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SYNTHESIS AND USE OF 3-MERCAPTOPROPYL MODIFIED MCM-41 FOR MERCURY REMOVAL FROM WASTEWATER

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A Thesis Submitted in Partial Fulfillment of the Requirements
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อ.ที่ปรึกษาวิทยานิพนธ์หลัก: ผศ.ดร.เฟื่องฟ้า อุ่นอบ, 124 หน้า

สังเคราะห์เอ็มซีเอ็ม-41ที่ดัดแปรด้วย 3-เมอร์แคปโทโพรพิลไทรเมทอกซีไซเลนซึ่งมีอะตอมของซัลเฟอร์ที่สร้างพันธะกับไอออนปรอทได้ดี โดยศึกษาวิธีสังเคราะห์ 3 วิธี คือ (1) วิธีคอนเวนชันนัลไฮโดรเทอร์มอลเทมเพลทโซลเจล (วิธีคอนเวนชันนัล) (2) วิธีออริจินอลสเต็ปเทมเพลทโซลเจล (วิธีสเต็ป) และ (3) วิธีกราฟท์ ซึ่งแบ่งย่อยเป็น วิธีกราฟท์โดยใช้เอ็มซีเอ็ม-41ที่เตรียมจากวิธีคอนเวนชันนัลไฮโดรเทอร์มอลเทมเพลทโซลเจล (วิธีกราฟท์-คอน) หรือเอ็มซีเอ็ม-41ที่เตรียมจากวิธีออริจินอลสเต็ปเทมเพลทโซลเจล (วิธีกราฟท์-สเต็ป) ในการสังเคราะห์วัสดุนี้มีการปรับเปลี่ยนปริมาณของ 3-เมอร์แคปโทโพรพิลไทรเมทอกซีไซเลน ทำการหาและเปรียบเทียบประสิทธิภาพในการเติมลิแกนด์บนวัสดุดูดซับของแต่ละวิธี พบว่าประสิทธิภาพในการเติมลิแกนด์เรียงลำดับดังนี้ วิธีคอนเวนชันนัล > วิธีกราฟท์-สเต็ป > วิธีสเต็ป > วิธีกราฟท์-คอน จากนั้นทำการหาและเปรียบเทียบประสิทธิภาพในการดูดซับไอออนปรอทของผลิตภัณฑ์ที่ได้ (เอ็มพี-เอ็มซีเอ็ม-41) พบว่าความจุการดูดซับปรอทเรียงลำดับดังนี้ เอ็มพี-เอ็มซีเอ็ม-41 สังเคราะห์ด้วยวิธีกราฟท์-สเต็ป > เอ็มพี-เอ็มซีเอ็ม-41 สังเคราะห์ด้วยวิธีกราฟท์-คอน > เอ็มพี-เอ็มซีเอ็ม-41 สังเคราะห์ด้วยวิธีสเต็ป > เอ็มพี-เอ็มซีเอ็ม-41 สังเคราะห์ด้วยวิธีคอนเวนชันนัล ซึ่งวิธีกราฟท์-สเต็ปเป็นวิธีที่เหมาะสมที่สุดในการเตรียมตัวดูดซับแม้ว่าประสิทธิภาพในการเติมลิแกนด์อยู่ในระดับปานกลางเมื่อเทียบกับวิธีการอื่น ทำการพิสูจน์เอกลักษณ์วัสดุดูดซับที่ได้ทั้งหมดด้วยเทคนิคการเลี้ยวเบนของรังสีเอกซ์ ฟูริเออร์ทรานสฟอร์มอินฟราเรด การวิเคราะห์หาพื้นที่ผิว และการวิเคราะห์เชิงความร้อน จากนั้นศึกษาปัจจัยที่มีผลต่อการดูดซับไอออนปรอท (II) ของเอ็มพี-เอ็มซีเอ็ม-41ได้แก่ พีเอชของสารละลาย เวลาในการกวน ไอออนรบกวนอื่นๆ พบว่าพีเอชที่เหมาะสมในการดูดซับคือ 5 – 8 การดูดซับทั้งหมดเข้าสู่สมดุลภายในเวลา 20 นาที คลอไรด์ไอออน (ที่ความเข้มข้น 0.1 และ 1.0 โมลาร์) ส่งผลให้ประสิทธิภาพในการขจัดลดลง 24 – 41 เปอร์เซนต์ พฤติกรรมการดูดซับปรอทบนเอ็มพี-เอ็มซีเอ็ม-41เป็นไปตามไฮโซเทอร์มแบบแลงเมียร์ และความจุการดูดซับไอออนปรอทสูงสุดเท่ากับ 1.25 มิลลิโมลต่อกรัม สามารถนำวัสดุนี้กลับมาใช้ซ้ำได้อย่างน้อย 4 ครั้ง และสามารถขจัดไอออนปรอท (II) ในน้ำเสียจริงจากโรงกลั่นน้ำมันได้

สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่อนิสิต ณัฐฐิดา ศิริวงศ์
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MCM-41 was synthesized and modified with sulfur-containing functional group (3-mercaptopropyltrimethoxysilane, MPTMS) which has a good affinity towards mercury ions. Three synthesis methods were studied; (i) Conventional hydrothermal templated sol-gel method (*Con*), (ii) Original stepped template sol-gel method (*Step*), and (iii) Grafting method that was divided into grafting method using MCM-41 prepared by conventional hydrothermal templated sol-gel method (*Graft-con*) and by original stepped template sol-gel method (*Graft-step*). The amount of MPTMS was varied in the synthesis. The efficiency of the method in ligand loading on the adsorbents was evaluated and compared. The ligand loading efficiency followed the order: *Con* method > *Graft-step* method > *Step* method > *Graft-con* method. The adsorption efficiency for mercury ions of the obtained products (MP-MCM-41) was evaluated and compared. The order adsorption efficiency of products followed MP-MCM-41 (*Graft-step*) > MP-MCM-41 (*Graft-con*) > MP-MCM-41 (*Step*) > MP-MCM-41 (*Con*). The *Graft-step* method was the most suitable method despite of fairly good ligand loading efficiency compared to other methods. All the obtained adsorbents were characterized by XRD, FT-IR, surface area analysis and thermal analysis. The factors that affect mercury(II) ions adsorption by MP-MCM-41 were studied i.e. the pH of solution, contact time, interfering ions. The suitable pH for adsorption was 5 – 8. Adsorption reached the equilibrium within 20 min. The presence of chloride ions (0.1 and 1.0 M) reduced the removal efficiency up to 24 – 41 %. The adsorption behavior of mercury on MP-MCM-41 at equilibrium followed Langmuir isotherm and the maximum mercury(II) ions adsorption capacity was 1.25 mmol/g. This material could be reused at least 4 cycies and it could remove mercury in real wastewater from refinery processes.

Field of study Petrochemistry and Polymer Science. Student's signature......Nattida S.......

Academic year.................2009................................ Thesis Advisor's signature.......F. Unob.......

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CONTENTS

Page

CHAPTERS

CHAPTERS **Page**

CHAPTER II THEORY AND LITERATURE REVIEWS……………….

CHAPTERS **Page**

CHAPTERS **Page**

LIST OF FIGURES

Figure **Page**

Figure **Page**

Figure **Page**

Figure **Page**

LIST OF TABLES

Table **Page**

LIST OF SCHEMES

LIST OF ABBREVIATIONS

g	gram
mg	milligram
µg	microgram
L	liter
mL	milliliter
min.	minute
h.	hour
ºC	degree Celsius
mol	mole
mmol	millimole
%mol	percentage of mole ratio
nm	nanometer
µm	micrometer
MCM-41	mobil crystalline material-41
MP-MCM-41	3-mercaptopropyl modified MCM-41
MPTMS	3-mercaptopropyltrimethoxysilane
MP	3-mercaptopropyl
USEPA	USA's environmental protection agency
CVAAS	cold vapor atomic absorption spectrometry
XRD	X-ray diffraction
FTIR	fourier transform infrared spectroscopy
BET	Brunauer-Emmett-Teller method
TGA	thermo gravimetric analysis
IUPAC	the international union of pure and applied chemistry
CTAB	hexadecyltrimethyl ammonium bromide
TEOS	tetraethylorthosilicate
DCM	dichloromethane
HSAB	hard-soft acid-base principle
cm^{-1}	unit of wave number
m^2/g	square meter per gram

LIST OF ABBREVIATIONS (continued)

cm^3/g	square centimeter per gram
M.W.	molecular weight
S.D.	standard deviation
M	molar
v/v	volume per volume

CHAPTER I

INTRODUCTION

1.1 Statement of the problem

The industries in Thailand that use mercury in production are divided into six types such as petroleum industry, chlorine and caustic soda industry, metal fused industry, pharmaceutical products industry, paper and pulp industry, paint industry and plastic industry. These industries are important for the economy of the country but they could also cause environmental problems especially water pollution. The contamination of heavy metals, in particular mercury in water is one of the problems concerned [1]. These heavy metals in water are harmful towards human life, animals and plant.

Mercury is a highly toxic substance and the major effects of mercury poisoning manifest as neurological and renal disturbances as it can easily pass the blood–brain barrier and affect the foetal brain. High concentration of Hg(II) causes impairment of pulmonary function and kidney, chest pain and dyspnousea [2]. Minamata disease caused by mercury can cause brain damage and death. The previous research reported the contamination of mercury in seawater in Thai gulf region [3]. Eastern Marine Fisheries Research and Development Center, Department of fisheries, reported that the amount of mercury in seawater in the eastern of Thai gulf between 1990-1999 at Rayong to Trad province contained 0.001-0.02 mg/L mercury in average, in particular at Mabtapud industrial park (0.001-0.07 mg/L) and at the middle of Thai gulf (0.001-0.07 mg/L). Since 1996, petroleum development project assigned that in the exploration, drilling oil and natural gas, the release and contamination of heavy metals, especially mercury is to be monitored in all three processes i.e. exploration, drilling and production [4]. Furthermore, all six industries that use mercury in production have to follow after the quality audition for contamination of mercury in seawater and accumulative toxin in aquatic animals.

To prevent a human from the danger of the contaminated mercury and the accumulation of mercury in an environment, the government released the law to control the mercury quantity in wastewater. In USA, the standard of USA’s Environmental Protection Agency (USEPA) states that wastewater from petroleum production activities must not have the contaminated mercury higher than 1.8 mg/L. The industrial factory in Thailand must have criterion to remove mercury in wastewater from the factory before direct releasing to a river or the ocean. The Ministry of Industry of Thailand announced the regulation for controlling of toxicity of the treated waste. The level of mercury has to be controlled must not be more than 5 μg/L for wastewater and 1 μg/L for drink water [5,6]. If the concentration of mercury from the wastewater has higher than the regulatory level, the waste will be categorized as the hazard wastewater which must retreat before the disposal. The method widely used for the determination of mercury concentrations is cold vapor atomic absorption spectrometry (CVAAS), due to its good accuracy and precision, high sensitivity and good selectivity [7]. This method is often chosen for comparing of the mercury concentration before and after treating the samples with wastewater.

Several methods have been used to remove heavy metals from wastewater, such as ion exchange, coagulation, chemical precipitation, solvent extraction and adsorption on various adsorbents [8]. One of which, adsorption is an efficient method and widely used to remove metals from effluent. In recent years, various adsorbents have been investigated, e.g. zeolites, silica gel, polymer bead, and clay minerals [8-14]. Many adsorbents for mercury ions showed several drawbacks like low mechanical and thermal stability and weak chemical affinity [8,14]. Mobil Crystalline Material-41 (MCM-41) has drawn a lot of interest due to its uniform structure and high surface area and the surface can be easily modified. Three methods of functionalization were used: (i) conventional hydrothermal templated sol-gel method, (ii) original stepped template sol-gel method and (iii) grafting method [15-18]. The attaching of ligand to MCM-41 is functionalization which is the ligand-MCM-41chemically bonded by attachment of silicane group with Si-O group, Si-O-Si group or –OH group of MCM-41. The ligand part is important for the extraction or chelation with the metal ions. It provides the binding site to form a complex with a metal ion. The affinity of mercury and ligand can be attributed to the type of donor atoms (hard or soft), oxidation state of the metal ion, the amounts of ligand and the metal atom, and pH of the solvent system. Sulfur-containing functional group (e.g. 3-mercaptopropyltrimethoxysilane, MPTMS) was chosen for surface modification to improve the affinity towards mercury ions [19].

This research focuses on the synthesis and characterization of 3-mercaptopropyl functionalized MCM-41 using three synthesis methods; the conventional hydrothermal templated sol-gel technology, the original stepped template sol-gel technology and the grafting method followed by the studies of the effect of various parameters that operated in the process of quantitative adsorption of mercury.

1.2 Objectives of the thesis

The objectives of thesis can be summarized as following:

1. To synthesize and characterize 3-mercaptopropyl functionalized MCM-41.
2. To study mercury removal performance of the 3-mercaptopropyl functionalized MCM-41 synthesized by the optimum method.

1.3 Scope of the thesis

The scope of this research was firstly synthesis of 3-mercaptopropyl functionalized MCM-41 using three synthesis methods; (i) conventional hydrothermal templated sol-gel method, (ii) original stepped template sol-gel method and (iii) grafting method (normal MCM-41 prepared from (i) and (ii)). In the synthesis of 3-mercapto propyl functionalized MCM-41, the optimum adding amount of 3-mercaptopropyl trimethoxysilane was determined by varying the amount of MPTS added in the synthesis (i.e. 0 – 20 %mol of MPTMS / MPTMS + TEOS for the conventional hydrothermal templated sol-gel method and the original stepped template sol-gel method and 0 – 20 mmol/g MCM-41 for grafting method). Secondly, the obtained products were characterized by X-ray diffraction (XRD), fourier transform infrared spectroscopy (FTIR) and surface area analysis (Brunauer-Emmett-Teller analyzer, BET). In addition, the attached amount of 3-mercaptopropyl on the adsorbents were measured by thermo gravimetric analysis (TGA) to compare the adding efficiency of functional group from three synthesis methods, to evaluate the adding amount of 3-mercaptopropyltrimethoxy silane for preparing materials which have the equal amount of functional group on adsorbents, and to choose the best condition for the next synthesis.

In the next step, the mercury ion adsorption efficiency of MCM-41 before and after surface modification was determined to find out the most appropriate conditions for synthesis. The amounts of mercury in solutions were measured by cold vapor atomic absorption spectrometry (CVAAS). The influence and factor effecting to the mercury ion absorption of functionalized MCM-41 were studied by using of the best obtained product from the best synthesis method. The factors that affect the adsorption were studied with batch system i.e. the pH of solution, stirring time, the presence of foreign ions (NO_3^-, SO_4^{2-}, Cl^-). The adsorption isotherms (Langmuir and Freundlich isotherm) were also studied. Finally, the reuse of 3-mercaptopropyl functionalized MCM-41 and the removal of mercury ion from refinery process wastewater were investigated.

1.4 The benefits of this thesis

To obtain suitable synthesis method of 3-mercaptopropyl functionalized MCM-41 and the adsorbents that could be used for removal of mercury (II) ions in wastewater.

CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Mobile crystalline material-41 (MCM-41)

In 1992, scientists from Mobil Oil Corporation first synthesized ordered mesoporous materials of the M41s family, one of which was MCM-41 [15, 20]. Mobile Crystalline Material-41 (MCM-41) is a silicate obtained by a templating mechanism. This material occupies a porous composite consisting of hexagonal arranged channels with diameters varied from 1.5 to 10 nm. The walls of the channels are amorphous SiO_2 [21]. MCM-41 has been used as adsorbents or catalysts in the varieties of processes. By changing the length of the template molecule, the width of the channels can be controlled to be within 2 to 10 nm. MCM-41 has attracted the attention because of its high specific surface area, high thermal and hydrothermal stability, possibility of controlling its pore size and its hydrophobicity and acidity. These characteristics have made MCM-41 a promising material as adsorbent, catalyst and/or support for use in industrial processes (e.g. adsorption, ion exchange) and environmental control [22]. MCM-41 is one of the members of mesoporous sieves which is one type of zeolite molecular sieves. In this study, MCM-41 was synthesized and modified with functional group for using as adsorbent for mercury. The classification or source of zeolite molecular sieves and background information of mesoporous materials should be studied before its application.

2.1.1 Zeolite molecular sieves [23, 24]

Zeolites, a type of molecular sieves, are crystalline aluminosilicates of alkali and alkaline earth metals. They occur in nature and can also be obtained from synthesis. The properties of zeolites i.e. high surface area, high sorption, ion exchange, and high acidity have been exploited for their applications such as oil refining (as adsorbents and cracking catalysts), petrochemical industry, and synthesis of chemicals.

Molecular sieves are porous materials that exhibit selective adsorption properties and are classified on the IUPAC definitions into three main types depending on their pore sizes; microporous material, mesoporous materials, and macroporous materials. Properties and examples of these materials are shown in Table 2.1.

Table 2.1 IUPAC Classification of porous materials

Type of materials	Pore size (nm)	Examples
microporous materials	< 2	zeolites, activated carbon
mesoporous materials	2 – 50	M4ls, SBA-15, pillared clays
macroporous materials	> 50	glasses

2.1.2 Mesoporous materials [24-26]

Mesoporous materials are a type of molecular sieves, such as silica, or modified layered materials such as pillared clays and silicates. The discovery of the hexagonal MCM-41 gave rise to analogous mesoporous structures with different pore orientations such as MCM-48 (cubic) and MCM-50 (lamellar). The slightly different forms of mesoporous silica are FSM and HMS, both of which are hexagonal arrayed mesoporous silicates. In general, all compounds are referred to as M41s materials. MCM-41 has proven to be more stable and easier to synthesize than the cubic, lamellar structures and other forms [25]. It has uniform pore sizes ranged from 2 to 50 nm and has found great utility as catalysts and sorption media because of the regular arrays of uniform channels. Large surface area is desirable for enhancing the reactions. A typical feature of mesoporous materials is extremely high surface area because of their porosity and the surface area of mesoporous materials are in range of 200 – 1000 m^2/g. In the case of MCM-41, it has surface area above 700 m^2/g [15].

2.1.2.1 Classification of mesoporous materials

Mesoporous materials can be classified by different synthetic procedures into three categories as described in Table 2.2.

Table 2.2 Classification of mesoporous materials by synthesis procedure

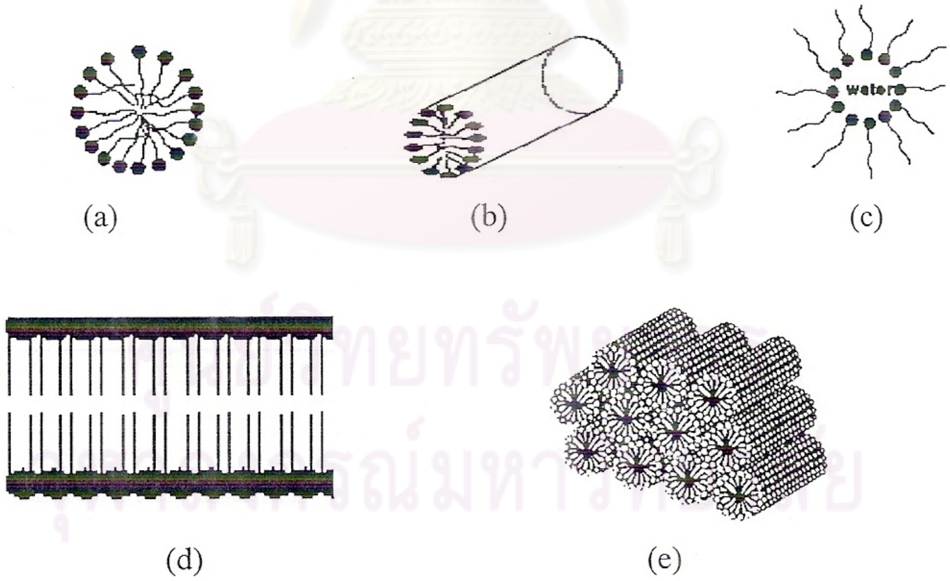
Assembly	Template	Media	Material
(a) Electrostatic	quaternary ammonium salt	base or acid	MCM-41
(b) H-bonding	primary amine	neutral	HMS
(c) H-bonding	amphiphilic triblock copolymer	acid (pH<2)	SBA-15

2.1.2.2 Synthetic strategies of mesoporous materials [26]

In general, the synthesis of MCM-41 involves the use of a surfactant in aqueous solution. MCM-41 is generally obtained by hydrothermal crystallization. The surfactant is used as a template around which a framework will form. The gel reaction of mesoporous materials usually contains cation (e.g. Si^{4+} of silicate materials, Al^{3+} of aluminate materials) to form the framework; anionic species (e.g. OH^- or F^-); organic template and solvent (generally water). Typically, the nature of template can be considered into two parts that are hydrophobic tail on the alkyl chain side and hydrophilic head on the other side. The examples of template used are primary, secondary, tertiary and quaternary amines, alcohols, crown or linear ethers, and polymer. An understanding of how organic molecules interact with each other and with the inorganic frameworks will increase the ability to design rational routes of synthesis of molecular sieve materials. The organic templates are frequently occluded in the pores of the synthesized material, contributing to the stability of mineral backbone. After that, the organic templates can be removed by extraction or calcination.

