coworkers [13] reported that the adsorption of formaldehyde by non-functionalized silica fibers was attributed to hydrogen bond between the silanol groups on the surface and hydrogen atom of formaldehyde as presented in Scheme 4.2.



Scheme 4.2 Chemical reaction between silica and formaldehyde [13].



Scheme 4.3 Hydration reaction of aldehyde to form diol.

In addition, formaldehyde dissolved in water often forms a diol with hydration reaction (Scheme 4.3). This diol form can also react to silica silanol groups through hydrogen bonding of the two hydroxyl groups. As a result, non-coated silica gel can slightly adsorb formaldehyde.

In Table 4.3, the silica-triethoxyoctylsilane could slightly extract formaldehyde in solution. Regarding the structure of triethoxyoctylsilane, it had no functional groups to interact with formaldehyde. The slight amount of formaldehyde may be extracted from solution by physisorption via Van der Waals forces or the remaining silanol groups on silica gel surface where was not modified with triethoxyoctylsilane.

4.2.2 Effect of formaldehyde solution pH

The effect of pH was investigated to obtain the suitable pH of the formaldehyde extraction, using the solution pH in the range of 4 to 9 at fixed contact time of 120 minutes. The initial concentration of formaldehyde was 100 mg/L. The experiment was performed by varying solution pH values and the results are shown in Figure 4.5.

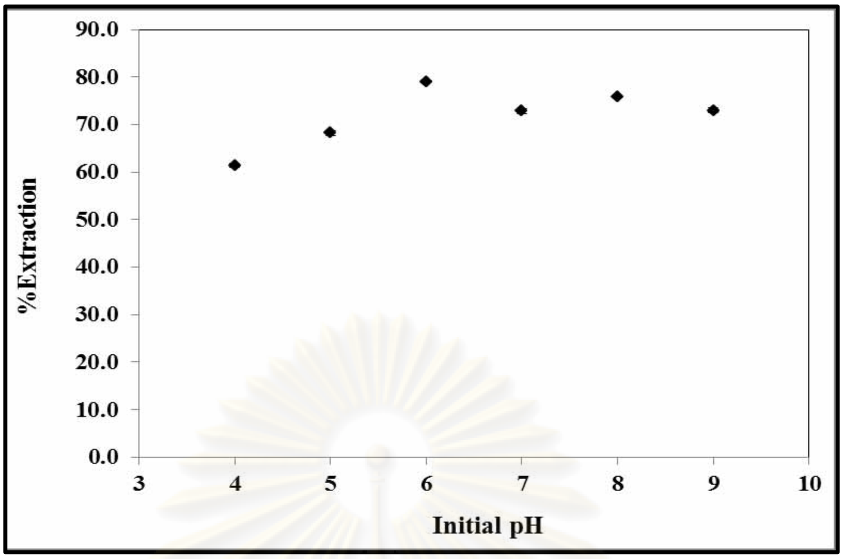


Figure 4.5 Effect of formaldehyde solution pH on extraction efficiency.

In order to obtain the optimum pH, the solution pH was varied from 4 to 9. Higher pH values were not studied because formaldehyde can undergo self oxidation-reduction reaction called Cannizzaro reaction [40], catalyzed by strong base in aqueous solution as shown in Scheme 4.4. When formaldehyde was changed from HCHO to $HCOO^-$ in the strong base solution, it would not interact with silica-PEI via imine formation.

$$2HCHO \xrightarrow{NaOH} HCOO^- + CH_3OH$$

Scheme 4.4 The Cannizzaro reaction of formaldehyde [40].

From the result in Figure 4.6, increasing the pH value of formaldehyde solution from 5 to 9 did not strongly affect the efficiency of silica-PEI in formaldehyde extraction. The final pH of all samples was in the range of 8.0-8.5 due to the basic properties of PEI on the adsorbent surface. The adsorption probably occurred under the same conditions despite of different initial solution pH values. This observation is an advantage in the application of the adsorbents in real sample that has wide range of pH. Normally, the pH of formaldehyde in water is around 6; therefore, formaldehyde solution pH 6 was chosen in the further extraction study.

4.2.3 Effect of extraction time

In this experiment, the effect of extraction time was investigated to determine the equilibrium time of the formaldehyde adsorption using the extraction time in the range of 5-480 minutes. The initial concentration of formaldehyde was fixed at 100 mg/L at pH 6.0. The experiment was performed by increasing extraction time until the constant value of extraction percentage was observed. The results are shown in Figure 4.6.

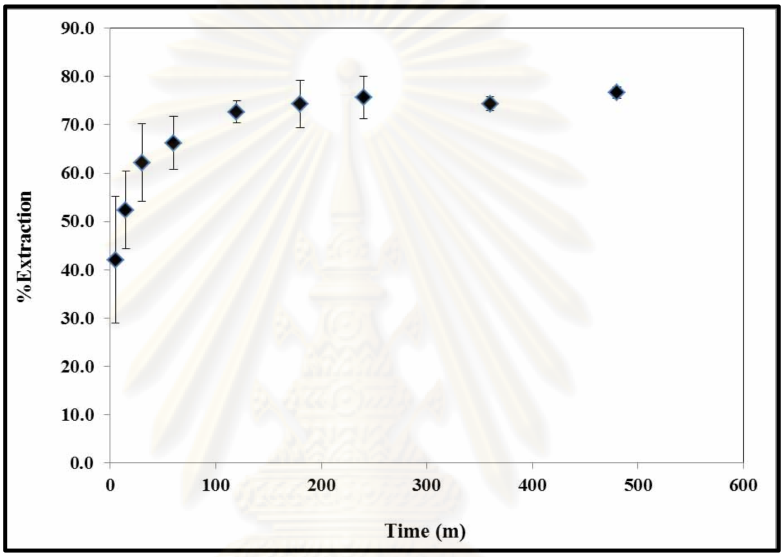


Figure 4.6 Effect of extraction time on extraction efficiency of formaldehyde by silica-PEI.

The extraction efficiency increased when increasing the extraction time due to the longer contact time between formaldehyde and amine groups. The adsorption reached the equilibrium after 120 minutes of formaldehyde extraction. Therefore, the extraction time of 120 minutes was chosen for extraction experiment.