2.1.2.3 The behavior of surfactant molecules in an aqueous solution

In a simple binary system of water-surfactant, surfactant molecules, at a particular concentration can aggregate to form micelles of various types. The shapes of micelle strongly depend on the concentrations as shown in Fig. 2.1.



(a) (b) (c)

(d) (e)

Figure 2.1 Phase sequence of the surfactant-water binary system (a) spherical micelle, (b) rod-shaped micelle, (c) reverse micelle, (d) lamellar phase, and (e) hexagonal phase.

At low concentration, they energetically exist as isolated molecules. With increasing concentration, surfactant aggregate together to form isotropic spherical and rod shaped micelles by directing the hydrophobic tails inside and turning the hydrophilic heads outside in order to decrease the system entropy. The initial concentration threshold at which those molecules aggregate to form isotropic micelle is called critical micelle concentration (CMC). The CMC determines thermodynamic stability of the micelles. When the concentration is continuously increased, the micellar shape changes from spherical or rod shape to hexagonal, lamellar, and inverse micelles. The particular phase present in a surfactant aqueous solution depends not only on the concentrations but also on the nature of surfactant molecules such as hydrophobic carbon chain length, hydrophilic head group, and counter ion. Moreover the ionic strength, pH value, and temperature including other additives are also the factors determining the shape of micelles.

2.1.2.4 Interaction between inorganic species and surfactant micelles [23, 27]

The major components of framework structure, mainly silicate, are present in aqueous solution as inorganic species. To acquire the desired structure, firstly the template forms the proper shape, and then the inorganic soluble species interact with the surfactant as shown in Table 2.3. The hybrid solids formed strongly depend on the interaction between surfactants and the inorganic precursors.

Table 2.3 Examples of interactions between the surfactant and the inorganic soluble species

Surfactant type	Inorganic type	Interaction type	Example materials
Cationic (S^+)	I^-	S^+I^-	MCM-41, MCM-48
	I^+X^-	$S^+X^-I^+$	SBA-1, SBA-2, zinc phosphate
	I^0F^-	$S^+F^-I^0$	silica
Anionic (S^-)	I^+	S^-I^+	Al, Mg, Mn, Ga
	I^-M^+	$S^-M^+I^-$	alumina, zinc oxide,
Neutral S^0 or N^0	I^0	S^0I^0 or N^0I^0	HMS, MSU-X, aluminum oxide
	I^+X^-	$S^0X^-I^+$	SBA-15

S^x or N^x : surfactant with charge of x

I^x : inorganic species with charge of x

X^- : halogenide anions

F^- : fluoride anion

M^{n+} : with charge of n

In the case of ionic surfactant (S^+ and S^-), the hydrophilic head mainly binds with inorganic species through electrostatic interaction. There are two possible formation routes. Firstly, direct pathway: surfactant and inorganic species of which charges are opposite interact together directly (S^+I^- and S^-I^+). Another is the indirect pathway, occurring when the charges of surfactant and inorganic species are the same. The counter ions in solution get involved as charge-compensating species such as the $S^+X^-I^+$ path takes place under acidic conditions in the presence of halogenide anions (X^- = Cl^- or Br^-) and the $S^-M^+I^-$ path is the characteristic pathway in basic media, in the presence of alkaline cation (M^+ = Na^+ or K^+). Fig. 2.2 shows the possible hybrid inorganic-organic interfaces.

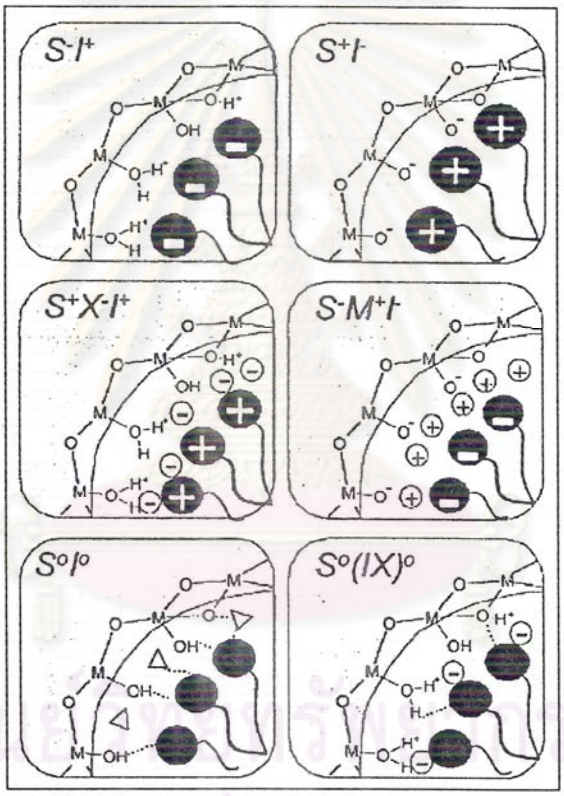


Figure 2.2 Schematic representation of the different types of silica-surfactant interfaces. Dashed line corresponds to H-bonding interactions [27].

Using non-ionic surfactant (S^0 or N^0), the main interaction between template and inorganic species is hydrogen bonding or dipolar, which is called neutral path i.e. S^0I^0 and $S^0X^-I^+$. Nowadays, non-ionic surfactants give important commercial advantages in comparison to ionic surfactants because they are easily removed, biodegradable, nontoxic, and relatively cheap.

2.1.2.5 Media for gel formation of mesoporous materials [28]

From classification of mesoporous materials by synthesis procedure in Table 2.2, gelation of MCM-41 could be prepared in base or acidic media. The formation of crystalline materials occurs by gel formation as following:

In the gelation step, alkoxide gel precursors in aqueous solution are hydrolyzed,

$$\equiv Si-OR + H_2O \rightleftharpoons \equiv Si-OH + ROH \tag{2.1}$$

and polymerized through alcohol or water producing condensations:

$$\equiv Si-OR + OH-Si\equiv \rightleftharpoons \equiv Si-O-Si\equiv + ROH \tag{2.2}$$

$$\equiv Si-OH + OH-Si\equiv \rightleftharpoons \equiv Si-O-Si\equiv + H_2O \tag{2.3}$$

The gel morphology is influenced by temperature, the concentrations of each species (such as functional group of ROH, the water/alkoxide molar ratio), and especially acidity:

- Acid product generally produces weakly-crosslinked gels which compact easily under drying conditions, yielding low-porosity microporous structures with pore diameter smaller than 2 nm.

- Using of neutral to base pH conditions results in relatively mesoporous structure after drying, as rigid clusters by a few nanometers across pack to form mesopores.

The synthesis in this thesis was performed using base solution because of the best gel formation [29].

2.1.2.6 Formation mechanism of mesoporous materials [15, 23, 25, 27]

Mechanism of mesoporous materials formation can be classified into three types based on the synthesis route (Fig. 2.3):

(a) Liquid crystal templating mechanism:

An example of the materials formed by this mechanism is MCM-41. From Fig. 2.3 (a), there are two main pathways. In the first pathway, liquid crystal phase is formed before silicate species are added (1) or another pathway is the addition of the silicate with surfactant resulting in the ordering of the subsequent silicate encased surfactant micelles (2).

(b) Folding sheet formation

An example of this mechanism is the formation of FSM-16 (see Fig. 2.3(b)). Ammonium surfactant intercalates into hydrate sodium silicate, which composes of single layered silica sheets called "kanemite" (ideal composition $NaHSi_2O_5.3H_2O$) to produce the lamellar-to-hexagonal phase in FSM-16. After the surfactants are ion exchanged into layered structure, the silicate sheets are thought to fold around the surfactants and condense into a hexagonal structure.

(c) Hydrogen-bonding interaction

HMS is one of the examples of mesoporous materials formed by this mechanism. Hydrogen bonding occurs between silicate and non ionic surfactant as shown in Fig 2.2 and Fig. 2.3(c). The neutral templating produces mesoporous materials with thicker walls and higher thermal stability as compared to the LCT derived silicates.

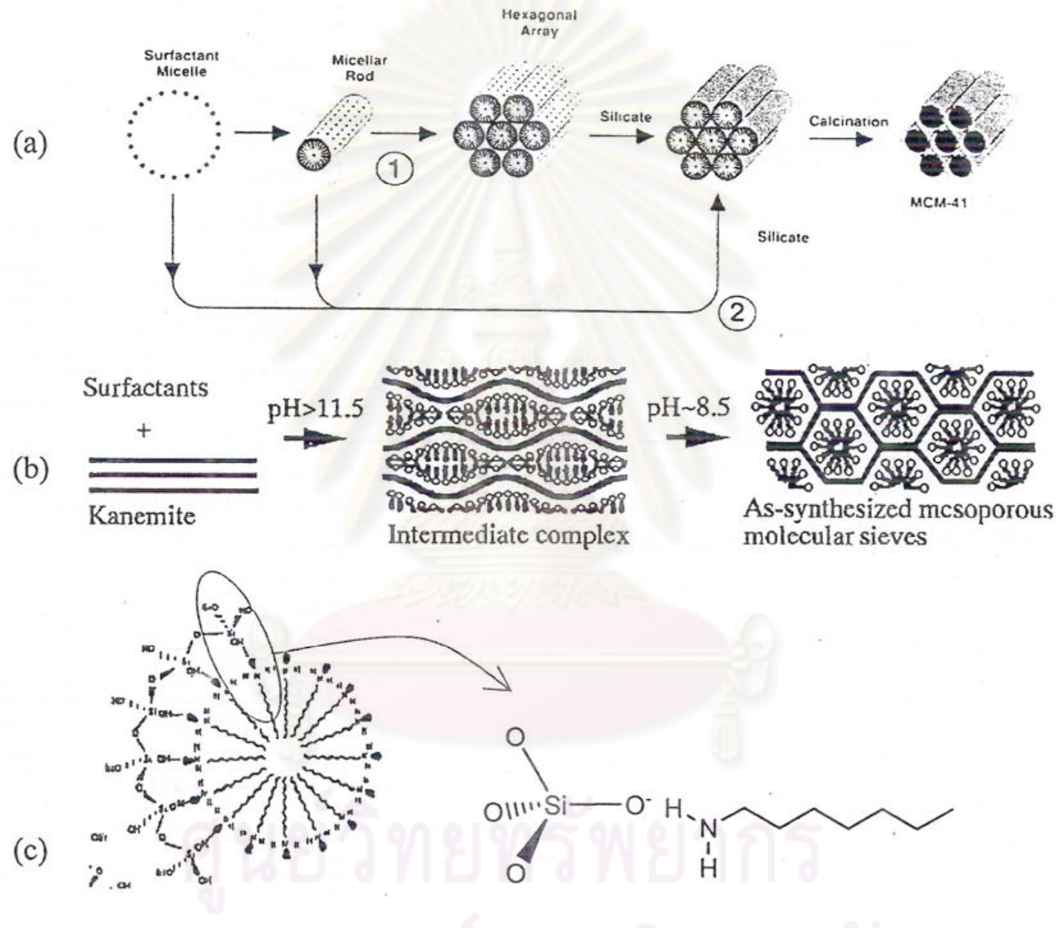


Figure 2.3 Mechanism of mesoporous material formation (a) LCT of MCM-41 formation, (b) Folding sheet formation of FSM-16 and (c) H-bonding interaction in HMS formation [15, 23, 27, 30]

For liquid crystal templating (LCT) mechanism in aqueous solution, a surfactant will form spherical micelles at small concentration. When the concentration of the surfactant increases, micellar rods are formed. This formation can use in a variety of orientations depending on the stacking ability of the surfactant due to their charge and shape [30].

The two pathways in Fig.2.3(a) can be explained in detail as following [15, 23]:

1.) A surfactant control mechanism.

In this route, inorganic material replaces the solvent (water) to create inorganic walls between the surfactant cylinders as surfactant arrays. The encapsulation of micelles by anionic silicate species occurs via electrostatic interaction with the cationic hydrophilic surfaces of the micelles.

2.) A silicate control mechanism.

In this second pathway, silicate species condense continuously around micelles. After that, they form rods and pack into a hexagonal structure. This pathway was unclearly postulated as a cooperative self assembly of the ammonium surfactant and the silicate precursor species. This is the generally favored pathway [23].

From Fig. 2.3 (a), the framework will condense around the micellar rods and a nonporous solid is formed. The surfactant template must be removed from the framework to produce the mesoporous materials. The method for template removal will depend on the desired morphology and the thermal stability of the synthesized products. The surfactant template in the framework can be removed by calcination. The synthesized products are heated to burn out the organic phase, resulting in the mesoporous framework [30]. The template can also be removed by extraction with solvents. Some of the effective solvents are ethanol or methanol with 10% hydrochloric acid [31]. Commonly used solvents are dichloromethane (DCM) and methanol [32].

Other type of structural orientation can be formed via the mechanism in Fig.2.3 (a). The surfactant type and concentration can be adjusted to yield cubic pore structures (MCM-48) or lamellar pore structures (MCM-50) but their structures are less stable and harder to synthesize, compared to MCM-41 [25].

MCM-41 has a honeycomb structure which is the result of hexagonal packing of unidimensional cylindrical pores as shown in Fig.2.4.

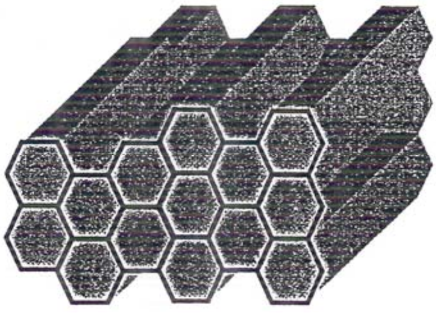


Figure 2.4 Hexagonal mesoporous structure.

Although some of mesoporous materials described above have the same hexagonal structure, they are different in the properties as shown in Table 2.4. The thermal and hydrothermal stability of material are based on the wall thickness. Therefore, MCM-41 possesses significantly higher surface area and exhibits higher thermal and hydrothermal stability than other materials. Furthermore, its pore size distribution is narrow.

Table 2.4 Properties of some hexagonal mesoporous materials [29]

Material	**Pore size (Å)**	**Wall thickness (nm)**	**BET specific surface Area (m^2/g)**
MCM-41	15-100	1-1.5	>1000
HMS	29-41	1-2	640-1000
FSM-16	50-300	no report	680-1000
SBA-15	15-32	3-6	630-1000

Table 2.5 Comparison of two well-known mesoporous materials, MCM-41 and SBA-15 in their characteristic properties [15, 33]

Properties	**MCM-41**	**SBA-15**
Pore size (Å)	15-100	46-300
Pore volume (ml/g)	>0.7	0.8-1.23
Surface area (m^2/g)	>1000	690-1040
wall thickness (Å)	10-15	31-64

According to the properties listed in Table 2.5, MCM-41 shows a better performance than SBA-15 and M41s in most of properties such as high surface area, narrow pore size distribution and high pore volume.

MCM-41 is the most studied with an increase progression in both theory and application. The synthesis of MCM-41 can be performed by various synthesis pathways using the surfactant templating method. MCM-41 has a uniform structure and specific surface area up to 1000 m^2/g. The pore diameter varies from 2 to 10 nm. It is used in different applications and it is a promising material regarding economic and environmental friendly processes. In present, surface modification is performed for various application such as adsorbent, catalytic support, and ion-exchange [15, 16].

The main structure of MCM-41 consists of Si-O bonds and surface silanol (Si-OH) species. There are several method to modify MCM-41 with functional groups. In previous research, the synthesis of modified MCM-41 was performed by mixing a variety of functional groups with the starting substance to add the desired molecule on the product by co-condensation. Some research found that a variety of functional groups should be added after crystalline structure formation to gain the desired functionalized product. The grafting of functional group on the surface of MCM-41 could be done via reactions with surface silanol species. However, surface modifications and the functionality will depend on the applications [30, 34, 35].

2.1.3 Synthesis method of MCM-41 and functionalized MCM-41 [9,15-18, 36-38]

The development in the synthesis of MCM-41 for using as heavy metal adsorbents is the continuous research. The synthesis methods can be divided into three different methods:

1. Conventional hydrothermal templated sol-gel method.

In this method, cetyltrimethyl ammonium bromide (CTAB) and tetraethyl orthosilicate (TEOS) as initial substance, and organic silicane (R-trimethyloxysilanes) are added to a base solution (aqueous ammonia or sodium hydroxide). The gel is form after stirring and the precipitate is obtained by heating of the gel in Teflon-lined stainless steel autoclave. Then, crystalline formation occurs by continuous heating about 72-144 h. The crystallization time depends on the type of silicanes. The removal of template from obtained product is finally performed.

<u>Removal of template</u>*: The solid product is recovered by filtration, washed with deionized water until the pH of the filtrate is neutral, and finally dried. The CTAB template can be removed by extraction with mixed solution of methanol and hydrochloric acid under reflux [31]. Final product is separated by centrifugation, washed with ethanol, dichloromethane, and finally dried.

2. Original stepped templated sol-gel method

CTAB is first dissolved in deionized water. Under continuous stirring, TEOS and base source (aqueous ammonia or sodium hydroxide) are added into the solution dropwise to produce a gel. Then, gel is transferred into a Teflon-lined stainless steel autoclave and heated about 30 h for hexagonal structure form crystallization. The organic silicane (R-trimethyloxysilanes) is added. The mixture is continuously stirred and heated for 1 h before being further heated at the beginning temperature for 24 h. The removal of template from obtained product is achieved by solvent extraction as described previously.

From topic 2.1.2.5, gelation can be prepared in base or acid media. This synthesis method 1 and 2 is performed by using base solution because of the best gel formation [28].

3. Grafting method

This method is to attach the functional group on normal MCM-41 obtained from method 1 or 2. The normal MCM-41 from method 1 or 2 is synthesized by using solely TEOS. Grafting method is divided into homogeneous and heterogeneous types. Homogeneous synthesis type is performed by attachment of the desired functional organic silicane (R-trimethyloxysilanes) on MCM-41. Heterogeneous type synthesis is carried out by first adding the starting organic silicane on MCM-41 and then functionalizing the attached starting organic group with the other function groups step by step to finally obtain the desired organic functional group. A higher metal adsorption capacity was observed when the adsorbents were synthesized by homogeneous synthesis type, compared to heterogeneous synthesis type [10, 11].

From previous research, the synthesis methods for functionalized MCM-41 were proposed but there is no comparison and conclusion on the best performance method in the preparation of modified MCM-41 for the use of adsorbents so far. Functionalized MCM-41 in this thesis is synthesized using three methods, characterized, and evaluated for the adsorption capacity for mercury ions. The results are compared and the most suitable method of synthesis is finally chosen.

2.2 Information of mercury

2.2.1 Mercury compounds

Mercury, which has several chemical forms, is a trace component of all fossil fuel source materials including coal, petroleum, oil shale, natural gas, gas condensates, and bitumen [39]. Mercury compounds are found in various forms. From a toxicological and environmental point of view, the most useful and commonly accepted classification is metallic mercury (liquid and vapor), inorganic salts (sulfides, chlorides, nitrates, and oxides), alkyl compounds such as those containing an ethyl or methyl group, alkoxyalkyl compounds, aryl compounds in particular the diphenylmercury. The various chemical forms of mercury exhibit significantly different chemicals and physical behavior [40].

Mercury is the only metallic element that is liquid at room temperatures. It also called quicksilver or hydrargyrum. The characteristics of mercury are atomic number of 80, atomic weight of 200.59, melting point of -38.8 ^{o}C, specific gravity of 13.55 g/cm, vapor pressure of 1.22 x 10^{-3} mmHg at 20 ^{o}C and the oxidation states of Hg^0, Hg^+ (mercurous) and Hg^{2+} (mercuric). Its valencies are of 1 and 2 [41]. Mercury capably forms hundreds of compounds depending on its own chemical properties. Mercury rapidly forms alloys known as amalgams with practically all metals except iron. Dental fillings are essentially amalgams of mercury and silver. And the importance is that all mercury compounds are volatile and usually decomposed to mercury. Mercury has a relatively high vapor pressure at room temperatures and the rate of vaporization increases with increasing of temperature [42].