4.2.4 Adsorption isotherms

In this experiment, adsorption of formaldehyde on silica-PEI surface was performed at constant temperature. The adsorption behavior of formaldehyde on adsorbent at equilibrium would reveal the adsorption mechanism. Langmuir and Freundlich isotherm models are commonly used in the study of adsorption behavior. Langmuir isotherm model is based on the assumption that sorbate species are chemically adsorbed on the adsorbent surface at a fixed number of active sites. Each site accommodates one sorbate molecule/ion and there is no interaction between them, therefore the monolayer of sorbate molecule covers the surface. While Freundlich isotherm model is based on the assumption that the uptake of sorbate molecule/ion occurs as multilayer adsorption. The experimental data were fitted to both adsorption isotherm models. The Langmuir adsorption isotherm model is described by Equation 4.3,

$$\frac{C}{q} = \frac{1}{bq_m} + \frac{C}{q_m} \qquad (4.3)$$

where C = equilibrium concentration of formaldehyde in aqueous solution (mg/L or mol/L)
q = adsorption capacity of adsorbent (mg/g or mol/g)
q_m = maximum adsorption capacity of adsorbent (mg/g or mol/g)
b = Langmuir constant related to energy of adsorption (L/mg or L/mol)

The linearized Langmuir isotherm allows the calculation of adsorption capacity (q_m) and the Langmuir constant (b). From the linear plot, the value of q_m and b could be calculated from the slope and intercept, respectively.

The linearized form of Freundlich isotherm is shown in Equation 4.4,

$$\log q = \log K_f + \left(\frac{1}{n}\right) \log C_e \qquad (4.4)$$

where K_f = Freundlich constant related to adsorption capacity (mg/g or mol/g)
n = the numerical value of Freundlich constant

In the Freundlich isotherm linear plot, the value of n and K_f could be calculated from the slope and intercept, respectively.

The experiment was performed at 25 ± 0.5 °C by adding the fixed weight of silica-PEI to solutions containing different initial concentrations of formaldehyde. The remained concentration of formaldehyde in solutions was determined by UV-Visible spectrophotometry. The adsorption capacities as a function of the equilibrium concentration are shown in Figure 4.7. The adsorption capacity for formaldehyde increased rapidly at low initial concentrations. The experimental data were plotted using Langmuir and Freundlich equation. Linear regression was performed to confirm the validity of both Langmuir and Freundlich isotherms. The Langmuir and Freundlich isotherm plots are shown in Figure 4.8 and 4.9, respectively. Then, the constant values of both isotherms models were calculated using linear equations obtained and the results are listed in Table 4.4 and 4.5.

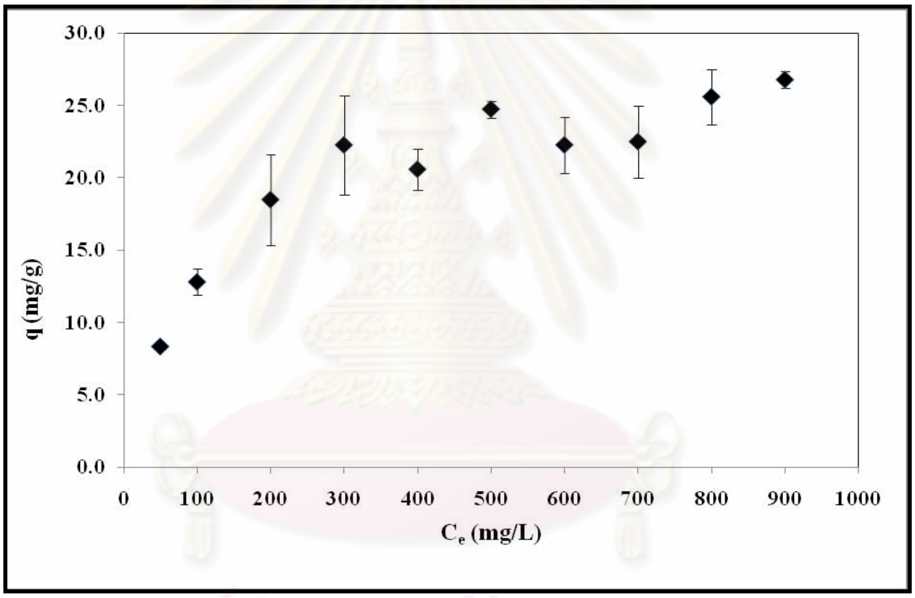


Figure 4.7 Adsorption isotherm of formaldehyde at 25 ± 0.5 °C.

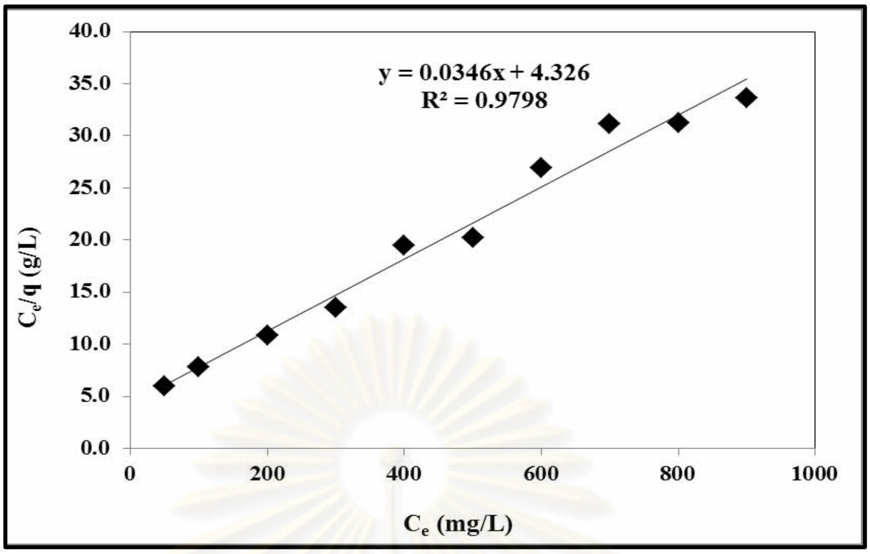


Figure 4.8 Langmuir isotherm plot of the adsorption of formaldehyde onto silica-PEI at 25 ± 0.5 °C.

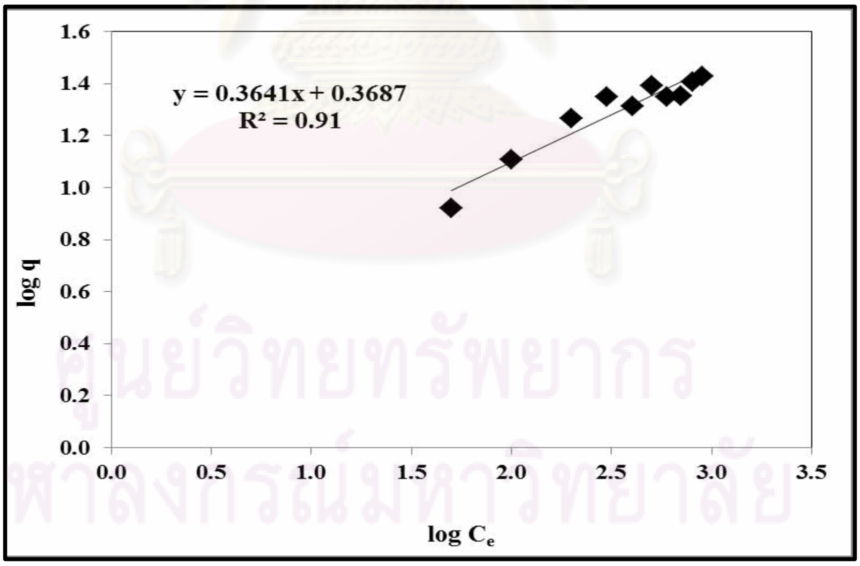


Figure 4.9 Fruendlich isotherm plot of the adsorption of formaldehyde onto silica-PEI at 25 ± 0.5 °C.

Table 4.4 The Langmuir isotherm parameters of the adsorption of formaldehyde at 25 ± 0.5 °C.

Linear equation	**R^2**	**b (L/mg)**	**$q_{max,cal}$ (mg/g)[a]**	**$q_{max,exp}$ (mg/g)[b]**	**R_L**
$y = 0.0346x + 4.326$	0.9798	8.00×10^{-3}	28.90	25.90	0.122-0.714

[a] The maximum adsorption capacity obtained from the calculation.

[b] The maximum adsorption capacity obtained from the experiment.

Table 4.5 The Freundlich isotherm parameters of the adsorption of formaldehyde at 25 ± 0.5 °C.

Linear equation	**R^2**	**K_f (mg/g)**	**1/n**	**n**
$y = 0.3641x + 0.3687$	0.9100	2.34	0.3461	2.75

From the results shown in Table 4.4 and 4.5, the correlation coefficients (R^2) obtained by fitting the experimental data to the Langmuir model, compared to the data fitting to the Freundlich model. These results indicate that the adsorption isotherm of formaldehyde fit to Langmuir model better than Freundlich model. Therefore, the adsorption behavior of formaldehyde on silica-PEI follows Langmuir model assumptions. It was assumed that the sorbate molecules are chemically adsorbed on the adsorbent surface. Thus, it indicates that the main adsorption mechanism of formaldehyde onto silica-PEI surface is chemisorption. The maximum adsorption capacity (q_{max}) of adsorbent for formaldehyde obtained from the experiment corresponds to q_{max} obtained from the calculation of Langmuir model. The adsorption reached a saturation of adsorption capacity at high equilibrium concentration with the monolayer coverage of formaldehyde on the silica-PEI surface. Moreover, the Langmuir isotherm model can be explained in term of an equilibrium parameter, R_L, given as Equation 4.5 [41],

$$R_L = \frac{1}{1 + bC_i} \tag{4.5}$$

where b = Langmuir constant related to energy of adsorption (L mol^{-1})
C_i = initial concentration of formaldehyde (mol L^{-1})

In this experiment, the values of R_L obtained from Langmuir model are in the range of 0 to 1 (R_L = 0.122 – 0.714) indicating that the adsorption of formaldehyde onto silica-PEI is favorable with increasing of adsorption capacity at higher initial concentrations. The parameter R_L is related to the type of isotherm as presented in Table 4.6.

Table 4.6 The value of R_L related to the type of isotherm [42]

Value of R_L	Type of isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

Finally, these results lead to the conclusion that the adsorption isotherm of formaldehyde onto silica-PEI followed Langmuir model and the maximum adsorption capacity of formaldehyde onto silica-PEI was 25.9 mg/g. The adsorption capacities of different adsorbents in formaldehyde adsorption are summarized in Table 4.7. Silica-PEI show relatively low adsorption capacity, compared to the other adsorbents.

The silica-PEI extracted formaldehyde via the chemical adsorption, which required the specific active sites from amine groups on PEI. The number of active sites for formaldehyde adsorption was limited by the coated amount of PEI, when compared to the other adsorbents such as activated carbon, which adsorbed formaldehyde via physical adsorption on porous surface. So that it can absorb formaldehyde in higher extent than silica-PEI.

Table 4.7 Comparison of adsorption capacity in formaldehyde adsorption

Type of adsorbent	**Adsorption capacity (mg/g)**	**Reference**
activated carbons from coffee residue	130	[8]
silylated graphite oxide	2280	[43]
activated carbon with amino groups	1-2	[44]
Rayon-based ACFs by p-aminobenzoic acid (PABA)	447.8	[45]
PAN-based activated carbon fibers (ACFs)	14.3	[46]
Silica-PEI	25.9	This work

4.3 Formaldehyde desorption study

The desorption of formaldehyde from the used silica-PEI was studied using batch method. After adsorption, the used silica-PEI was washed with de-ionized water, then separated and mixed with hydrochloric acid. Hydrochloric acid was successfully used as eluent for formaldehyde desorption as reported previously in other researches [13, 47]. The adsorption of formaldehyde on silica-PEI via imine formation was reversible. This reaction could return formaldehyde and R-NH_3^+ was formed by using acid as catalyst in aqueous solution [48] as shown in Scheme 4.5. As a result, the amount of desorbed formaldehyde can be determined and the reuse of silica-PEI is possible.

$$\underset{\text{imine}}{\text{-R-N=CH}_2} + H_2O + H^+ \longrightarrow \text{-R-NH}_3^+ + \underset{\text{formaldehyde}}{\text{HCHO}}$$

Scheme 4.5 The reaction of imine in acid solution [48].