2.2.2 Mercury in petroleum

Mercury is a metallic compound found in a wide range of petroleum industry such as in crude oil, condensate, natural gas, wastewater and soil around platform. Mercury compounds are found in various forms such as elemental, ionic and organometallic forms. Form and quantities of mercury depend on the source. For example, amounts of mercury in natural gas and condensate are generally 10-3000 ppb [43], 0.5-10 ppb in crude oil [44], and 3-4 ppb in crude oil processed by United State refineries in 2004 [45].

Elemental mercury is highly adsorptive and it adsorbs on metallic surface and on solid materials suspended in liquids. Elemental mercury can precipitate as mercury (sulfur) complexes (HgX where X is an organic sulfide, thiol, thiophene or mercaptan) occurring in some crude oils and condensates. Boiling points of Hg^0 in distillation of crude oil is 357 ^{o}C [46].

The presence of mercury from petroleum drilling in neighboring waters would affect marine lives. In the Gulf of Thailand, mercury substance was first found in petroleum drilled from the Gulf many years ago and the offshore gas production units have discharged mercury-contaminated water into the sea resulting in the increasing amount of this heavy metal in aquatic animals around platforms.

2.2.3 Disadvantages of mercury compounds in petroleum

1. Effects of mercury on processing [46]

Mercury has several detrimental impacts on processing operation.

1) Equipment may be damaged because mercury accumulates in equipment constructed of various metals, especially aluminum, by forming an amalgam with the metal, for example, in the ethylene production [47]. The failures occur, at the LNG plant at Skikda, Algeria, from tube corrosion in the exchangers [48].

2) Mercury in gas plant products may affect downstream processes. The risk of mercury contamination occurs in process feed especially gas plant process that used for chemical manufacture (such as olefins, ethylene, aromatics and MTBE).

3) Mercury contaminates treatment processes such as molecular sieve and glycol dehydration units, and amine acid gas removal system. Spent molecular sieve adsorbent and contaminated treatment liquids are difficult to eliminate and regenerate.

4) Mercury deposition in equipment is a threat for health and safety of workers involved in maintenance or inspection activities. Sludge containing mercury from water treatment system, desalters, separators, and heat exchangers is a toxic waste that is needed special treatment and disposal.

5) Wastewater streams which contain high levels of mercury must be treated to remove mercury before discharging. Thus, the plant operational expense increases.

2. Catalyst deactivation [30, 49]

Catalytic process such as hydrogenation can be deactivated by mercury poisoning. Poisoning is catalyst deactivation due to the adsorption of impurities from the feed stream, such as nitrogen, sulfur, oxygen, and metal. The metal impurities can permanently deposit on the active sites of the catalyst and cause a loss of catalytic activity. Several researchers studied an effect of mercury on catalyst deactivation. Mercury poisoning of catalysts reduces the catalyst life.

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3. Health and safety risk [50]

Mercury compounds are extremely toxic to human and animals, especially its organic compounds. They damage nervous system on inhalation or ingestion of ionic mercury and absorption of them. Mercury in oil and condensate can be emitted in air upon combustion, causing air pollution, wastewater and soil. Mercury and it compounds are neurotoxins or neurological dysfunction. The period of time between exposure and exhibition of symptoms varies depending on the type of mercury species and content of exposure. Hg^0 is readily absorbed into the blood stream via the lungs.

The major mercury specific considerations for health and safety of workers in petroleum processing are revealed by oil field manufacturer. Estimation of the potential risk to oil field workers due to mercury compounds in petroleum liquids is uncertain because of the lack of data or uncompleted data reported by the manufacturer.

2.2.4 Control of mercury in the environment [5, 6]

Hazardous wastewater is a waste that is harmful to human, animal, or living organisms in environment such as water containing pesticides from agricultural activities, the by-products of manufacture, and heavy metal contaminated water. The contamination of heavy metals in water especially mercury is a critical environmental problem [51]. This research emphasizes on the removal of mercury from wastewater before releasing to the environment. In Thailand, the residual concentration of mercury in released water has to be within the limit of the regulations of the Pollution Control Department, PCD. The acceptable maximum concentration of mercury in drinking water and industrial wastewater is 0.001 mg/ L and 0.005 mg/L, respectively [5, 6].

2.3 Removal of mercury

2.3.1 Background information of mercury removal

Mercury can be removed by different methods depending on its form. Elemental mercury is eliminated by using sulfur supported on solid material and ionic or inorganic mercury can be removed by ion-exchange or reduced to elemental Hg using a reducing reagent such as Sn(II). However, ion-exchange cannot remove elemental mercury. The removal of all mercury species from wastewater is more complicated, especially in the presence of organometallic compounds. Organometallic mercury cannot be removed by ion-exchange because of the covalent nature of Hg-C bonds. One method is adsorption onto an ion-exchange resin containing chemically bound active -SH groups [52]. The removal of mercury occurs via chelation mechanism.

The chelation mechanism concerns coordination of the electron donor atoms or the ligands and metal electron acceptor. The examples of electron donor atoms in chelating ligands are sulfur (e.g. S in thiols, thiocarbamates and thioethers), nitrogen (e.g. N in azo groups, nitriles, imino and amines groups) and oxygen (e.g. O in hydroxyl, ether, phenolic, carboxylic and carbonyl groups). The chelating ligands can coordinate with different metal ions with different affinity. It can be explained by the hard-soft acid-base principle (HSAB). Pearson proposed that “hard acids bind strongly to hard bases and soft acids bind strongly to soft bases” [53]. The interaction between hard acid and hard base occurs via electrostatic interactions while interaction of soft acids and soft bases occurs via covalent bonds. In the case of the borderline acids, which have intermediate characteristics, they show an affinity for both hard and soft bases. The selectivity of chelating ligand toward metal ion corresponds to the HSAB principle. The relation of hard-soft acids and hard-soft base are shown in Table 2.6.

Table 2.6 The classification of hard-soft acids and hard-soft bases [53]

Acids	**Bases**
Hard	
H^+, Li^+, Na^+, K^+(Rb^+, Cs^+)	NH_3, RNH_2, N_2H_4
Be^{2+}, $Be(CH_3)_2$, Mg^{2+}, Ca^{2+}, Sr^{2+}(Ba^{2+})	H_2O, OH^-, O^{2-}, ROH, RO^-
Se^{3+}, La^{3+}, Ce^{4+}, Gd^{3+}, Lu^{3+}, Th^{4+}, U^{4+}, UO_2^{2+}, Pu^{4+}	R_2O
Ti^{4+}, Zr^{4+}, Hf^{4+}, VO^{2+}, Cr^{3+}, Cr^{6+}, MoO^{3+}, WO^{4+}, Mn^{2+}, Mn^{7+}, Fe^{3+}, Co^{3+}	CH_3COO-, CO_3^{2-}, NO_3^-, PO_4^{3-}, SO_4^{2-}, ClO_4^-
BF_3, BCl_3, $B(OR)_3$, Al^{3+}, $Al(CH_3)_3$, $AlCl_3$, AlH_3, Ga^{3+}, In^{3+}	F^- (Cl^-)
CO_2, RCO^+, NC^+, Si^{4+}, Sn^{4+}, CH_3Sn^{3+}, $(CH_3)_2Sn^{2+}$	
N^{3+}, RPO_2^+, $ROPO_2^+$, As^{3+}	
SO_3, RSO_2^+, $ROSO_2^+$	
Cl^{3+}, Cl^{7+}, I^{5+}, I^{7+}	
HX (hydrogen-bonding molecules	
Borderline	
Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}	$C_6H_5NH_2$, C_5H_5N, N_3^-, N_2
Rh^{3+}, Ir^{3+}, Ru^{3+}, Os^{2+}	NO_2^-, SO_2^{2-}
$B(CH_3)_3$, GAH_3	Br^-
R_3C^+, $C_6H_5^+$, Sn^{2+}, Pb^{2+}	
NO^+, Sb^{3+}, Bi^{3+}	
SO_2	
Soft	
$Co(CN)_5^{3-}$, Pd^{2+}, Pt^{2+}, Pt^{4+}	H^-
Cu^+, Ag^+, Au^+, Cd^{2+}, Hg^+, Hg^{2+}, CH_3Hg^+	R^-, C_2H_4, C_6H_6, CN^-, RNC, CO
BH_3, $Ca(CH_3)_3$, $GaCl_3$, $GaBr_3$, GaI_3, Tl^+, $Tl(CH_3)_3$	SCN^-, R_3P, $(RO)_3P$, R_3As
CH_2, carbenes	R_2S , RSH , RS , $S_2O_3^{2-}$
π acceptors: trinitrobenzene, chloroanil, etc.	I^-
HO^+, RO^+, RS^+, RSe^+, Te^{4+}, Rte^+	
Br_2, Br^+, I_2, I^+, ICN, etc.	
O, Cl, Br, I, N, RO, RO_2	
M^0 (metal atoms) and bulk metals	

R refers to hydrocarbon compounds.

Furthermore, the binding ability between the chelating ligands attached onto the solid support and the metal ions in solution also depends on many factors as followings:

- Charge, size, and nature of the metal ions
- Nature of the donor atoms present in the ligand
- Nature of the solid support (e.g. hydrophlilicity of adsorbent should be considered in case of the extraction in the aqueous solution.)
- The pH of solution

Many researches show that the sulfur atoms in chelating ligands have higher affinity toward mercury ions than nitrogen and oxygen atoms [13, 54]. The selectivity of sulfur atoms in chelating ligands (such as R_2S , RSH , RS , $S_2O_3^{2-}$) toward mercury ions (Hg^+, Hg^{2+}, CH_3Hg^+) can be explained by the HSAB principle. In previous research, it was found that elemental mercury could be rapidly captured on sulfur-based trapping masses in the gas phase [43]. This technique is not easily adapted to liquid applications because of the low solubility of elemental sulfur in the aqueous solution. Then, the trapping agent must be anchored to the supported material. Consequently, a ligand containing sulfur atom is modified onto the surface of material and/or strongly attached on the supported material.

2.3.2 Methods of mercury removal [55]

Several methods have been proposed for mercury removal from wastewater around platform. They can be classified into two methods as followed.

1. Chemical treatment
    - Precipitation
    - Coagulation treatment
    - Reduction processes
2. Adsorption
    - Adsorption by adsorbent
    - Ion exchange

2.3.2.1 Chemical treatment

Chemical treatment concerns the use of chemicals to convert mercury compounds in petroleum to the form which is easy to remove from sample. The chemical substance used is usually a sulfur compound. The reaction between mercury and sulfur compounds is shown below.

$$Hg + S_x^{2-} \longrightarrow HgS + S_{x-1}^{2-} \; ; \quad \text{where } x = 3\text{-}6 \qquad (2.4)$$

Mercuric sulfide (HgS) precipitates can be removed easily by solid-liquid separation. The disadvantage of chemical treatment method is the contamination of the treated product or water with the chemicals used [56].

Precipitation method

The addition of sulfide to precipitate highly insoluble mercury sulfide is the common precipitation treatment reported. The effective of precipitation, with minimizing sulfide dosage, occurs in the near-neutral pH range. Optimum pH of 8.5 is suggested [57]. By using this method, the user may encounter certain difficulties. The formation of insoluble mercury sulfide complexes occurs at high levels of excess sulfide with the difficulty of monitoring excess sulfide levels and the problem of toxic sulfide residual in the treated effluent. This method requires precipitate separation by filtration or activated carbon polishing treatment [58].

Coagulation treatment

Coagulation has been reported useful for a variety of mercury contained wastewater by using aluminum sulfate (alum), iron sates and lime. The concentration of mercury in effluent achieved by alum treatment can be in a range of 1.5-102 μg/L, and 0.5-12.8 μg/L by iron treatment. This method requires separation unit to remove the precipitates.

Reduction processes

Inorganic mercury can be converted to the metallic form by reduction, and separated by filtration or other solids separation techniques. Reducing agents available are aluminum, zinc, hydrazine, stannous chloride and sodium borohydride. Reduction processes cannot effectively reduce the mercury levels to below 100 μg/L. The operating costs are high due to the cost of reducing agents and the second stage polishing by the rigorous treatment methods.

2.3.2.2 Adsorption

Adsorption is a phenomena of the sorption that occurs between solid phase and the liquid or gas phase. The removal of mercury by adsorption does not contaminate the effluent with other chemicals compared to chemical treatment. Then, this method appears to be suitable method for refinery wastewater treatment and it is chosen to study in this research. Among the more common type of adsorption methods is the adsorption by adsorbents and ion exchangers.

Adsorption by adsorbent

Many adsorbents were used for mercury adsorption such as activated carbon, zeolite, silica, clay, polymer bead and etc. Activated carbon is widely used as adsorbent for mercury removal but its cost is high. The effectiveness of adsorption depends on initial form and concentration of mercury, dosage and type of adsorbents, and contact time between adsorbent and mercury contained wastewater. Increasing adsorbent dosage and increasing contact times improve removal efficiency. The result from adsorption indicated that crystalline materials showed good adsorption efficiency [9 - 11].

Ion exchange

This treatment of inorganic mercury involves the formation of a negatively charged mercuric chloride complex by addition of chlorine or chloride salts, followed by the removal of the mercuric chloride complex on an anion exchange resin. In wastes where the amount of chloride is not high, cation exchange resins are more effective. Common used resins contain mercapto group (R-SH), for example, polythiolstyrene resins are highly specific for mercuric ion [59]. This method requires pretreatment of mercurous and organic mercury. The operating costs were reported as very high.

Among the processes shown, the adsorption by using adsorbents have the capability to reduce mercury to the concentration range of 0.25 – 20 μg/L as shown in Table 2.7.

Table 2.7 The summary of treatment technology for mercury [55]

Treatment methods	Lower limit of treatment capability Hg (µg/L)
1. Chemical treatment	
- Sulfide precipitation	10 – 20
- Alum coagulation treatment	1 – 10
- Iron coagulation treatment	0.5 – 5
2. Adsorption	
- Adsorption by adsorbent	
- High initial Hg	20
- Moderate initial Hg	2.0
- Low initial Hg	0.25
- Ion exchange	1 – 5

The effectiveness and the operating cost of each type of methods depend on the chemical nature and initial concentration of mercury, the presence of other constituents in the wastewater that may interfere the specific treatment and the degree of mercury removal that must be achieved.

In this research, the adsorption method using crystalline material for mercury removal is studied.

2.4 Adsorption [60]

The removal of mercury by adsorption provides a high efficiency of mercury removal and easily applies to the large scale treatment. The adsorption method depends on type of adsorbent and condition used. Then, behavior and mechanism of adsorption should be understood before using the adsorbent for mercury removal. The adsorption can occur via physisorption or chemisorption.

Physisorption

Physisorption (or physical adsorption) occur when the attraction between adsorbates (liquid or gas phase) and adsorbents is van der Waals force, generating from the electrostatic force and London dispersion force. It does not involve a significant change in the electronic orbital patterns of the species involved. When the concentration of adsorbates increases, the multilayer sorption on the adsorbent surface can be obtained. The reaction is called outer-sphere surface reaction or non-specific (Fig. 2.5(a)). The analytes independently adsorb on the adsorbents surface and the adsorption is reversible. The reversibility of reaction depends on the attraction forces of analytes with adsorbent, temperature, and the concentration of analytes.

Chemisorption

Chemisorption (or chemical adsorption) involves the covalent or chemical bonds between adsorbent and analytes, which is stronger than van der Waals force in physisorption. The mechanism may occur when the surface of adsorbents has active sites specific for analytes. The adsorption of analytes occurs in the monolayer regime and the reaction is irreversible. Chemisorption can be called inner-sphere surface reaction (Fig. 2.5(b)).

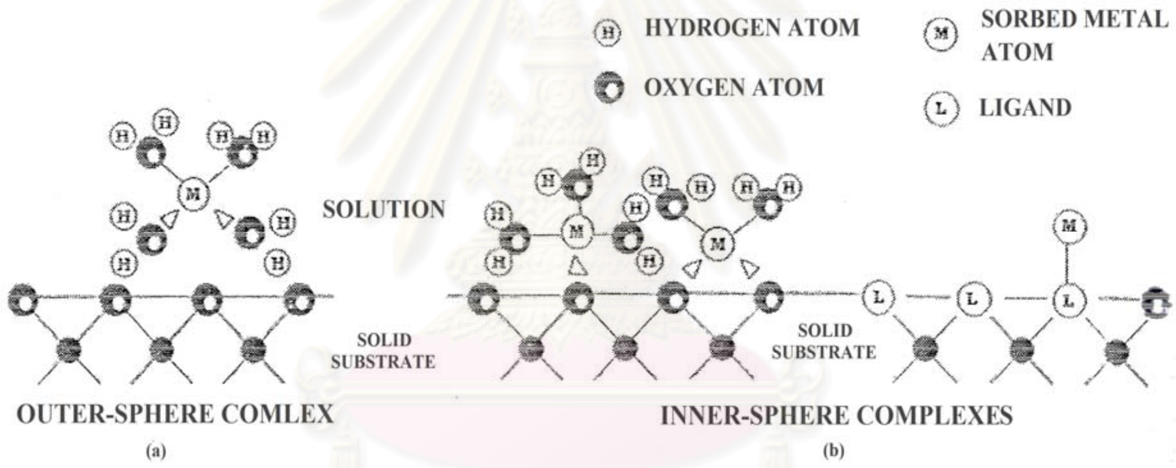


Figure 2.5 The outer-sphere (a) and inner-sphere (b) surface reaction [60].

2.4.1 Rate of mass transfer

Mass transfer is the phenomena involving the transfer of analytes in liquid or gas phase to adsorbent surface. The mass transfer is devided in three steps: (i) bulk transport, (ii) film transport and (iii) intraparticle transport (see in Fig. 2.6). It is important to understand the adsorption kinetics in order to predict the time for adsorption equilibrium to occur. The rate determining step of mass transfer at equilibrium is the slowest step of the adsorption mechanism. Each steps of adsorption are shown in Fig. 2.6.

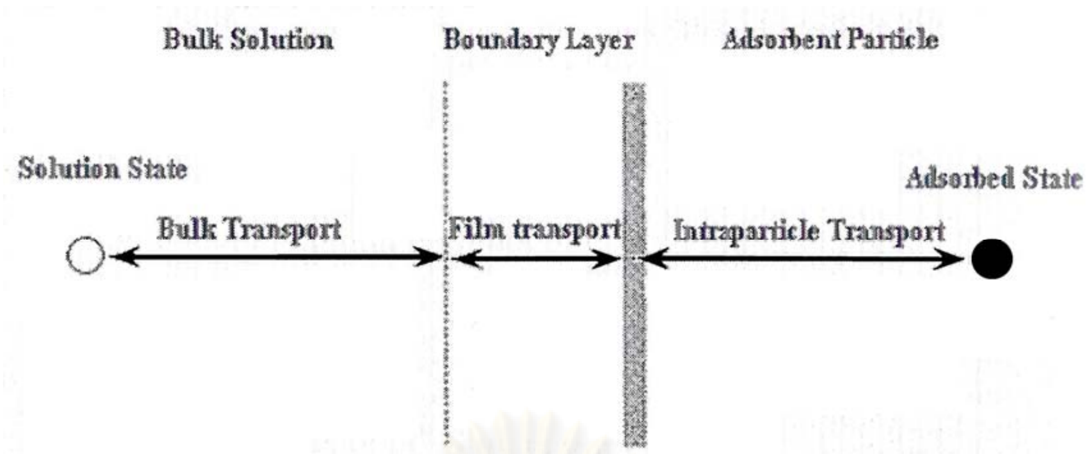


Figure 2.6 The steps of adsorption on the adsorbent surface [61].

(i) Bulk transport

This step is the very fast process. It occurs when analytes move from the bulk solution to the surface of the boundary layer.

(ii) Film transport

Film transport may occur slowly. It can be considered as the step which controls the adsorption rate. It is the process involving the transportation of the analytes from the boundary layer to the surface of adsorbent. It is called film diffusion or external diffusion.

(iii) Intraparticle transport

This step is one of the steps that can be the rate determining steps of adsorption. It is called the internal diffusion. It occurs when the analytes transport from adsorbent surface to the inside or into the pores of adsorbent and react with the active sites.

2.4.2 Adsorption isotherms [62]

Adsorption isotherms are often used to describe the adsorption equilibrium on the adsorbent surface. The adsorption isotherm is considered in the relation of the amount of analyte on adsorbent and the concentration of analytes in solution at equilibrium. The experimental data can be used to fit to adsorption isotherm models such as Langmuir and Freundlich models as shown in Fig. 2.7 and 2.8.