The concentration of desorbed formaldehyde was determined. The effects of HCl concentration and desorption time were studied. The formaldehyde desorption efficiency is presented in term of percentage of desorption calculated from Equation 4.6,

$$\%\text{elution} = \frac{n_{eluted}}{n_{adsorbed}} \times 100 \qquad (4.6)$$

where n_{eluted} = the amount of formaldehyde eluted from the adsorbent (mg)
$n_{adsorbed}$ = the amount of formaldehyde adsorbed on the adsorbent (mg)

4.3.1 The effect of hydrochloric concentration

Hydrochloric acid (HCl) at various concentrations (0.05 M, 0.1 M, 0.3 M, 0.5 M, 1.0 M and 2.0 M) were used to elute the adsorbed formaldehyde. The efficiencies in elution are shown in Figure 4.10.

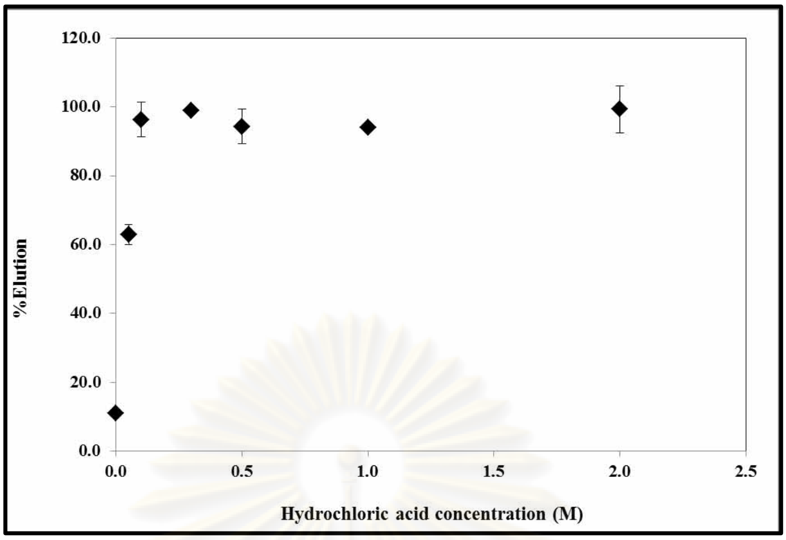


Figure 4.10 The effect of HCl concentrations on the percentage of elution (desorption time 60 minutes).

Hydrochloric acid could elute about 90-100% of formaldehyde from the used adsorbents. Using hydrochloric acid with low concentrations (0.1-1.0 M) was sufficient for elution and an increase in acid concentrations from 0.1 M to 2.0 M did not improve the elution efficiency significantly. Therefore, 0.1 M HCl was selected as the suitable eluent.

4.3.2 Desorption time

The effect of desorption time was investigated using 0.1 M hydrochloric acid as eluent to obtain the suitable time that allows the maximum desorption. Desorption time was varied in the range of 5-120 minutes. The results are shown in Figure 4.11.

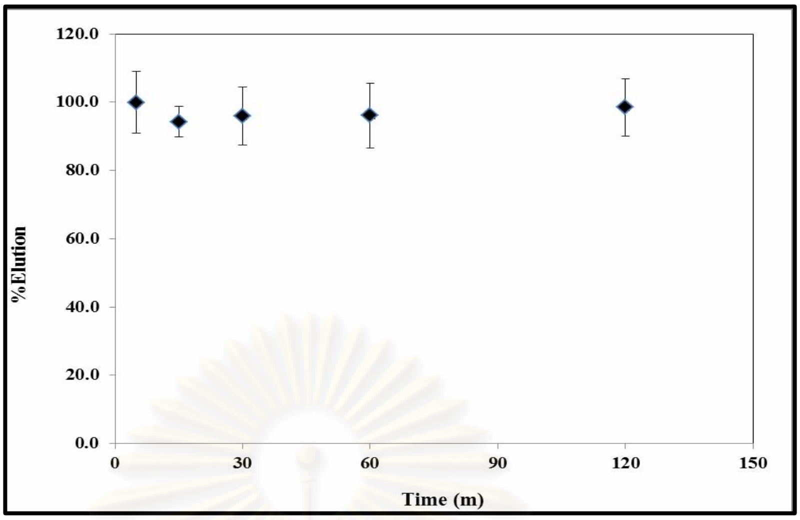


Figure 4.11 The relationship between desorption time and the percentage of elution.

Figure 4.11 presents the percentage of formaldehyde elution at different times. The percentage of formaldehyde elution was not significantly different when increasing the desorption time. Consequently, it may conclude that elution time did not affect the elution efficiency. In summary, the elution with a short time (about 5 minutes) and low acid concentration (0.1 M) can be applied for desorption.

4.4 Reusability of adsorbent

The adsorbent reusability is an important and desired property of adsorbents. The reuse of adsorbent was investigated and the experiment was performed using the same adsorbent for repeated cycles of adsorption/desorption. The initial concentration of formaldehyde used in the adsorption was 100 mg/L. The eluent of 0.1 M hydrochloric acid was used for formaldehyde and 5 minutes desorption time was also used.

It was found that the percentage extraction decreased from 68.26 to 6.16 in the second cycle of adsorption and the percentage of the first cycle of elution was about 90. After formaldehyde elution with hydrochloric acid, the amine groups on the silica-PEI were protonated (Scheme 4.5) to ammonium species which would not form imine with formaldehyde. Therefore, the percentage of adsorption in the second cycle decreased. Under this experimental conditions, the silica-PEI gave the highest extraction efficiency for formaldehyde extraction only for the first time application.

CHAPTER V

CONCLUSION

5.1 Conclusion

The silica-PEI adsorbent was prepared by coating of the polyethyleneimine on the triethoxyoctylsilane modified silica gel. Then, the obtained product was crosslinked with epichlorohydrin solution. The modified adsorbents in each step were characterized by Fourier transforms infrared (FT-IR) spectrometer, thermogravimetric analysis (TGA) and elemental analysis. The results from all characterization techniques confirmed the successful preparation of the polyethyleneimine-coated silica gel.

The silica-PEI was applied as adsorbent for extraction of formaldehyde in aqueous solution using batch method before its determination by UV-Visible spectrophotometry. The effects of pH of formaldehyde solution and extraction time as well as the adsorption isotherms were investigated. The adsorption behavior and suitable conditions of silica-PEI in extraction of formaldehyde in aqueous solution are summarized in Table 5.1.

Table 5.1 The adsorption behavior and suitable conditions of the extraction of formaldehyde

Parameters	Formaldehyde adsorption
Solution pH	4-9
Extraction time	120 minutes
Adsorption isotherm	Langmuir
Maximum adsorption capacity (mg/g)	25.9 mg/g

The adsorption of formaldehyde onto silica-PEI occurred mainly via the schiff base (imime) formation and hydrogen bonding between PEI and formaldehyde molecule. The silica-PEI show higher efficiency in formaldehyde adsorption than non modified silica.

Lastly, the elution of adsorbed formaldehyde was studied. Hydrochloric acid was used for elution of formaldehyde with a high desorption efficiency. Under the optimum condition for elution which is 0.1 M hydrochloric acid and the elution time of 5 minute, the percentage of elution was about 90-100%.

In conclusion, the polyethyleneimine-coated silica gel was successfully prepared as a novel adsorbent for adsorption of formaldehyde in water.

5.2 Suggestion of future work

- The present method should be applied to the extraction of formaldehyde in real sample such as, tap water and industrial wastewater.
- The effect of matrix compositions of water sample and other kinds of wastewater on formaldehyde extraction should be investigated.
- This study points out to a need for further study on more various aldehyde compounds.

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APPENDICES

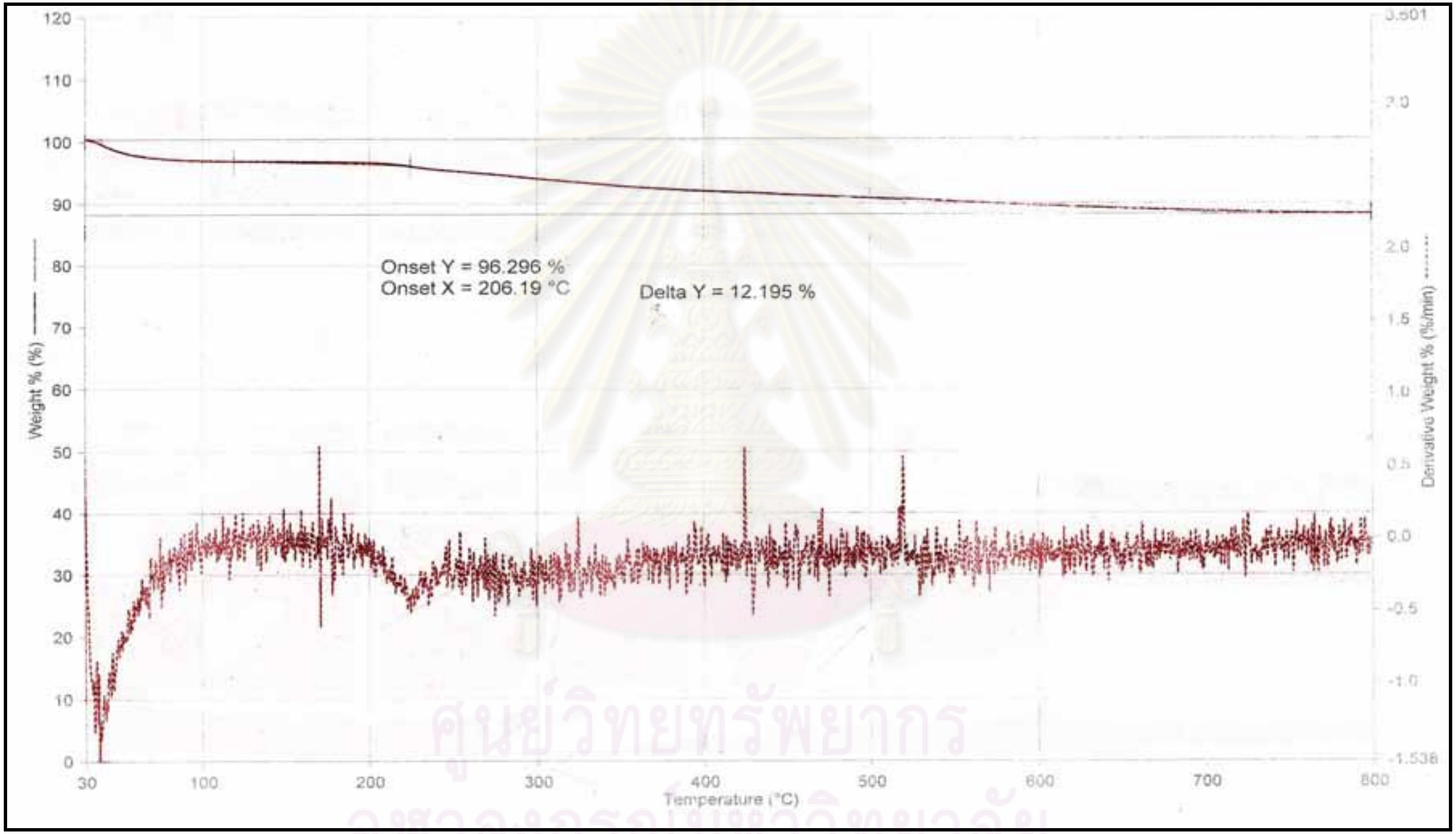

Figure A.1 The thermogram of silica-PEI prepared using PEI amount of 0.050 g.