2.4.2.1 Langmuir isotherm

The Langmuir model derived for adsorption is initially based on the assumptions: (i) the adsorption takes place at specific sites of adsorbent and no further adsorption can occur at that sites (ii) the energy of adsorption is constant and independent of the extent of homogeneous surface, and (iii) the phenomena of adsorption is the monolayer and the maximum adsorption capacity of the adsorbent for that analyte at equilibrium can be predicted. The common form of the Langmuir relation was shown in equation 2.5 [63].

$$q = \frac{q_m b C_e}{1 + b C_e} \tag{2.5}$$

In gas/solid interface, the Langmuir equation is based on an equilibrium between condensation and evaporation of adsorbed molecules, considering a monomolecular adsorption layer. The equation 2.5 can be rearranged into the form of linear equation, as shown in equation (2.6).

$$\frac{C_e}{q} = \frac{1}{b q_m} + \frac{C_e}{q_m} \tag{2.6}$$

where C_e = equilibrium concentration of the analyte 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 the affinity of binding sites (L/mg or L/mol)

A relation plotting between C_e/q and C_e yield a straight line with a slope of $1/q_m$ and intercept of $1/bq_m$, as shown in Fig. 2.7(b).

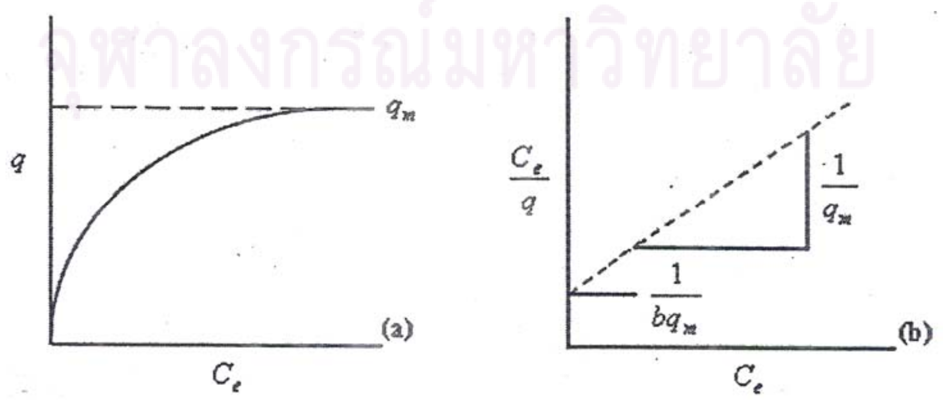


Figure 2.7 The shape (a) and the linear plot (b) of Langmuir adsorption isotherm [64].

2.4.2.2 Freundlich isotherm

The Freundlich model was derived theoretically by assuming the adsorption of analytes on heterogeneous surface or surface active sites of varied affinities. The general form of the Freundlich equation is shown in equation 2.7.

$$q = K_f C_e^{1/n} \tag{2.7}$$

The linear equation of the Freundlich isotherm is in logarithmic form, as shown in equation 2.8.

$$\log q = \log K_f + \frac{1}{n} \log C_e \tag{2.8}$$

where K_f = Freundlich constant related to adsorption capacity (mg/g or mol/g)

n = Freundlich constant related to adsorption intensity

A relation plotting between log q and log C_e gives a slope of $\frac{1}{n}$ and intercept of log K_f, as shown in Fig. 2.8(b) .

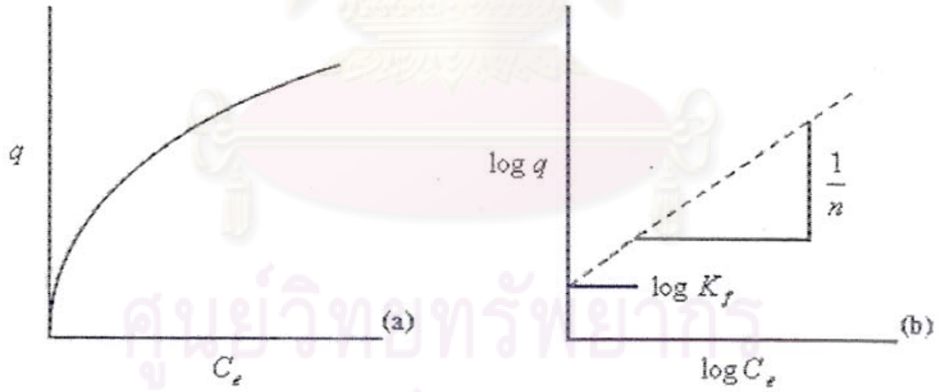


Figure 2.8 The shape (a) and the linear plot (b) of Freundlich adsorption isotherm [64].

2.5 Characterization techniques of functionalized MCM-41

2.5.1 X-ray diffraction technique (XRD) [65]

X-ray powder diffraction (XRD) is a reliable technique that can be used to identify mesoporous structure. Typically, the XRD pattern of hexagonal symmetry show five well-resolved peaks that can be indexed to the corresponding lattice planes of miller indices (100), (110), (200), (210), and (300). These XRD peaks appear at small angle (2θ angle between 2 and 5 degree) because the materials are not crystalline at atomic level, therefore diffraction at higher angles are not observed. Fig. 2.9 shows that a monochromatic beam of X-ray incident on the surface of crystal at an angle, θ. The scattered intensity can be measured as a function of scattering angle 2θ.

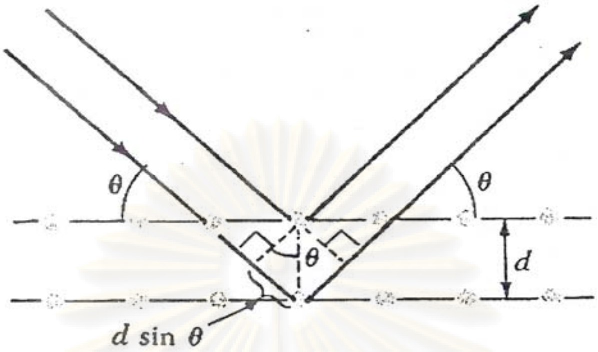


Figure 2.9 Diffraction of X-ray by regular planes of atoms.

The resulting XRD pattern efficiently indicates the different phases present in the sample structure. Using this method, Bragg's law is able to determine the inter planar spacing of the samples, from diffraction peak according to Bragg's angle.

$$n\lambda = 2d\sin\theta \tag{2.9}$$

When n is the order of the diffracted beam, λ is the wavelength; *d* is the inter planar distance of the crystal (the *d*-spacing) and *θ* is the angle between the incident beam and these planes.

2.5.2 Nitrogen adsorption-desorption technique [66, 67]

The N_2 adsorption-desorption technique is used to determine the physical properties of mesoporous molecular sieves, that are surface area, pore volume, pore diameter and pore-size distribution of solid. Adsorption of gas by a porous material is described by an adsorption isotherm, the amount of adsorbed gas by the material at a fixed temperature as a function of pressure. Porous materials are frequently characterized is terms of pore sizes derived from gas adsorption data. The IUPAC classification of adsorption isotherms is shown in Fig.2.10.

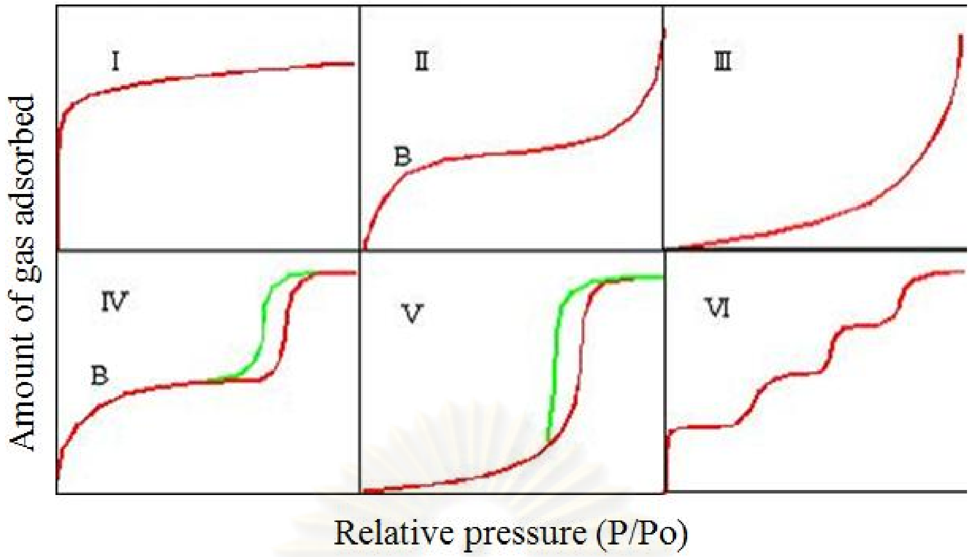


Figure 2.10 The IUPAC classification of adsorption isotherm [66].

Types of adsorption isotherms are described in Table 2.8 based on the strength of the interaction between the sample surface and the adsorbate. Pore size distribution is measured by using nitrogen adsorption/desorption isotherm at relative pressures (P/P_o) ranging from 0.05 – 0.1. The large uptake of nitrogen at low P/P_o indicates the filling of the micropores (<20 Å) in the adsorbent. The linear portion of the curve represents multilayer adsorption of nitrogen on the surface of the sample, and the concave upward portion of the curve represents the filling of mesoporous and macropores. The multipoint Brunauer Emmett and Teller (BET) method is commonly used to measure total surface area.

$$\frac{1}{W[(P_0/P)-1]} = \frac{1}{W_m C} + \frac{C-1}{W_m C}(P/P_0) \qquad (2.10)$$

W is the weight of nitrogen adsorbed at a given P/P_o and W_m is the weight of gas to give monolayer coverage, and C is a constant related to the heat of adsorption. A slope and intercept are used to determine the quantity of nitrogen adsorbed in the monolayer manner and calculate the surface area. For a single point method, the intercept is taken as zero or a small positive value, and the slope from the BET plot is used to calculate the surface area. The surface area reported depends on the method used, as well as the partial pressures. The data are summarized in Table 2.8.

Table 2.8 Features of adsorption isotherms

Type	**Interaction between sample surface and gas adsorbate**	**Porosity**	**Example of sample-adsorbate**
I	relatively strong	Micropores	activated carbon-N_2
II	relatively strong	Non porous	oxide-N_2
III	weak	Non porous	carbon-water vapor
IV	relatively strong	Mesopore	silica-N_2
V	weak	Micropores	oxide-Ar, carbon-Ar, oxide-N_2, carbon-N_2
		Mesopore	activated carbon-water vapor
VI	relatively strong sample surface has an even distribution of energy	Non porous	graphite-Kr

2.5.3 Fourier transforms infrared spectroscopy (FTIR) [68]

FTIR is a powerful tool for identifying types of chemical bonds in a molecule by producing an infrequency in the infrared absorption spectrum. The vibration of bond can occur due to the interaction of infrared radiation with a sample molecule. Infrared spectrometry finds its widest application in the analysis of organic and polymeric materials, but it is also useful for molecular sieves and organometallic compound characterization. Samples for FTIR can be prepared in many ways. For liquid samples, the easiest way is to place one drop of sample between two plates of sodium chloride (salt). Salt is transparent to infrared light. The drop forms a thin film between the plates. Solid samples can be milled with potassium bromide (KBr) to form a very fine powder. This powder is then compressed into a thin pellet and analyzed. KBr is also transparent in FTIR [68]. The IR band of mesoporous materials correspond to O–H stretching of the surface silanol groups, stretching vibrations of siloxane (–Si–O–Si–), Si–O bond stretching of the silanol groups, deformation vibrations of adsorbed water molecules and the remaining adsorbed water molecules. The attachment of functional group onto mesoporous materials could be confirmed by FTIR [69, 70].

2.5.4 Thermogravimetric analysis (TGA) [71]

TGA is a simple analytical technique that measures the weight loss (or weight gain) of a material as a function of temperature. The material testing was performed by placing mesoporous materials into an alumina cup that is supported on, or suspended from an analytical balance located outside the furnace chamber. The sample cup is heated according to a predetermined thermal cycle. After materials are heated, they can loose weight due to a simple process such as drying, or from chemical reactions that liberate gasses. Some materials can gain weight by reacting with the atmosphere in the testing environment. Using TGA signal, the TGA curve can be plotted between percent weight change on the Y-axis against the reference material temperature on the X-axis [71, 72]. For the characterization of functionalized MCM-41, TGA have two main utilities. Firstly, it is employed to study of thermal decomposition of MCM-41 and the hydrophilicity of synthesized materials by losing of water molecule at temperature about 100 °C. Secondly, the amount of functional group on adsorbent can be determined by calculating from the percent weight loss of TGA curve [19].

2.6 Literature reviews on removal of mercury by adsorption

The removal of mercury has been investigated for many years. Many adsorbents have been developed for removal of mercury ions from wastewater in petroleum industry. The improvement of adsorption efficiency of the adsorbents has also been reported.

Regarding the selectivity of adsorbents toward mercury, elemental mercury is readily captured on sulfur-based trapping masses in the gas phase [43]. This technique is not easily applied to liquid applications because of the solubility of elemental sulfur in the aqueous solution. Therefore, the trapping agent must be anchored to a support material for capture of elemental mercury. Moreover, the other substrates (e.g. clay, activated carbon, polymer, and silica gel) were also modified for removal of mercury(II) ions. The functional groups of the modification reagent must contain the sulfur, nitrogen and/or oxygen atoms such as 2-mercaptobenzothiazole [73], procion brown MX 5BR [14], diethanolamine (EDA) [74], dithizone [12], 2-mercaptobenzimidazole (MBI) [8, 13], and 3-mercaptopropyltrimethoxy silane (MPTMS) [75 - 80]. The modified materials and their adsorption capacity for mercury ions are listed in Table 2.9.

Table 2.9 The adsorption capacity of the other modified materials (e.g. clay, activated carbon, polymer, and silica gel) for mercury(II) ions removal

Adsorbents	**Type of organofunctionalized**	**Adsorption condition**			**Ref.**
		pH	**Time** (min)	**Adsorption capacity** (mmol / g)	
Clay	2-mercaptobenzothiazole (MBT)	3 - 6	30	0.0135	[73]
Montmorillonite clay	3-mercaptopropyltrimethoxysilane (MPTMS)	Not shown	Not shown	0.325	[75]
Fluorohectorite clay	3-mercaptopropyltrimethoxysilane (MPTMS)	Not shown	1,080	0.74	[76]
Clay	2-mercaptobenzimidazole (MBI)	4 - 8	360	0.145-0.178	[8]
Smectite clay	3-mercaptopropyltrimethoxysilane (MPTMS)	2 - 9	Not shown	0.60	[77]
Activated carbon	Sulphurised	6	240	1.137	[81]
Furfural activated carbon	–	5.5	60	0.87	[82]
Furfural-based activated carbon	–	2 - 5	Not shown	0.87	[83]
Polymer membranes	procion brown MX 5BR	2 - 6	45	0.34	[14]
Polymer bead	polyethyleneimine (PEI)	5	60	1.67	[84]
Polymer bead	diethanolamine (EDA)	5.4	420	1.10	[74]
Silica gel	3-mercaptopropyltrimethoxysilane (MPTMS)	7	480	0.70	[78]
Silica gel	3-mercaptopropyltrimethoxysilane (MPTMS)	Not shown	Not shown	0.40	[79]
Silica gel	dithizone	6	30	0.32	[12]
Silica gel	1,5 diphenylcarbazide (DPC)	6	30	0.028	[85]
Silica gel	2-mercaptobenzimidazole (MBI)	Not shown	Not shown	(Homo) 1.42 (Hetero) 1.35	[13]
Silica gel	2-(3-(2-aminoethylthio)propylthio) ethanamine (AEPE)	3	60	(Hetero) 0.79	[17]
Organoceramic	3-mercaptopropyltrimethoxysilane (MPTMS)	3 - 5	Not shown	3.63	[80]

Homo = Synthesis by *Graft* method (homogeneous type)   Hetero = Synthesis by *Graft* method (heterogeneous type)

From the comparison of previous results, some researchers found that sulfur atoms have the lone pair electrons that can be used in the binding with mercury ions according to the hard-soft acid-base principle [53] and have higher affinity toward mercury ions than nitrogen and oxygen atom.

Many materials have been developed for mercury removal from wastewater in petroleum industry but the adsorption efficiency of those materials were not high enough. Many adsorbents for mercury removal showed several problems like low mechanical and thermal stability and weak chemical affinity. To increase adsorption efficiency, the modified materials should have high surface area and the ordered structure such as zeolite. Some research groups are interested in the synthesis of zeolite such as MCM-41, SBA-15, HMS and M41s. Recently, MCM-41 has drawn a lot of interest due to its high surface area, uniform structure and the surface can be easily modified. Zeolite materials can be used as adsorbent and could be synthesized or modified the surface by three methods; (i) conventional hydrothermal templated sol-gel method, (ii) original stepped template sol-gel method and (iii) grafting method.

1. *Conventional hydrothermal templated sol-gel method (Con)*

MCM-41 can be prepared by *Con* method. Beck *et al*. (1992) [15] synthesized, characterized, and proposed mechanism of formation of a new family of silicate/aluminosilicate mesoporous molecular sieves designated as M41s. MCM-41, one member of this family, exhibits a hexagonal arrangement of uniform mesopores. Chen *et al*. (2002) [18] prepared MCM-41 by the conventional hydrothermal templated sol-gel method and studied the property of MCM-41 by XRD and BET. The obtained materials retained ordered channels and large BET surface area even after thermal treatment at 1000 ^oC for 1 h in air.

The modification of zeolite with functional group can also performed by *Con* method. Huang *et al*. (2004) [38] synthesized MCM-41 modified with cationic silane, tri methoxysilypropyl-*N*, *N*, *N*-trimethoxyl ammonium chloride by the conventional hydro thermal templated sol-gel method and used it as adsorbent for removal of benzoic acid and toluene. The obtained material was characterized by XRD, FTIR and BET. The adsorption capacity of benzoic acid and toluene were 0.20 and 0.21 mmol/g, respectively. Evangelista *et al*. (2007) [86] synthesized HMS modified with 2-mercaptothiazoline using the conventional hydrothermal templated sol-gel method and used it for Hg(II) ions adsorption. The obtained material contained 0.89 mmol of active 2-mercaptothaiazoline groups per gram of silica and was able to adsorb mercury 2.34 mmol/g at pH 5.

2. *Original stepped template sol-gel method* (*Step*)

The *Step* method was proposed later for the modification of zeolite with organic functional groups. Nei *et al*. (2005) [19] synthesized and studied the property of 3-mercaptopropyl functionalized SBA-15 prepared by original stepped template sol-gel method. They reported that the surface area and pore volume of the obtained materials decreased by increasing the adding amount of 3-mercaptopropyltrimethoxysilane from 5 to 20 % mol ratio. Furthermore, surface area and pore volume decreased up to 76% at 20 % mol ratio.

3. *Grafting method* (*Graft*)

Grafting method has been widely used in the modification of inorganic materials, including zeolite. Antochshuk *et al*. (2003) [9] synthesized 1-benzoyl-3-propylthiourea functionalized MCM-41 by heterogeneous grafting method for mercury removal. This material was prepared via a two step modification by attachment of aminopropyl functional group and subsequent conversion into a thiourea ligand. It had a surface area of 380 m^2/g and mesopores diameter of 3.0 nm. The maximum Hg(II) ions adsorption capacity of this material was 5.0 mmol/g. The adsorbent regeneration was performed by using slightly acidified aqueous thiourea solution.

Sierra *et al*. (2006) [10] prepared MCM-41 and SBA-15 modified by 2-mercapto pyridine for mercury removal from wastewater. Two grafting methods were used; homogeneous method by grafting mercaptopyridine functional group on MCM-41 and SBA-15 and heterogeneous method by grafting the starting functional group first on MCM-41 and SBA-15 before adding the other functional groups step by step until mercaptopyridine was obtained. The modified materials were characterized and tested for Hg(II) ions adsorption. Mercury(II) ions adsorption capacity was 0.12 and 0.16 mmol/g for modified MCM-41 and SBA-15 prepared by homogeneous synthesis method and 0.09 and 0.08 mmol/g for modified MCM-41 and SBA-15 prepared by heterogeneous synthesis method, respectively. The same materials and methods were used in the modification with 2-mercaptothiazoline by Sierra *et al*. [11]. Mercury(II) ions adsorption capacity of MCM-41 and SBA-15 modified with 2-mercaptothiazoline by homogeneous synthesis method was 0.70 and 1.10 mmol/g and 0.25 and 0.12 mmol/g by heterogeneous synthesis method.

In most researches, one synthesis method was chosen to modify the zeolite materials. There is no finite conclusion on the most suitable synthesis method. The comparison of these three synthesis methods was demonstrated by Zhang *et al*. (2005) [16]. They prepared the modified MCM-41 using the conventional hydrothermal templated sol-gel method, the original stepped template sol-gel method and the grafting method. The functional groups for surface modification were phenyl, 3-aminopropyl, 3-chloropropyl and *N*-aminoethylaminopropyl. The results showed that modified MCM-41 obtained from the original stepped template sol-gel method was the best synthesis method for gas adsorption. This method could produce the materials that have high thermal stability and high attached amount of functional group on surface while it could reduce the synthesis time. Those materials were tested for carbon dioxide adsorption.

However there is no comparison of synthesis methods for preparation of adsorbents for adsorption of analytes from solutions. This thesis focused on the synthesis of functionalized MCM-41 as adsorbents for mercury removal from water. 3-mercaptopropyl was chosen as functional group to be modified on MCM-41 and it has never used to modify on MCM-41 before. The functional group for material modification should have donor atom that have high affinity toward mercury. Regarding the nature of donor atoms (i.e. sulfur, oxygen, and nitrogen), the order of soft Lewis base is S > N > O. In complexes between mercury(II) ion and sulfur donor atoms on the functional groups, mercury is referred to as soft acids and sulfer as soft bases in hard-soft acid-base principle [53].

In this study, 3-mercaptopropyl functionalized MCM-41 was prepared by three different methods; (i) conventional hydrothermal templated sol-gel method, (ii) original stepped templated sol-gel method and (iii) grafting method. The efficiency of the methods in ligand loading was compared. The most suitable method of synthesis was chosen in respect to high ligand loading efficiency and high adsorption capacity of the obtained materials for mercury ions.

CHAPTER III

EXPERIMENTALS

In this study, MCM-41 and 3-mercaptopropyl functionalized MCM-41 were prepared and used as adsorbents for the mercury removal. The experiment was divided into five steps.

1. Synthesis of MCM-41 and 3-mercaptopropyl functionalized MCM-41 (MP-MCM-41) by three methods.
2. Characterization of the obtained adsorbents.
3. Adsorption study
4. Reusability of the adsorbents.
5. Application to real wastewater samples from refinery process.

The detail of the experiments was explained in the following:

3.1 Chemicals and instruments

3.1.1 Chemicals

The reagents and solvents in all experiments were of analytical grade and summarized in Table 3.1.

Table 3.1 Chemicals and suppliers

Chemicals	Suppliers / Grade
Mercury standard solution, $Hg(NO_3)_2$ (1000 mg L^{-1})	Merck, Germany / for analysis
Hexadecyltrimethylammonium-bromide	Merck, Germany / for synthesis
Tetraethyl orthosilicate 98%	Merck, Germany / for analysis
(3-Mercaptopropyl)trimethoxysilane	Fluka Chemies A.G., Switzerland / for synthesis
Ammonia solution 25%	Merck, Germany / for analysis

Table 3.1 Chemical and suppliers (continued)

Chemicals	**Suppliers / Grade**
Calcium hydride	Fluka Chemies A.G., Switzerland / Assay ≥ 95% (gas-valumetric)
Toluene	CARLO ERBA, Italy / GR ACS
Ethanol	Merck, Germany / A.R.
Methanol	Merck, Germany / A.R.
Dichloromethane	Fisher Chemicals, England / A.R.
Acetone	Fisher Chemicals, England / A.R.
Hydrochloric acid 37%	Merck, Germany / for analysis
Sulfuric acid 95-97%	Merck, Germany / for analysis
Nitric acid 65%	Merck, Germany / for analysis
Sodium hydroxide	Merck, Germany / for analysis
Sodium chloride	Merck, Germany / for analysis
Sodium sulfate	Merck, Germany / for analysis
Sodium nitrate	Fluka Chemies A.G., Switzerland / purum p.a. > 99%
Tin (II) chloride dihydrate	CARLO ERBA, Italy / RPE-ACS
Potassium bromide	Merck, Germany / for IR spectroscopy
Potassium permanganate	Merck, Germany / for analysis
Potassium persulfate	Merck, Germany / for analysis
Hydroxylammonium chloride	Merck, Germany / for analysis
Triethoxyoctylsilane	Merck, Germany / for synthesis

****** Toluene was dried over calcium hydride under nitrogen atmosphere of moisture removal before used.

3.1.2 Instruments

All equipments, used in the adsorbents preparation were listed as follows in Table 3.2.

Table 3.2 Equipments for the adsorbents preparation

Equipments	Manufacture : Model
Stirrer / Hot plate	CORNING : PC-420 and PC-620
Oven	Memmert : UM 500
Digital balance	Mettler : AT 200
Desiccator	Aris : DC56LA
Centrifuge	Sanyo : Centaur 2
Vacuum pump	Buchi : V-700

The analytical instruments used for the characterization and the measurements were listed in Table 3.3.

Table 3.3 Analytical instruments

Equipments	Manufacture : Model	Purpose
X-ray diffractometer (XRD)	Rigaku : 1200+	crystallinity study
Fourier transforms infrared spectrometer (FTIR)	Nicolet : Impact 410	functional group and bonds identification of MCM-41
Thermogravimetric analyzer	Perkin-Elmer : Pyris 1 TGA	measurement of functional group amounts into adsorbent
Surface area analyzer	BEL Japan : BELSORP-mini	surface area, pore volume, pore diameter determination
pH meter	Hanna instruments : pH 211	pH measurement
Cold vapor atomic absorption spectrometer (CVAAS)	Perkin-Elmer : Analyst 300 coupled with FIAS400 system	mercury (II) ion determination

3.1.3 Preparation methods of chemicals and reagents

All solutions were prepared by using deionized (DI) water.

a) Mercury solutions

Mercury standard solution (1000 mg/L) in 2 M HNO_3 was used to prepare the mercury solution of required concentrations (40 – 420 mg/L) by dilution with DI water. The pH value of the mercury solutions were adjusted by sodium hydroxide and nitric acid solutions.

b) Sodium hydroxide solutions

Sodium hydroxide solutions (1, 5 and 10 %w/v) for pH adjustment were prepared daily by dissolving the appropriate amount of NaOH in DI water.

c) Nitric acid solutions

Nitric acid solutions (1, 5 and 10 %v/v) for pH adjustment were prepared daily by direct dilution from the concentrated solution (65%).

d) Hydrochloric acid solutions

Hydrochloric acid solutions (10 %v/v for template removal and 3 %v/v for acid carrier in mercury determination by CVAAS) were prepared daily by direct dilution of the concentrated solution (37%).

f) Solutions containing different salts

The solutions containing sodium salt of desired anion (NO_3^-, SO_4^{2-} and Cl^-) of 0.1 and 1.0 M, used for the studies of interfering ions effect were prepared by dissolving the appropriate amount of sodium nitrate, sodium sulfate and sodium chloride in DI water.

i) Potassium permanganate solutions

Potassium permanganate, mercury-free, solution (5% w/v) was prepared by dissolving 5 g of potassium permanganate in 100 mL DI water.

j) Potassium persulfate solutions

Potassium persulfate solution (5% w/v) was prepared by dissolving 5 g of potassium persulfate in 100 mL DI water.

h) Sodium chloride-hydroxylammonium chloride solution

Sodium chloride-hydroxylammonium chloride solution was prepared by dissolving sodium chloride (12 g) and hydroxylammonium chloride $(NH_2OH)HCl$ (12 g) in DI water and dilution to 100 mL. (Hydroxylamine sulfate may be used in place of hydroxylammonium chloride.)

e) Tin (II) chloride solutions

$SnCl_2$ (100 g) were dissolved in 200 mL of 37% (v/v) HCl. The mixture was stirred continuously until homogeneous solution was obtained. Then, the volume was adjusted to 1000 mL by DI water. The solution should be stirred continuously during use for good homogeneity.

g) Mercury working standard solutions

Mercury working standard solutions were prepared by successive dilutions of the stock mercury solution to obtain a working standard containing 0.05, 0.1, 0.15, 0.20, 0.25 and 0.30 mg/L Hg. The working standard solutions should be prepared freshly before use.

3.2 Synthesis of MCM-41 and 3-mercaptopropyl functionalized MCM-41 by three methods

1. Conventional hydrothermal templated sol-gel method (or *Con*): In this method, the organic functional molecules are added in the mixture of CTAB, NH_3 and TEOS at the beginning before the formation of the main structure of MCM-41.

2. Original stepped template sol-gel method (or *Step.*): In this method, after the hexagonal main structure were initially formed, the organic functional molecules are

added. Then the final product was obtained after letting the mixture to crystallize and react for certain period of time.

3. Grafting method (or *Graft*): In this method, the organic functional molecules are added to the solid MCM-41. It can be divided into two types, depending on the type of MCM-41 as follows;

- Grafting the organic molecules on bare MCM-41 prepared from *Con* method (or *Graft-con*)
- Grafting the organic molecules on bare MCM-41 prepared from *Step* method (or *Graft-step*)

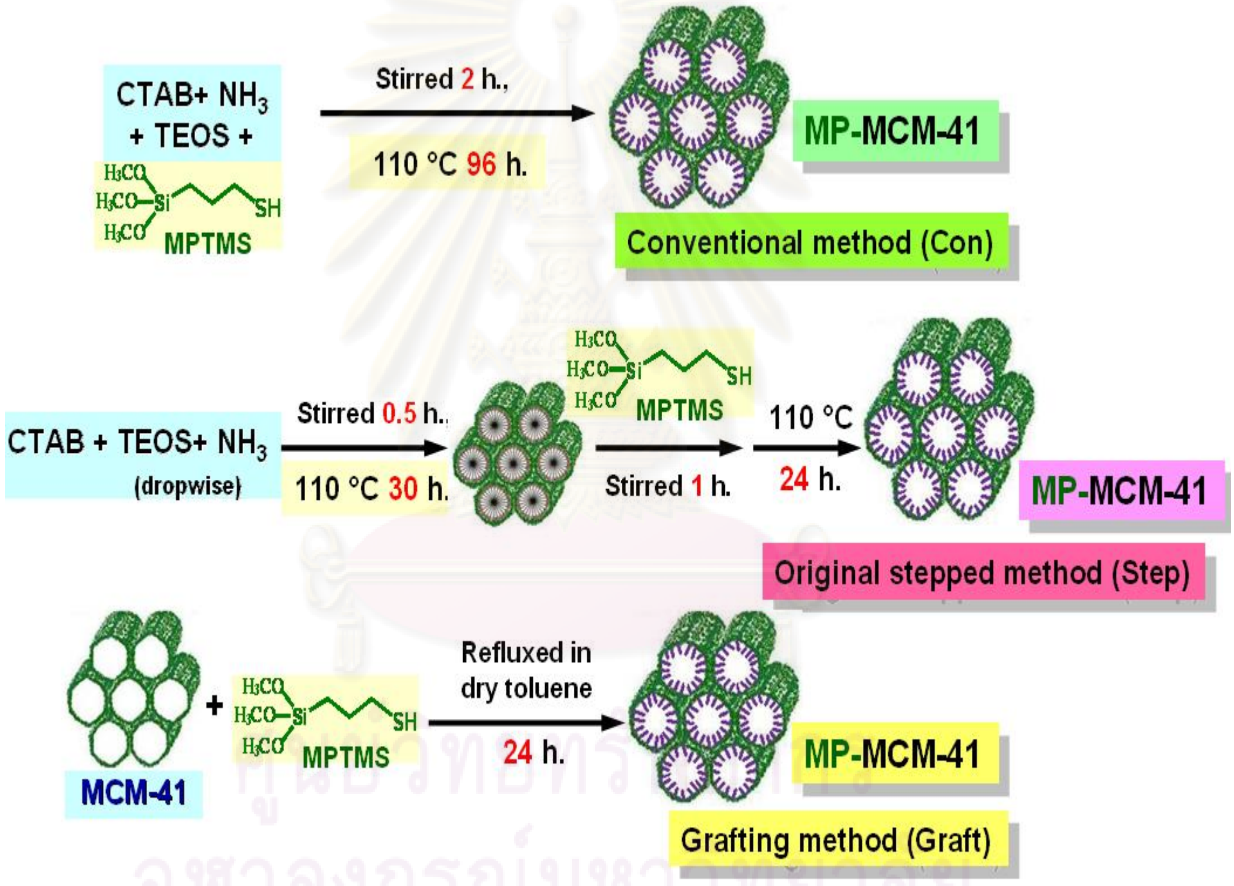
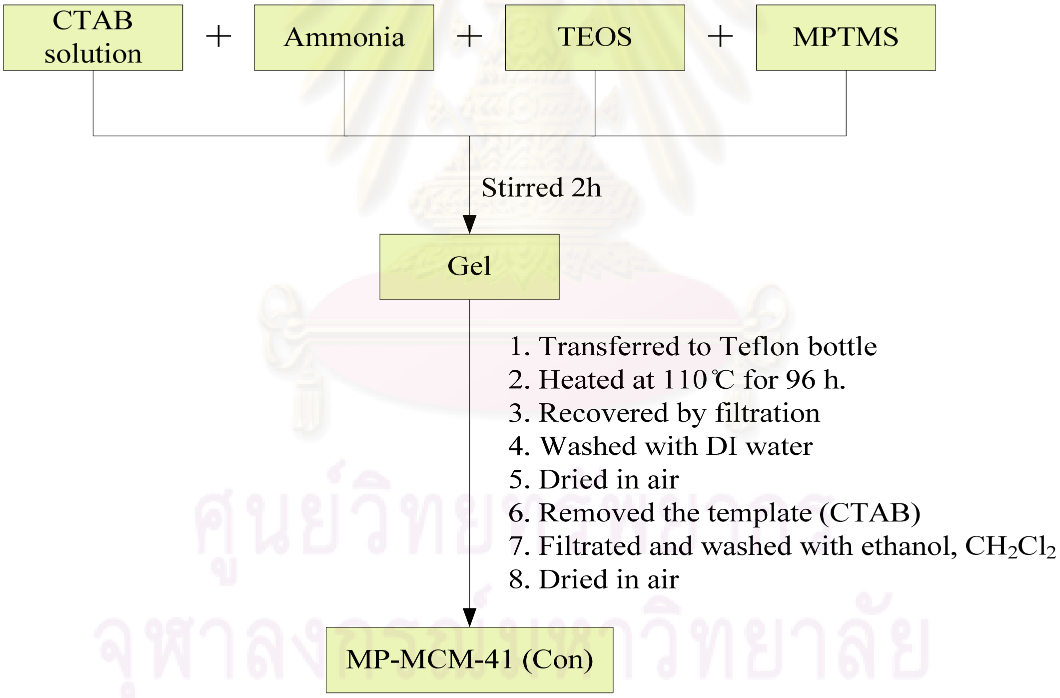


Figure 3.1 Methods of preparation of 3-mercaptopropyl functionalized MCM-41.

1. Conventional hydrothermal templated sol-gel method (Con)

A typical synthetic procedure was carried out as described [18]: ammonia (15.39 mL, 0.8 mol) and hexadecyltrimethyl ammonium bromide (CTAB) (2.19 g, 10 mmol) were dissolved in 102.6 mL deionized water under electromagnetic stirring until homogeneous. Then tetraethyl orthosilicate (TEOS) (9.98 mL, 90 mmol) and 3-mercaptopropyl trimethoxysilane (MPTMS) (0.94 mL, 10 mmol) were added into the solution. After 2 h of continuous stirring, a gel with a molar composition TEOS:MPTMS:CTAB:NH_4OH:H_2O of 0.9:0.1:0.12:8:114 was obtained. In this way, the mole ratio TEOS:MPTMS was 0.9:0.1 or the quantity of MPTMS added was 10 % mole of the total number of moles of TEOS and MPTMS. To add more MPTMS to the mixture, the amount of TEOS was reduced proportionally. The adding amount of MPTMS was varied in the range of 5 to 20 % mole. The obtained gel was transferred into a Teflon bottle and heated at 110 °C for 96 h. The solid product was recovered by filtration, washed with deionized water until the pH of filtrate was neutral, and finally dried. Thereafter, template (CTAB) was removed.

The procedure of conventional hydrothermal templated sol-gel method (or *Con*) was concluded in the scheme 3.1.



Scheme 3.1 The procedure of conventional hydrothermal templated sol-gel method.

MCM-41 and functionalized MCM-41 were prepared by using the original stepped template sol-gel technology [15, 16]. The normal MCM-41 was synthesized by using solely TEOS as silica source, while MPTMS was added together with TEOS to prepare MP-MCM-41.

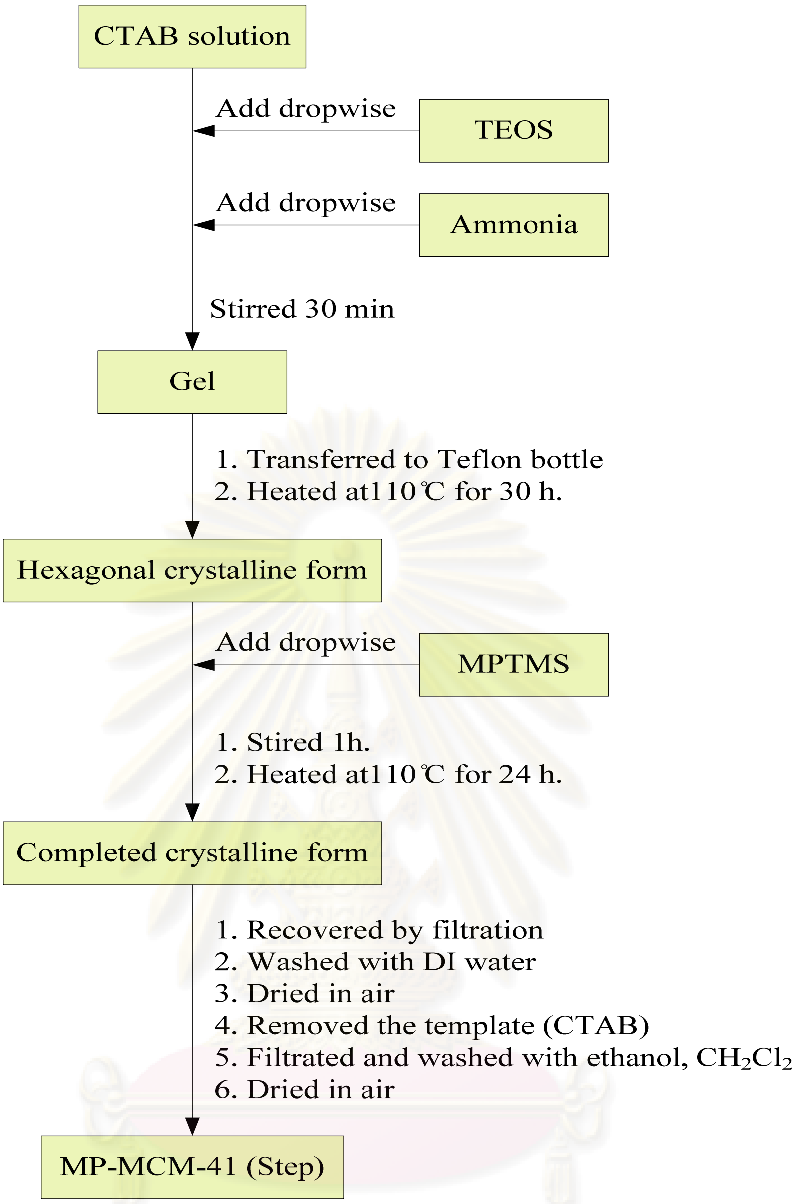
2. *Original stepped template sol-gel method (Step)*

In this method, the synthesis was performed as done in the conventional templated sol-gel method, but divided into two steps. The molar proportion of the starting materials used in conventional method was also applied. The adding amount of MPTMS was varied in the range of 5 to 10 %mol. Firstly, CTAB was dissolved in deionized water until homogeneous. Under continuous stirring, TEOS and then ammonia were added into the surfactant solution dropwise to produce a gel in 30 min. The stirring time of 30 min for gel formation was the most suitable condition to obtain the good order of crystalline structure of MCM-41 (the results showed in Fig.A1, appendix). The gel was transferred into a Teflon bottle and heated in oven at 110 °C about 30 h for hexagonal structure formed crystallization. After the typical MCM-41 hexagonal structure formed, the Teflon bottle containing the product was cooled and MPTMS was added. The solution mixture was electromagnetically stirred for 1 h and subsequently, the solution mixture was let to crystallize and to react at 110 °C for 24 h. The resulting solid was recovered by filtration, washed with deionized water until the pH of the filtrate was neutral, and finally dried. Next step, template (CTAB) was removed. The normal MCM-41 was also prepared by this way but using solely TEOS in every step.