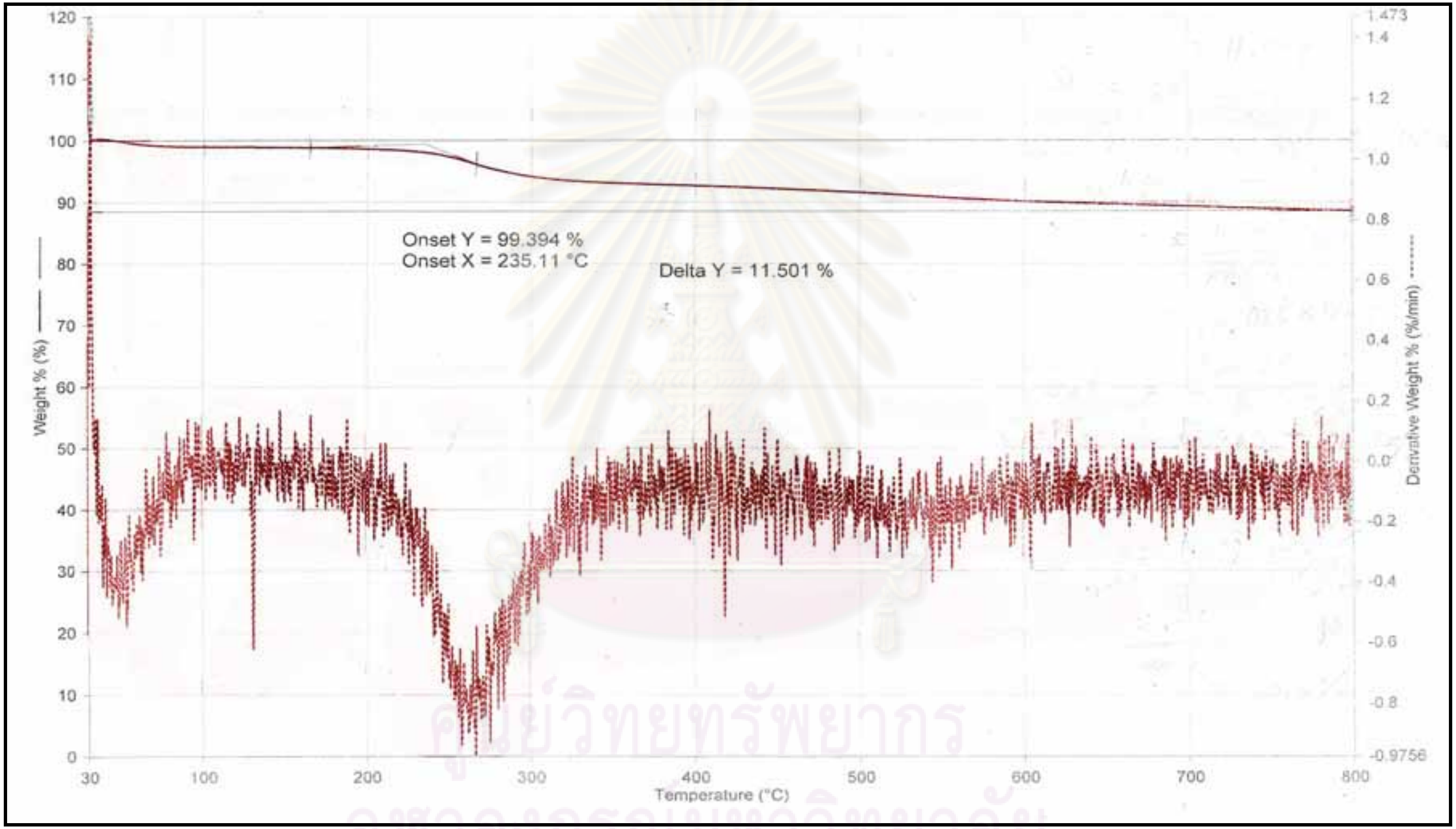

Figure A.2 The thermogram of silica-PEI prepared using PEI amount of 0.100 g.

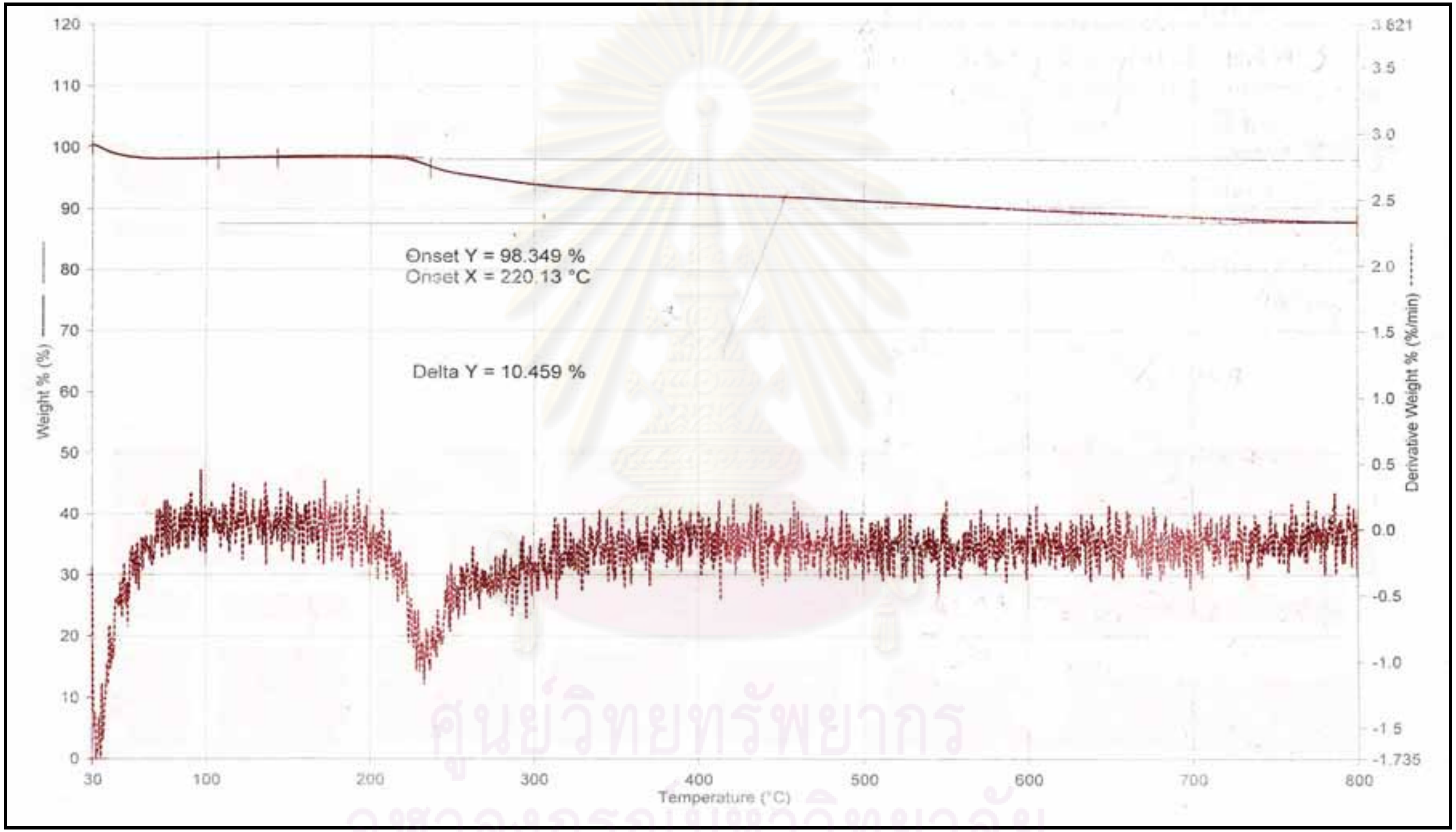

Figure A.3 The thermogram of silica-PEI prepared using PEI amount of 0.250 g.