Removal of template:

The templates or CTAB were removed from the solid product obtained from the conventional hydrothermal templated sol-gel method or the original stepped template sol-gel method by extraction using the mixture of methanol and hydrochloric acid under reflux [31, 37-38]. Final product was separated by centrifugal filtration, washed with ethanol, dichloromethane, finally dried, and kept in a desiccator.

The procedure of original stepped template sol-gel method (or *Step*) was concluded in the scheme 3.2.

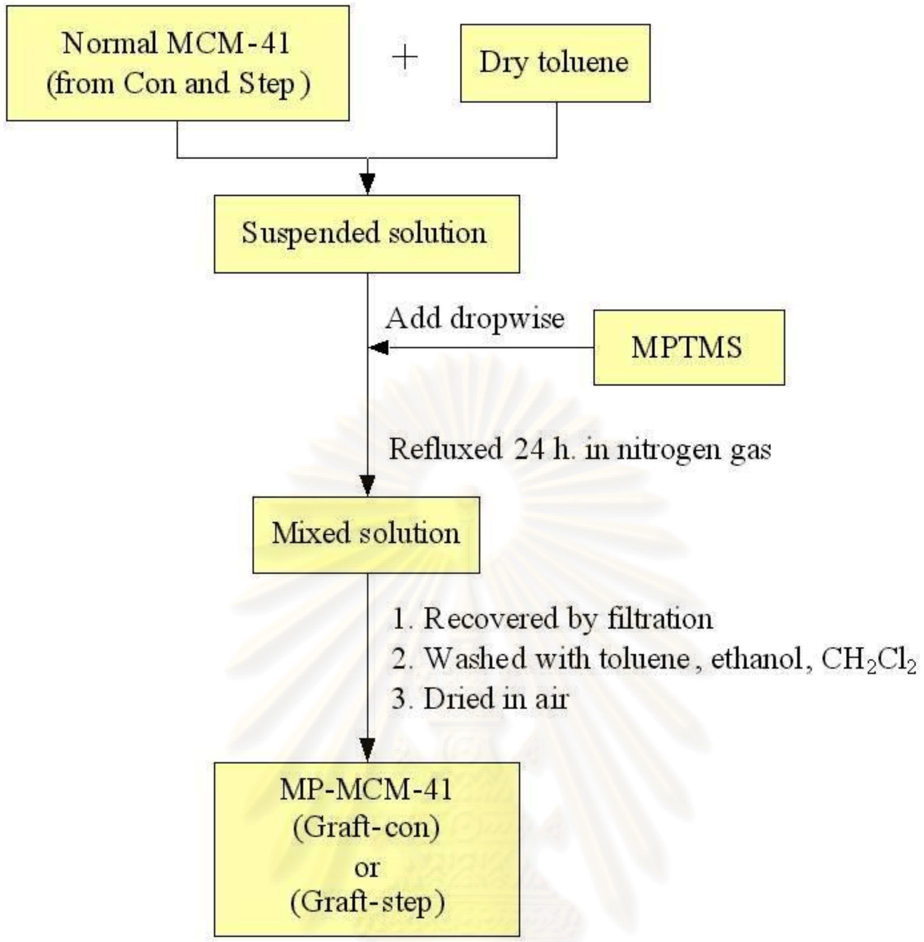


Scheme 3.2 The procedure of original stepped template sol-gel method.

3. Grafting method **(*Graft*)** [8-10, 16, 36, 70]

The normal MCM-41 synthesized by conventional hydrothermal templated sol-gel method (1) or original stepped template sol-gel method (2) was suspended in boiling dry toluene and then MPTMS was added dropwise at a quantitative ratio of 1.87 mL of MPTMS : 2.25 g of MCM-41 or 10 mmol MPTMS : 1.12 g MCM-41. The number of MPTMS moles was varied in the range of 4.46 to 17.86 mmol : 1 g MCM-41. The reflux lasted for 24 h under nitrogen atmosphere and the solid product was recovered by filtration, washed orderly with toluene, ethanol and dichloromethane, and finally dried in air.

The procedure of grafting method was concluded in the scheme 3.3.



Scheme 3.3 The procedure of grafting method.

The amount of MPTMS attached on adsorbent was measured by thermo gravimetric analysis (TGA) to compare the adding efficiency of the three synthesis methods. Then the relationship between the adding amount and the attached amount of each method was determined. To test the accuracy of the equations, the preparation of MP-MCM-41 containing equal amount attached was tempted. To test the validity of the equations obtained, other organic functional group was added instead of MPTMS. Triethoxyoctylsilane (TEOTS) was chosen as organic functional group and the TEOTS modified MCM-41 was prepared by (i) conventional hydrothermal templated sol-gel method, (ii) original stepped template sol-gel method and (iii) grafting method. The adding amount of TEOTS was calculated using the previously obtained equations in order to obtain the equal amount of TEOTS attached in the final products. Then the amount of TEOTS attached on the obtained TEOTS-MCM-41 was determined by TGA.

Finally, the best synthesis method was chosen to prepare MP-MCM-41 for mercury removal.

3.3 Characterization of the adsorbents

The characterization of all synthesized MCM-41 was performed by powder X-ray diffraction (XRD) technique. XRD patterns could identify the specific crystallization of MCM-41 structure. FT-IR spectrometry was used to confirm their functional groups existence. The surface area and pore size of the adsorbents were determined by nitrogen gas adsorption–desorption isotherms using a surface area analyzer. The amount of 3-mercaptopropyl functionalized on MCM-41 was determined by thermogravimetric analysis.

The instruments and techniques used to characterize the adsorbents were specified in the following.

3.3.1 X-ray diffraction (XRD)

The structure of synthesized mesoporous materials were identified by using a Rigaku D/MAX-220 Ultima+ X-ray diffractometer (XRD) equipped with Cu K_α radiation (40 kV 30 mA) and a monochromater at 2 theta angle between 1.5 to 8 degrees. The scattering slit, divergent slit and receiving slit were fixed at 0.5 degree, 0.5 degree, and 0.15 mm, respectively. X-ray diffraction patterns provide the information about the structure and crystallization of MCM-41 and 3-mercaptopropyl functionalized MCM-41.

3.3.2 Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared spectra were recorded on Nicolet FT-IR impact 410 spectrophotometer. The solid samples were prepared by pressing the sample with KBr. Infrared spectra were recorded between 400 cm^{-1} to 4,500 cm^{-1} in transmittance mode. The FT-IR technique was used to characterize functional groups of MCM-41 and 3-mercaptopropyl functionalized MCM-41.

3.3.3 Nitrogen adsorption (Brunauer-Emmett-Teller method (BET))

The determination of BET specific surface area, pore volume and pore diameter of the adsorbents were performed by using a BEL Japan, BELSORP-mini instrument. The sample weight was near 20 mg and weighed exactly after pretreatment at 400 ^{o}C for 3 h before each measurement. The principle of this method is the adsorption of a particular molecular species from a gas or liquid onto the surface. Based upon one adsorbed layer, the quantity of adsorbed material gave directly the total surface area of the sample.

3.3.4 Thermogravimetric analysis (TGA)

Thermogravimetric measurements were performed by using Pyris 1 Thermal gravimetric analyzer. The sample was heated from 20 ^{o}C to 800 ^{o}C with a heating rate of 20 ^{o}C/min under nitrogen atmosphere. The percentage weight loss at different temperatures was shown in a thermogram. The amount of 3-mercaptopropyl (mmol) per adsorbent (g) were calculated from TGA.

3.4 Adsorption study

Mercury (II) ion content in solutions was measured by a cold vapor atomic absorption spectrometer, which is located at department of geology, Chulalongkorn University.

The adsorption of mercury (II) ions in aqueous solutions by 3-mercaptopropyl functionalized MCM-41 was studied using batch method. The adsorbent (0.01 g) was added to 10 mL of solution containing mercury (II) ions. The initial concentration of mercury(II) ions ranged from 40 to 420 mg L^{-1}. The initial pH values of mercury(II) ion solutions were 6.0 ± 0.2. The contact time of 120 min was applied to assure the adsorption equilibrium. Thereafter, adsorbents were separated from metal ion solutions by centrifugation at 3000 rpm for 10 min. The pH of solutions at equilibrium was also measured. The adsorption experiments were performed in triplicate. The initial and residual concentration of mercury in solutions was determined by CVAAS. The conditions for measurement of mercury(II) ion concentration in aqueous solutions by CVAAS are shown in Table 3.4.

Table 3.4 CVAAS conditions for measurement of Hg concentration in aqueous solutions

Parameters	**Operating conditions**
Wavelength (nm)	253.7
Slit width	0.70
Lamp type	Hallow Cathode Lamp (HCL)
Lamp current (mA)	8
Argon flow-rate (min^{-1})	100
Working range ($mg\ L^{-1}$)	0.05-0.3

** The detection limit was 0.03 μg/mL, calculated from:

$$\text{Signal}_{\text{LOD}} = \text{Signal}_{\text{blank}} + 3\ (\text{S.D. of Signal blank})$$

where LOD is the Limit of detection, Signal $_{\text{blank}}$ is the average signal of blank (n=10), S.D. is the standard deviation of blank signal (n=10).

To generate cold vapor of Hg^0, hydrochloric acid carrier solution and tin (II) chloride dihydrate solution as the reducing agent were used. The vapor was swept through a long path quartz cell by argon carrier gas and the absorbance at 253.7 nm was measured.

3.4.1 Evaluation of the adsorption capacity of the adsorbents obtained from different preparation methods

The mercury (II) ions adsorption efficiency of MCM-41 before and after surface modification were determined using above mentioned adsorption procedure. The initial concentration of mercury(II) ions solution was 210 mg/L. The most appropriate method of synthesis should give the adsorbents that have high adsorption capacities. Therefore, the adsorption capacity of MP-MCM-41 obtained from three synthesis methods using different adding amount of 3-mercaptopropyl trimethoxysilane was evaluated. Then, the adsorption capacity of the adsorbents prepared by the three methods to have the same 3-mercaptopropyl content was compared.

Then, the adsorbent that has the best performance was used in adsorption study. The influence of the factors affecting the mercury(II) ion adsorption was investigated using batch system. The parameters studied are listed as followed,

- pH of solution	1-8
- contact time	2-150 min.
- Effect of foreign ion	NO_3^-, SO_4^{2-}, Cl^-
- Adsorption Isotherms	Langmuir, Freundlich isotherms

3.4.2 Effect of pH

The effect of the solution pH on the mercury(II) ions adsorption was investigated in the range of pH 1.0 – 8.0 and pH more than 8.0 causes precipitation of metal ions. The adjustment of pH was made with sodium hydroxide solutions (1, 5 and 10 %w/v) and nitric acid solutions (1, 5 and 10 %v/v). The contact time was 120 min. The initial concentration of mercury(II) ions solution was 210 mg/L. The amount of MP-MCM-41 was 0.01 g for 10 mL of mercury(II) ions solution in each testing sample.

3.4.3 Effect of contact time

The effect of contact time on the mercury (II) ions adsorption was investigated by varying time in the range of 2 – 150 min. The solution pH was 6.0 ± 0.2. The initial concentration of mercury (II) ions and the amount of adsorbent were the same as that mentioned in 3.4.2.

3.4.4 Effect of foreign ions

The effect of foreign ions were studied by adding the sodium salt of different anions (NO_3^-, SO_4^{2-} and Cl^-) in the concentration of 0.1 or 1.0 M in the mercury (II) ions solution. The solution pH was 6.0 ± 0.2. The stirring time was 120 min. The initial concentration of mercury (II) ions and the amounts of adsorbent were the same as that mentioned in 3.4.2.

3.4.5 Adsorption isotherms

The initial concentration of mercury (II) ions of 40 – 420 mg/L in 10 mL solution was used for adsorption isotherm study. The initial pH was 6.0 ± 0.2 and the temperature was controlled at 25.0 ± 0.5 ^{o}C. The stirring time was 120 min to assure the adsorption equilibrium. The amount of adsorbent was 0.01 g. MP-MCM-41 used in this study was obtained from the most suitable synthesis method with suitable amount of MPTMS adding.

Two models of adsorption isotherm were adopted; Langmuir isotherm and Freundlich isotherm. The remaining mercury concentrations at equilibrium and mercury adsorption capacities were used to plot as suggested in Langmuir and Freundlich relationships. The best fit model would describe the adsorption behavior of mercury (II) ions on the MP-MCM-41.

3.5 Reusability of 3-mercaptopropyl functionalized MCM-41

The reusability of the best adsorbent obtained from the best synthesis method was studied. The experiments were performed as the following:

1. The volume of 10 mL of mercury solutions (210 mg/L) was added to test tubes. This reusability experiments were performed in triplicate.

2. In each tube, the amount of 0.01 g of the adsorbent was added to the solutuion and the mixture was stirred for 2 h.

3. Sample and the adsorbent were separated by centrifugation at 3000 rpm for 10 min then mercury content in sample was determined by CVAAS.

4. The used adsorbent from the first adsorption experiment was regenerated by using 10 mL of 4% thiourea in 0.1 M HCl. The mixture was stirred for 2 h in batch method. The solid was separated and used in the next adsorption experiments.

5. The amount of mercury in regeneration solution was measured to determine the desorption efficiency in first cycle.

6. The adsorption/desorption cycles were performed consecutively until the adsorption percentage was less than 50 percent.

3.6 Application to real wastewater sample from refinery process

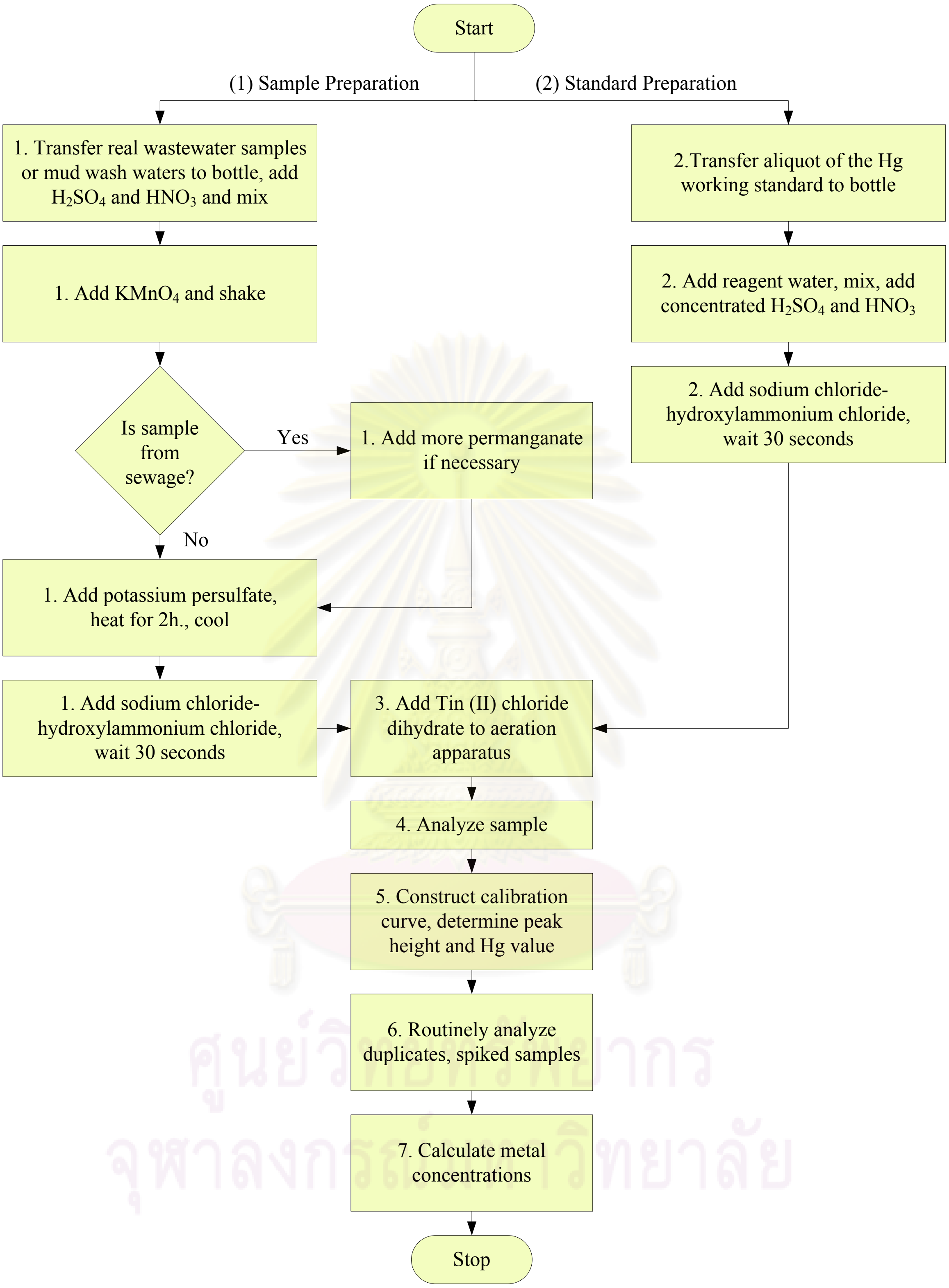
The real wastewater samples and mud wash water employed in this study were collected from crude distillation units of refinery at Chonburi and Rayong province, Thailand. The selected adsorbent was applied to remove mercury from the wastewater. Before application in adsorption experiments, the wastewater samples and mud wash water were filtered and the pH of the samples was measured. The mercury concentration in samples was determined by CVAAS [7]. Sample digestion and oxidization was performed to reduce analytical interferences and to ensure that the mercury in the sample was converted to the mercuric ion form and dissolved in aqueous media. Wastewater samples and mud wash water were digested with sulfuric acid, nitric acid, permanganate solution, and persulfate solution, respectively. After the reaction was complete, the residual permanganate was reduced with hydroxylamine. Thereafter, the obtained transparence aqueous solution was used for determination of initial mercury(II) ions in real wastewater samples and mud wash water.

The digestion method used in this study was adapted from ASTM D3223-02 [87] which is a standard method for determination of total mercury in water and from method 7470A of United States Environmental Protection Agency (USEPA) [88] which is a manual for determination of mercury in liquid waste (ground waters, certain solid and sludge-type wastes). At last, the digestion method was also adapted from ASTM F885-88 [89] which is a standard test method for analysis of metals in refuse-derived fuel by atomic absorption spectroscopy. The digestion procedure is described in scheme 3.4 and performed as the following.

Digestion procedure

1. Real wastewater sample or mud wash water (100 mL) was transferred into a 250-mL round-bottomed flask.
2. The concentrated sulfuric acid (H_2SO_4) (5 mL) was added, followed by the concentrated nitric acid (HNO_3) (2.5 mL). After each addition, mixing of the mixed solution was performed by shaking.
3. Potassium permanganate solution ($KMnO_4$) (15 mL) was added to sample flask. The sample flask was vigorously shaken and another portion of potassium permanganate solution was added if necessary, until the purple color persisted for at least 15 min.
4. Potassium persulfate solution ($K_2S_2O_8$) (8 mL) was added to sample flask. The sample flask was heated for 2 h in a water bath maintained at 95 ^{o}C.
5. Thereafter, the sample flask was cooled and then sodium chloride-hydroxylammonium chloride solution (6 mL) was added to reduce the excess of permanganate.
6. After a delay of at least 30 sec, the transparent aqueous solution was obtained and used for determination of initial mercury(II) ions of real wastewater and mud wash water samples by CVAAS.

For adsorption study, the water samples were filtered and used in the adsorption without any sample preparation. The sample of 10 mL was extracted by 0.01 g of the selected adsorbent for 2 h. After the adsorption equilibrium was reached, the adsorbent were separated from sample by centrifugation at 3000 rpm for 10 min and then mercury content in sample was determined by CVAAS. The adsorption experiments were performed in triplicate.



Scheme 3.4 Digestion procedure for determination of total mercury in real wastewater (adapted from [88]).