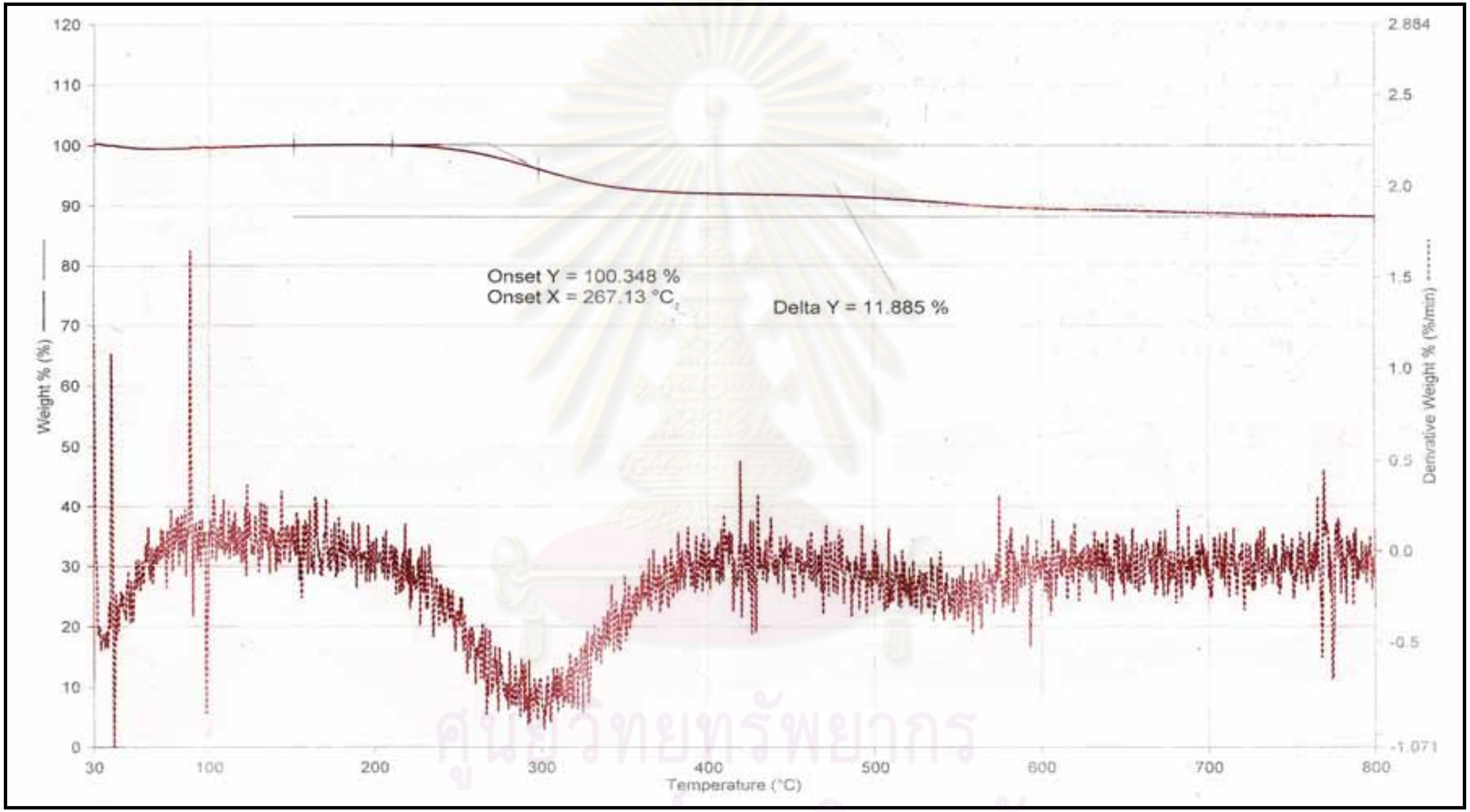

Figure A.4 The thermogram of silica-PEI prepared using PEI amount of 0.500 g.

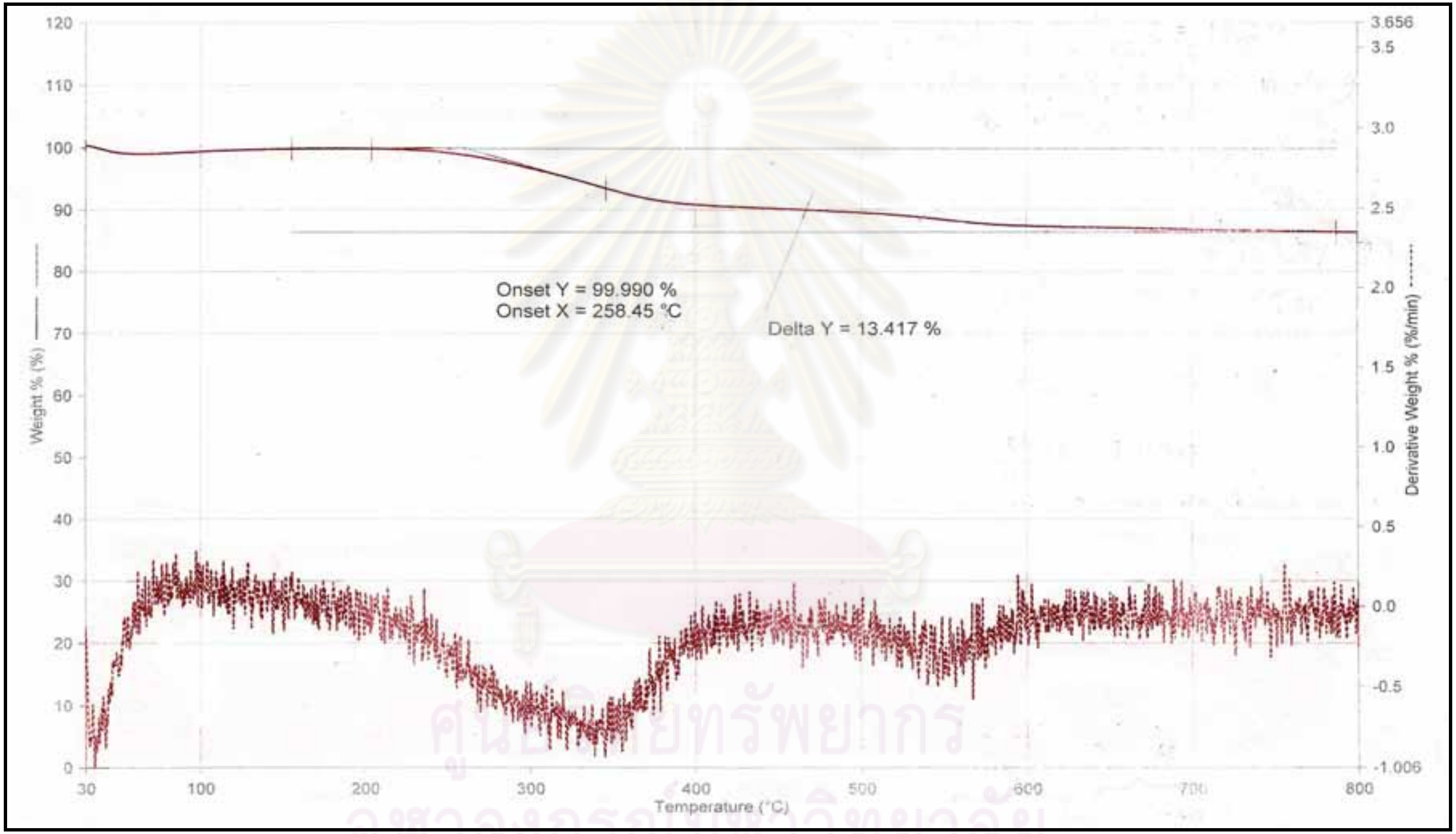

Figure A.5 The thermogram of silica-PEI prepared using PEI amount of 0.750 g.

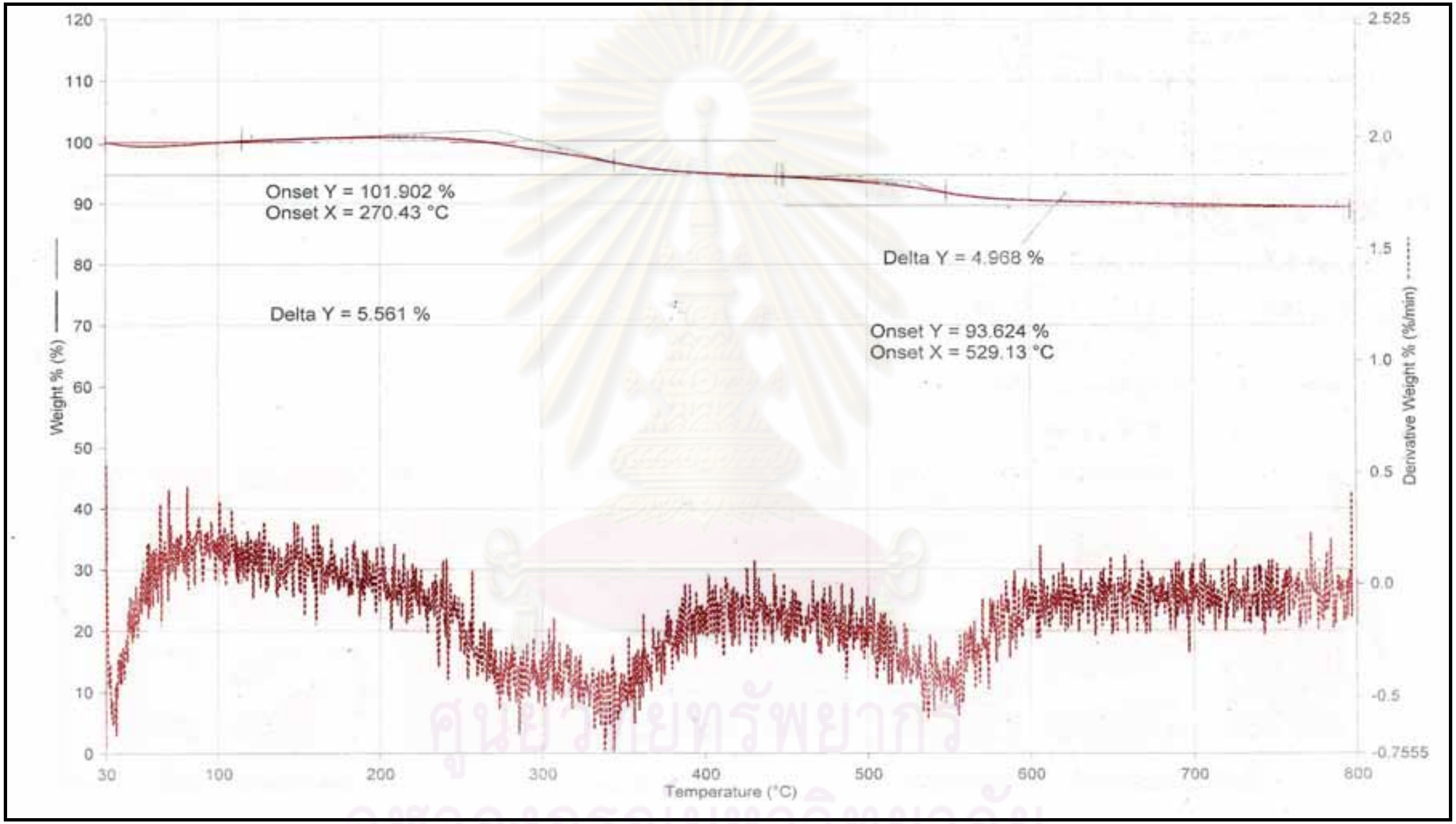

Figure A.6 The thermogram of silica-PEI prepared using PEI amount of 1.000 g.

VITA

Miss Sopida Sriviriyakul was born on December 6, 1985 in Bangkok, Thailand. She graduated with a Bachelor of Science degree from Mahidol University in 2007. After that, she has been a graduated student at the Program in Petrochemistry and Polymer Science Chulalongkorn University and become a member of Environmental Analysis Research Unit. She finished her Master’s degree of Science in 2010.