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Synthesis of 3-mercaptopropyl modified MCM-41 (MP-MCM-41)

MP-MCM-41 adsorbents were synthesized by three different methods;

1. Conventional hydrothermal templated sol-gel method (or *Con*)
2. Original stepped template sol-gel method (or *Step*)
3. Grafting method which is divided into two types, depending on the type of MCM-41 as followed;
    - Grafting the organic molecules on bare MCM-41 prepared from *Con* method (or *Graft-con*)
    - Grafting the organic molecules on bare MCM-41 prepared from *Step* method (or *Graft-step*)

4.1.1 Comparison of methods of synthesis

Procedure and preparation time of conventional hydrothermal templated sol-gel method (Method 1, *Con*) and original stepped template sol-gel method (Method 2, *Step*) are compared in Table 4.1.

Table 4.1 Comparison of *Con* and *Step* methods of preparation of MP-MCM-41

Condition	**Method 1 (*Con*)**	**Method 2 (*Step*)**
Gel preparation	Mix all substrate	Add TEOS and then NH_3 dropwised to the solution of CTAB
mixing time for gel formation	2 h	0.5 h
Crystallization time	96 h	30 h
Adding of 3-mercaptopropyltrimethoxysilane (MPTMS)	At the beginning	After crystallization formation and mixing for 1 h
Heating time after adding MPTMS	-	24 h
Total time for synthesis	98 h	55.5 h

Gel from *Step* method forms rapidly in 5 – 10 min after adding ammonia solution and it appears in murky white color. On the other hand, gel from *Con* method forms after stirring for 1 h. Crystallization period and the step of adding MPTMS in each synthesis methods are shown in Fig.4.1.

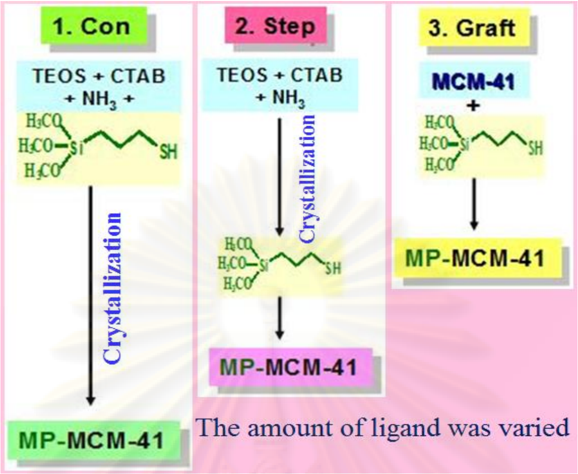


Figure 4.1 The step of adding MPTMS and crystallization period for each synthesis methods.

In conclusion, synthesis of MP-MCM-41 by *Con* method is easier than the other methods but the crystallization time is long. The synthesis by *Step* method requires short crystallization time but the procedure for preparation has many steps. The synthesis by *Graft* method requires long time due to many steps of synthesis but it is expected to have good dispersion of functional group on surface.

In the synthesis of MP-MCM-41, the adding amount of MPTMS was varied as 5, 10, 15 and 20 % mol for *Con* method and *Step* method. In the case of *Graft* method, the number of MPTMS moles was varied as 4.46, 8.93, 13.39 and 17.86 mmol/ g MCM-41 (or 5 – 20 mmol **:** 1.12 g MCM-41).

The suitable synthesis method of MP-MCM-41 adsorbents should have the following features;

- It should have good adding efficiency of functional group to yield the adsorbents that have relatively high ligand loading.

- The obtained product from that method maintains the good order of crystalline structure of MCM-41. This feature is required due to the good benefit of high surface area in adsorption and the fast adsorption kinetics.

- The obtained product from that method should have high adsorption capacity with reasonable adding amount of ligand.

4.12 Characterization of MCM-41 and MP-MCM-41 obtained by variation of the adding amount of MPTMS

The MP-MCM-41 prepared by *Con* and *Step* method will be called MP-MCM-41 (*Con*) and MP-MCM-41 (*Step*), respectively. The normal MCM-41 synthesized by *Con* and *Step* method are named MCM-41 (*Con*) and MCM-41 (*Step*) and when the normal MCM-41 are used in the grafting method, the product will be called MP-MCM-41 (*Graft-con*) and MP-MCM-41 (*Graft-step*), respectively. It should be noted that the normal MCM-41 prepared by *Step* method was synthesized by adding TEOS in the 2nd step instead of MPTMS.

Table 4.2 The adding amount of MPTMS and TEOS for synthesis by *Con* and *Step* method

Synthesis method	**Adsorbents**	**Amount of MPTMS**	**Amount of TEOS**
Con method	MCM-41 (*Con*)	0	100 % mol
	MP-MCM-41 (*Con*) 5 %	5 % mol	95 % mol
	MP-MCM-41 (*Con*) 10 %	10 % mol	90 % mol
	MP-MCM-41 (*Con*) 15 %	15 % mol	85 % mol
	MP-MCM-41 (*Con*) 20 %	20 % mol	80 % mol
Step method	MCM-41 (*Step*) 5 %	0	95 % mol (1st step) 5 % mol (2nd step)
	MCM-41 (*Step*) 10 %	0	90 % mol (1st step) 10 % mol (2nd step)
	MCM-41 (*Step*) 15 %	0	85 % mol (1st step) 15 % mol (2nd step)
	MCM-41 (*Step*) 20 %	0	80 % mol (1st step) 20 % mol (2nd step)

Table 4.2 The adding amount of MPTMS and TEOS for synthesis by *Con* and *Step* method (continued)

Synthesis method	**Adsorbents**	**Amount of MPTMS**	**Amount of TEOS**
Step method	MP-MCM-41 (*Step*) 5 %	5 % mol (2nd step)	95 % mol (1st step)
	MP-MCM-41 (*Step*) 10 %	10 % mol (2nd step)	90 % mol (1st step)
	MP-MCM-41 (*Step*) 15 %	15 % mol (2nd step)	85 % mol (1st step)
	MP-MCM-41 (*Step*) 20 %	20 % mol (2nd step)	80 % mol (1st step)

Table 4.3 The adding amount of MPTMS and the starting material for synthesis by *Graft* method

Synthesis method	**Adsorbents**	**Amount of MPTMS***	**Starting material**
Graft method	MP-MCM-41 (*Graft-con*) 4.46 mmol/g	4.46 mmol/g	MCM-41 (*Con*)
	MP-MCM-41 (*Graft-con*) 8.93 mmol/g	8.93 mmol/g	MCM-41 (*Con*)
	MP-MCM-41 (*Graft-con*) 13.39 mmol/g	13.39 mmol/1g	MCM-41 (*Con*)
	MP-MCM-41 (*Graft-con*) 17.86 mmol/g	17.86 mmol/1g	MCM-41 (*Con*)
	MP-MCM-41 (*Graft-step*) 4.46 mmol/g	4.46 mmol/1g	MCM-41 (*Step*) 5 %
	MP-MCM-41 (*Graft-step*) 8.93 mmol/g	8.93 mmol/1g	MCM-41 (*Step*) 10 %
	MP-MCM-41 (*Graft-step*) 13.39 mmol/g	13.39 mmol/1g	MCM-41 (*Step*) 15 %
	MP-MCM-41 (*Graft-step*) 17.86 mmol/g	17.86 mmol/1g	MCM-41 (*Step*) 20 %

* mmol MPTMS used per one gram of MCM-41

4.1.2.1 X-ray diffraction technique

X-ray diffraction technique was used to characterize the structure of unmodified and modified MCM-41. All obtained adsorbents show highly ordered mesoporous MCM-41 specific structure (Fig. 4.2- 4.3). The XRD patterns of MCM-41 and MP-MCM-41 displayed a well-resolved pattern at low 2θ with a very sharp diffraction peak corresponding to miller indices (100) at 2.12° and three additional high order peaks (110), (200), and (210) with lower intensities at 3.66°, 4.24° and 5.58°, respectively. The results are in agreement with the previous researches [16-18, 31, 38]. The *d*-spacing values for the XRD peaks were 41.64, 24.02, 21.78 and 15.80 Å, respectively. The XRD patterns of MCM-41 (*Con*) and MCM-41 (*Step*) are shown in Fig. 4.2. The normal MCM-41 (*Step*) shows slightly lower intensity and broader corresponding peaks, compared to MCM-41 (*Con*). This is probably because the addition of TEOS in the second step distorts the regular liquid crystalline array of the template and lowers the order of crystalline structure of MCM-41. Then, the structure of product from *Step* method is slightly disordered.

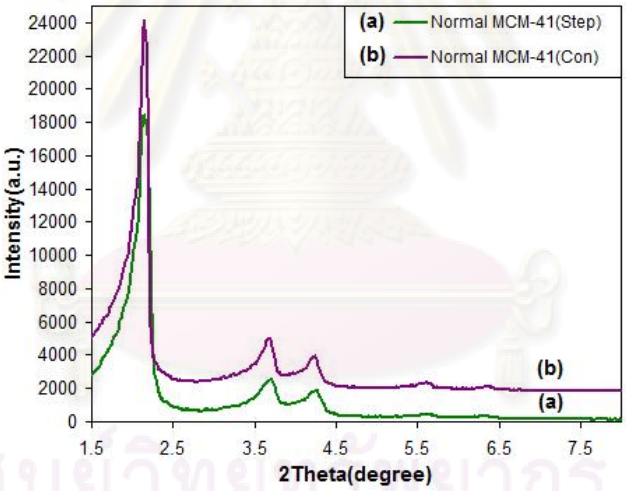


Figure 4.2 XRD patterns of (a) normal MCM-41 (*Con*) and (b) MCM-41 (*Step*).

When modified with 3-mercaptopropyl, a considerable decrease in the XRD peaks intensity was observed as shown in Fig. 4.3. A decrease in peak intensity may indicate that the functionalization occurred inside the mesopore channels. The results are in agreement with the previous researches [10, 11, 16, 70]. Nevertheless, the typical hexagonal structure was preserved in the products after modification.

Comparing different adding amount of 3-mercaptopropyltrimethoxysilane, the XRD peaks intensity of MP-MCM-41(*Con*) and MP-MCM-41(*Step*) decreased in increasing of the adding amount of functional group [19]. It indicates that the amount of 3-mercaptopropyltrimethoxysilane affected the order of MCM-41 hexagonal structure.

The XRD peak intensity of MP-MCM-41 (*Graft*) slightly decreased in particular the miller indices (100), compared to normal MCM-41. The peaks intensity of MP-MCM-41(*Graft*) decreased when the adding amount of 3-mercaptopropyltrimethoxysilane was increased. This is probably due to the insertion of functional group mainly inside the mesopore channels. The decrease in intensity at miller indices (100) was less obvious in XRD patterns of MP-MCM-41 (*Graft*), compared to those of MP-MCM-41(*Con*) and MP-MCM-41(*Step*). It can be explained that MP-MCM-41(*Graft*) was prepared from the staring material which was highly ordered.

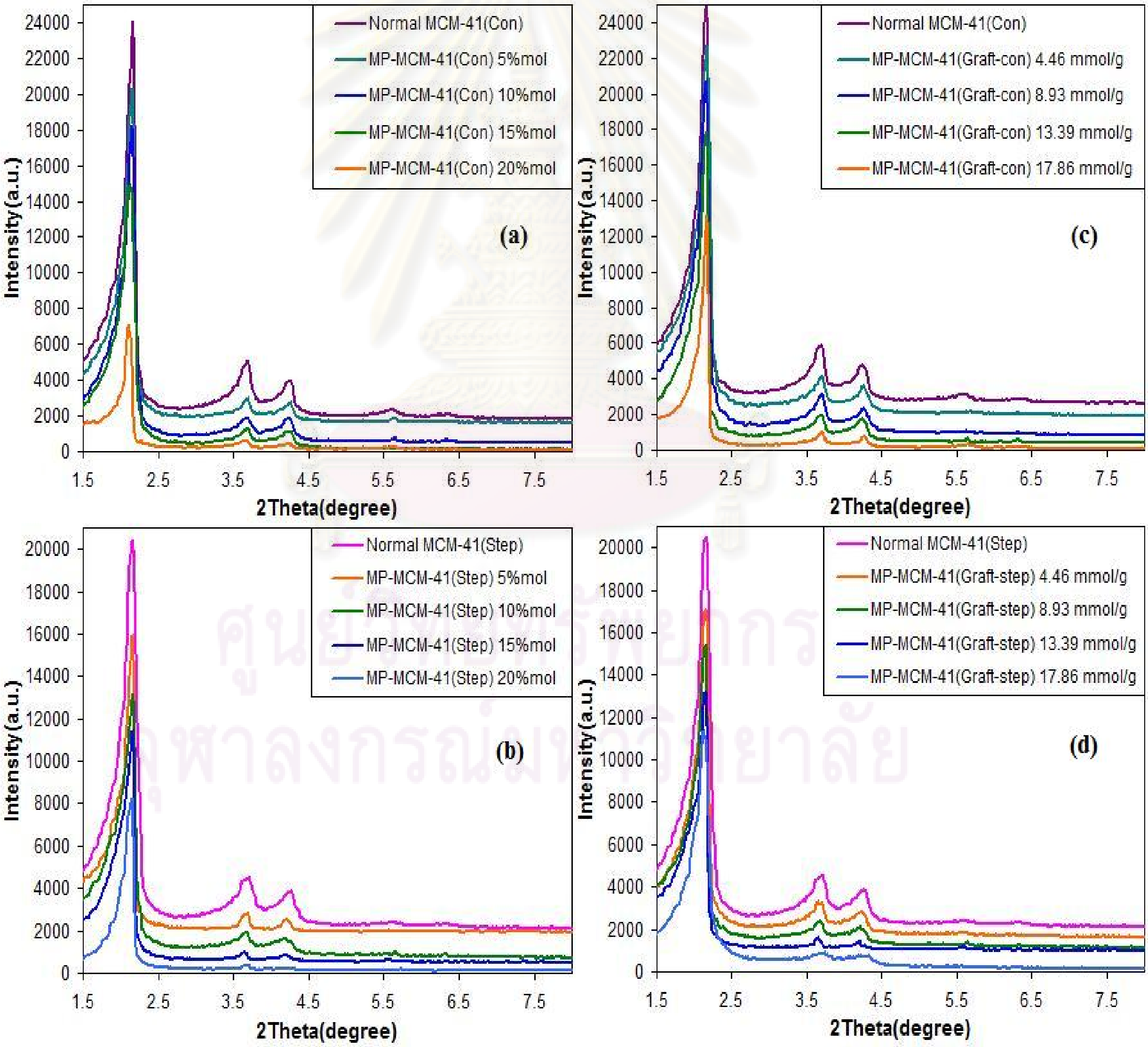


Figure 4.3 XRD patterns of MCM-41 and MP-MCM-41 from (a) *Con* method, (b) *Step* method, (c) *Graft-con* method and *Graf-step* method.

When the high adding amount of 3-mercaptopropyl group on adsorbent was used such as 20 % mol MPTMS in *Con* and *Step* method, and 17.86 mmol/1g in *Graft* method, the order of crystalline structure of MCM-41 was altered significantly and the obtained adsorbents seem not to be suitable for using as adsorbent.

4.1.2.2 Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FT-IR) was used in this research to correctly confirm the presence of specific organic functional groups as well as the 3-mercaptopropyl group on adsorbents. The assignments for the FT-IR bands of unmodified MCM-41 and the new bands appeared after functionalization with 3-mercaptopropyltrimethoxysilane are listed in Table 4.4.

Table 4.4 FT-IR vibration band position and their assignments for MCM-41 and MP-MCM-41 [10-11, 16, 68-70]

Adsorbents	Absorption frequency (cm^{-1})	Remarks and assignments
Normal MCM-41	3420 – 3200	O-H bond stretching of the surface silanol groups and/or the remaining adsorbed water molecules
	1630	deformational vibrations of adsorbed water molecules of MCM-41
	1230 and 1070	asymmetric stretching vibrations of Si-O-Si bridges
	954 and 800	symmetric stretching vibrations of Si-O bridges
MP-MCM-41[a]	2925	asymmetric stretching vibrations of CH_2
	2859	symmetric stretching vibrations of CH_2
	2571	stretching of S-H
	690	CH_2 rocking vibrations of Si–CH_2R

[a] New band appeared after functionalization with MPTMS

The FT-IR spectra of MCM-41, prepared by *Con* method and *Step* method are shown in Fig. 4.4-4.5. The signal of O-H bond stretching bands of the surface silanol groups were observed in MCM-41(*Con*) and MCM-41(*Step*). The intensity of O-H bond stretching band of MCM-41(*Step*) increased when increased the adding amount of TEOS (Fig. 4.5).

The FT-IR spectra of MP-MCM-41, prepared by *Con*, *Step* and *Graft* method with different adding amount of 3-mercaptopropyltrimethoxysilane are shown in Fig. 4.6-4.9. The signal of O-H bond stretching bands corresponding to silanol groups were observed in all adsorbents and the band intensity decreased when the MCM-41 was functionalized with MPTMS (Fig. 4.6-4.9). It indicates that the silanol groups on MCM-41 were modified with the functional group. The new bands appeared at 2925 and 2859 cm^{-1} in the spectra of MP-MCM-41 correspond to the aliphatic C-H stretching vibration. The intensity of this band increased sharply when increased the adding amount of MPTMS, indicating the increasing amount of MPTMS attached on the products. The CH_2 rocking vibration of Si–CH_2R was present at 690 cm^{-1} in the spectra of MP-MCM-41. A very weak S-H stretching peak was also observed at 2571 cm^{-1} for MCM-41 containing 3–mercaptopropyl groups [19, 69].

By the results in Fig. 4.8 and 4.9, the bands at 2925 and 2859 cm^{-1} of C-H stretching vibration and band at 2571 cm^{-1} of S-H stretching of MP-MCM-41(*Graft*) were clearly seen, unlike in MP-MCM-41(*Con*) and MP-MCM-41(*Step*). The FT-IR results indicate that the amount of functional groups attached on the surface of MP-MCM-41(*Graft*) was higher than on surface of MP-MCM-41(*Con*) and MP-MCM-41(*Step*).

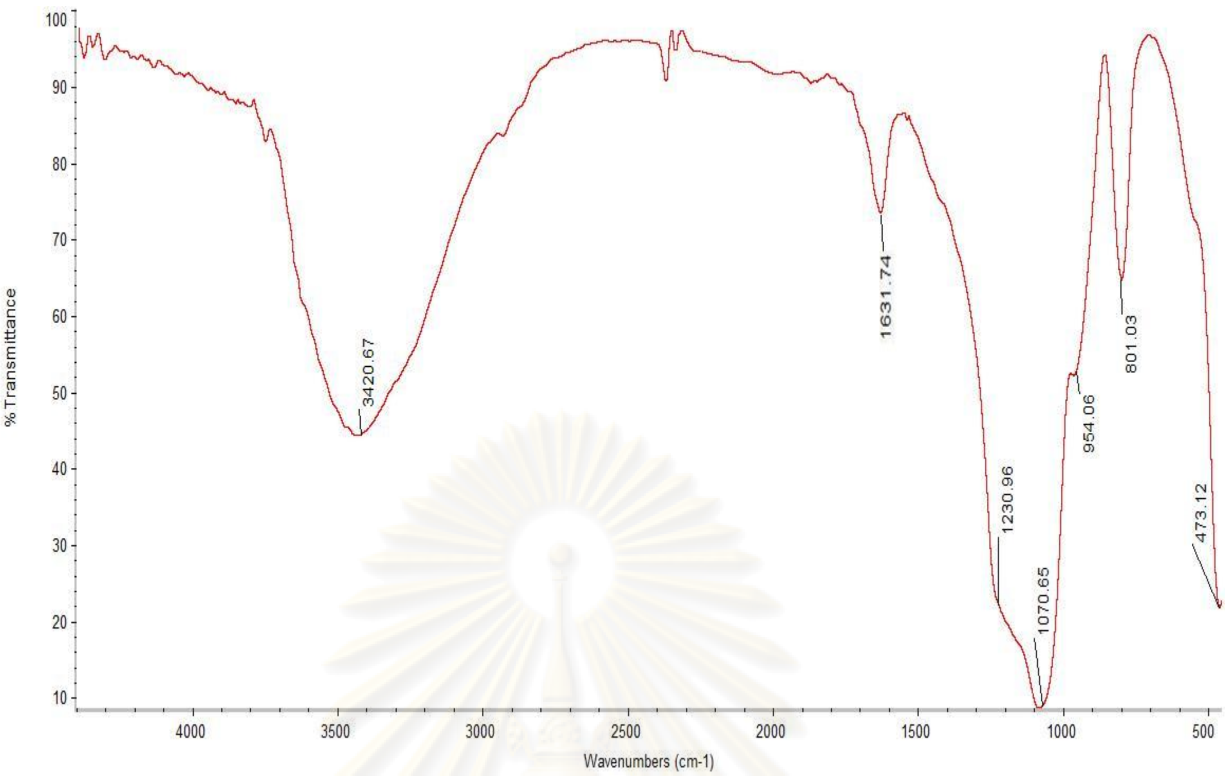


Figure 4.4 FT-IR spectrum of normal MCM-41 (*Con*).

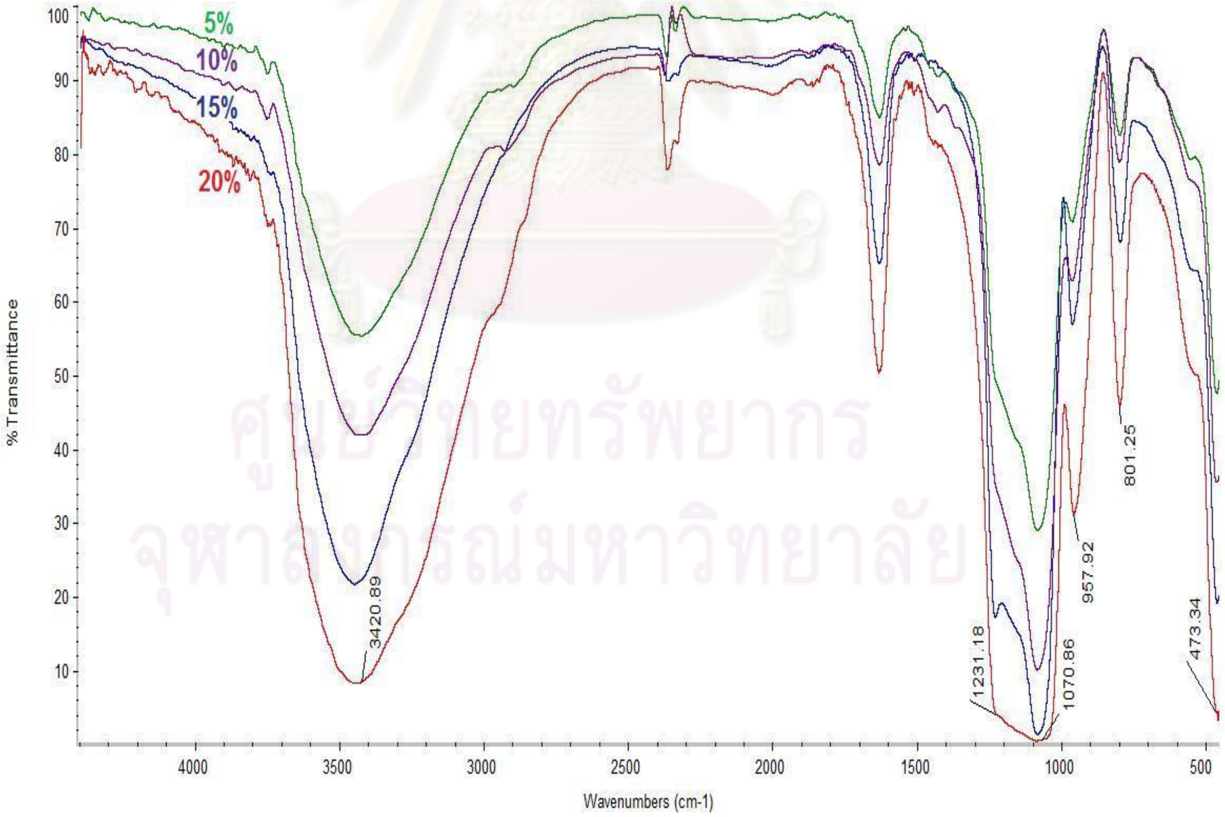


Figure 4.5 FT-IR spectra of normal MCM-41 (*Step*) prepared by different amount of TEOS added in the 2nd step.

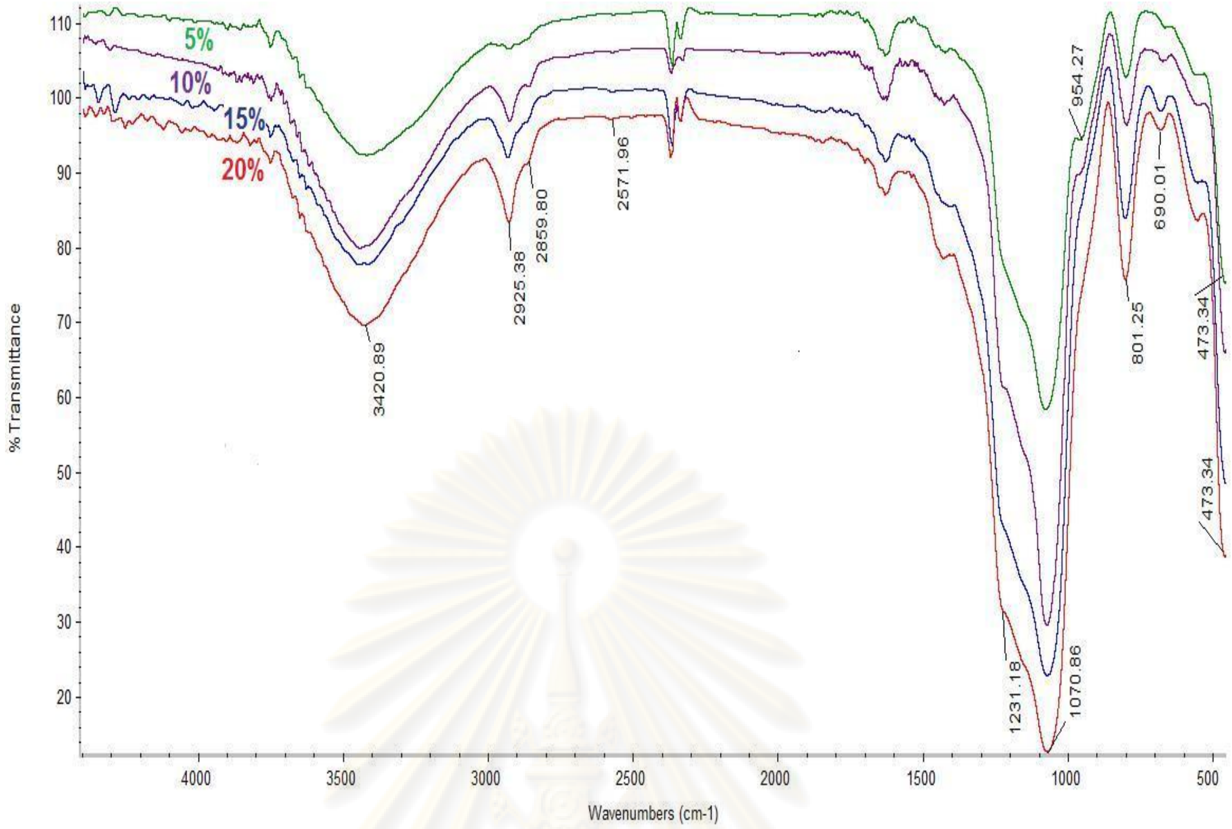


Figure 4.6 FT-IR spectra of **MP-MCM-41** (*Con*) with different amount of MPTMS added.

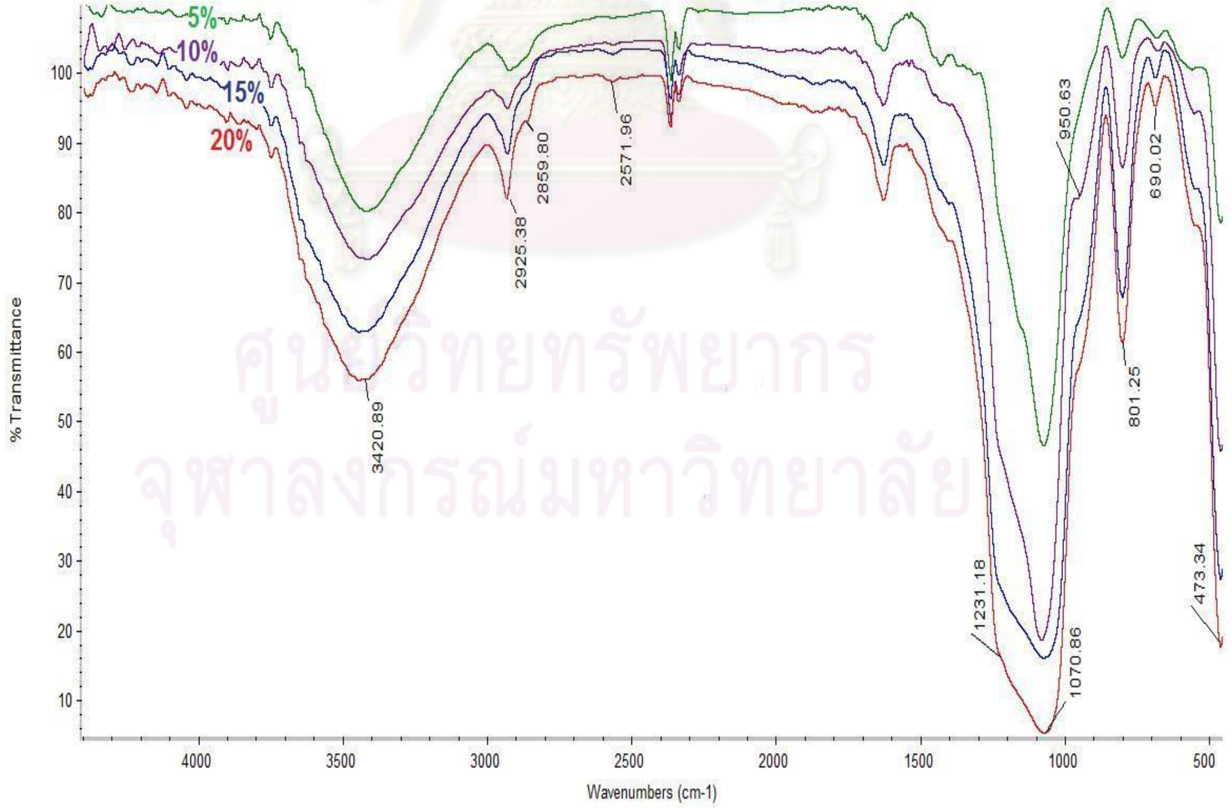


Figure 4.7 FT-IR spectra of **MP-MCM-41** (*Step*) with different amount of MPTMS added.

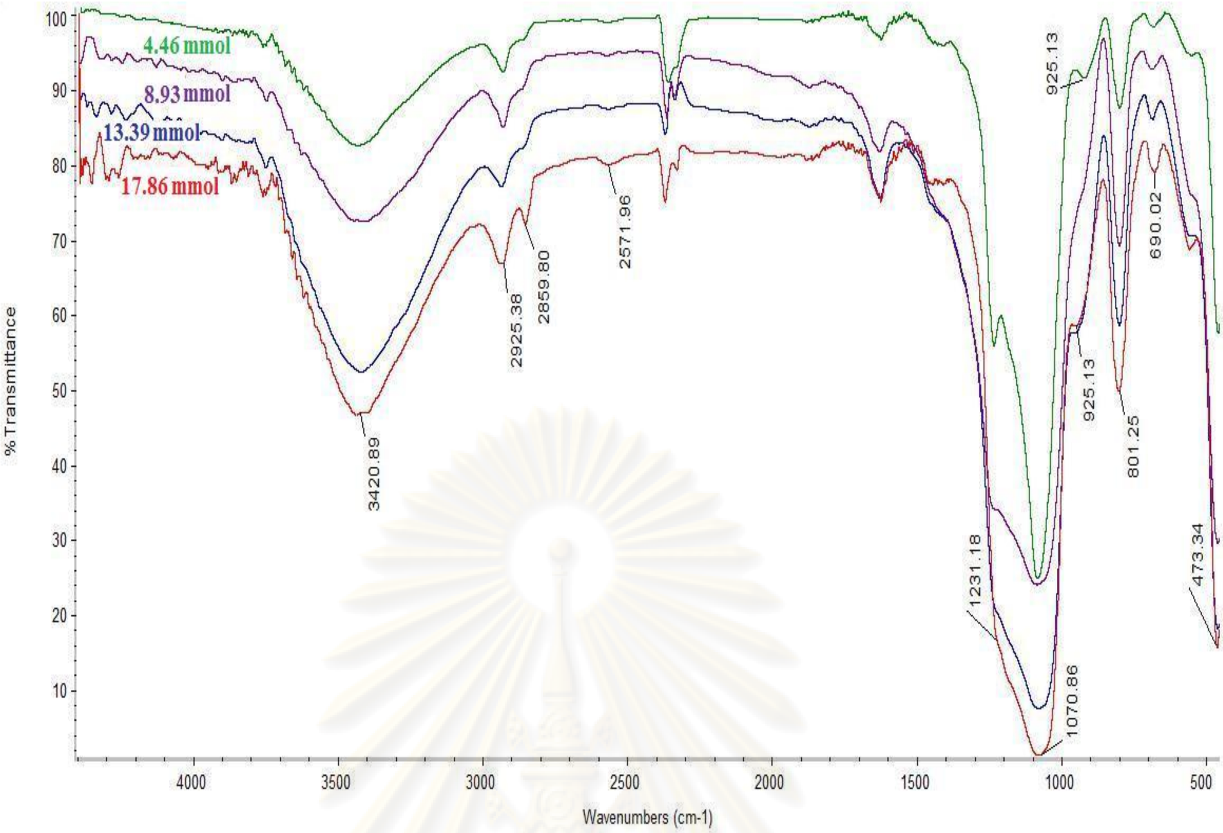


Figure 4.8 FT-IR spectra of **MP-MCM-41** (*Graft-con*) with different amount of MPTMS added.

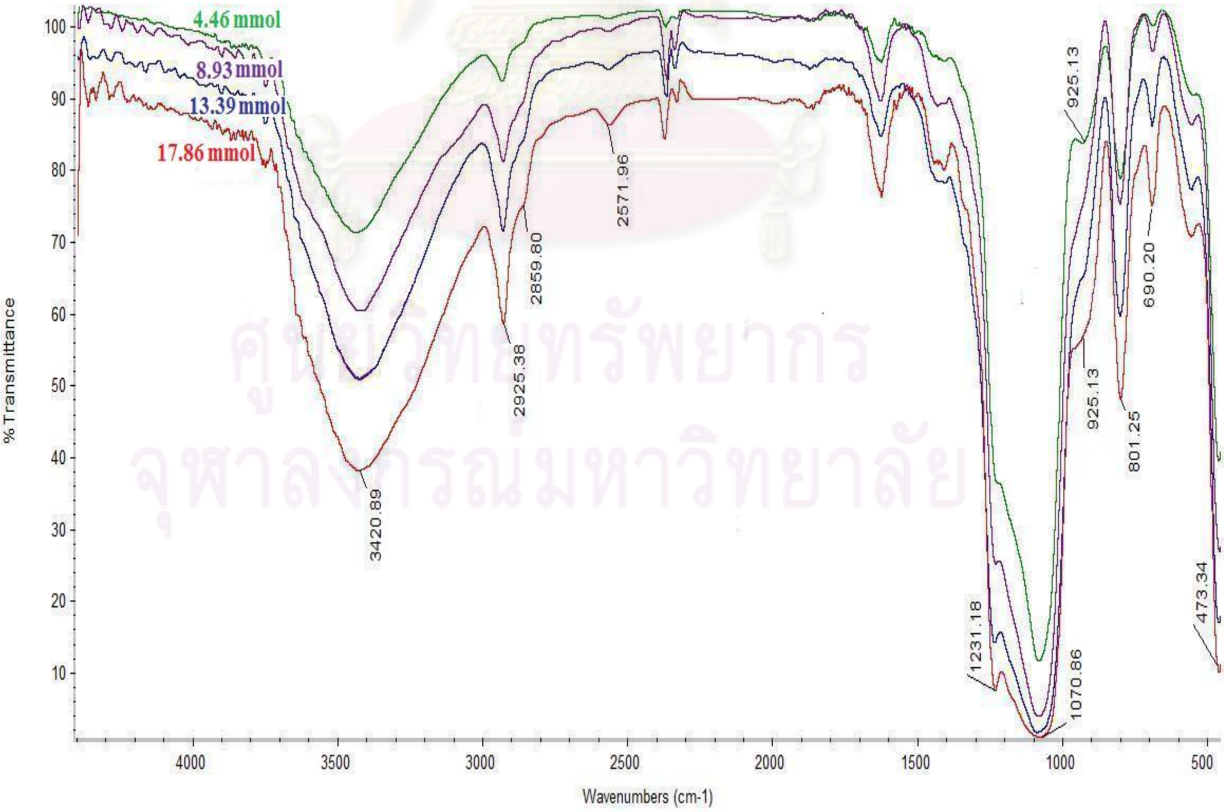


Figure 4.9 FT-IR spectra of **MP-MCM-41** (*Graft-step*) with different amount of MPTMS added.

In conclusion, FT-IR characterization shows the success of the synthesis of modified MCM-41 and confirmed the attachment of 3-mercaptopropyltrimethoxysilane on the adsorbents.

4.1.2.3 Surface area analysis

Surface area analysis by Brunauer-Emmett-Teller method (BET) was used in this research with the objective to compare the surface area, pore volume and pore diameter of MCM-41 and MP-MCM-41. The results are shown in Table 4.5. The BET surface area in the range of 857 - 1297 m^2/g was expected for hexagonal mesoporous materials [9-11, 15-18, 70]. MP-MCM-41 from all synthesis methods had lower surface area and pore volume and smaller in pore diameter, compared to normal MCM-41. The results show that the surface properties of MP-MCM-41 were clearly different from those of the unmodified MCM-41. The modification results in a reduction in surface area and pore volume, probably due to the occupation of the functionalized molecules on the surface and inside the pores of the adsorbents. The results in Table 4.5 are the average values of the experimental data *(n=2)* that are shown in detail in Table A1 (see appendix).

Table 4.5 Physical parameters of the adsorbents measured by nitrogen adsorption–desorption isotherms

Sample	**Adding reagent**	**Surface analysis**		
		Surface area (BET) (m^2/g)	**Total Pore volume** (cm^3/g)	**Pore diameter** (nm)
Normal MCM-41(*Step*)	5 to 20 % TEOS (in the 2nd step)	1296 to 963	1.16 to 0.80	4.1 to 3.7
Normal MCM-41(*Con*)	100 % TEOS	857 – 906	0.73 – 0.80	3.5 – 3.7
MP-MCM-41 (*Con*)	5 % to 20 % MPTMS	843 to 690	0.71 to 0.43	3.5 to 2.2
MP-MCM-41 (*Step*)	5 % to 20 % MPTMS	831 to 670	0.64 to 0.35	3.3 to 2.1
MP-MCM-41 (*Graft-con*)	4.46 to 17.86 mmol MPTMS/g MCM-41	842 to 685	0.70 to 0.36	3.4 to 2.1
MP-MCM-41 (*Graft-step*)	4.46 to 17.86 mmol MPTMS/g MCM-41	815 to 514	0.61 to 0.32	3.2 to 1.9

The surface area of MCM-41(*Step*) decreased when the adding amount of TEOS in the second step increased. It is probably due to the insertion of TEOS added in 2nd step on the surface of framework or between Si-O-Si bond of framework during crystalline formation, resulting in smaller pore diameter and lower surface area. Compared to MCM-41(*Step*), surface area of MP-MCM-41(*Step*) decreased after functionalization with MPTMS. The methoxy terminal of MPTMS might involve in the formation of inorganic framework or attach on the previously formed framework. The 3-mercaptopropyl branch might also react with the hydrophilic groups of template through H-bonding to form the complex structure [19], resulting in the occupation of space inside the pore and therefore reduction of surface area and porosities of MP-MCM-41(*Step*).

In the case of MP-MCM-41(*Con*), surface area of the obtained products also decreased when the adding amount of MPTMS increased especially at the adding amount of MPTMS of 15 and 20%mol. The presence of MPTMS, instead of TEOS, in the gel formation and crystallization step seems to alter the surface properties of the products.

In the case of MP-MCM-41(*Graft-con*) and (*Graft-step*), surface area of the obtained products decreased when increased the adding amount of MPTMS due to the attachment of MPTMS on the pore surface of MCM-41[17, 70]. The surface area and porosities of MP-MCM-41(*Graft-step*) decreased in higher extent than MP-MCM-41(*Graft-con*). The results reveal that the amount of MPTMS attached on the pore surface of MP-MCM-41(*Graft-step*) seems to be higher than on MP-MCM-41 (*Graft-con*) when used the same adding amount.

The nitrogen adsorption-desorption isotherm of the obtained products are shown in Fig. 4.10. The N_2 adsorption-desorption isotherms of MCM-41 (*Con*) and MCM-41 (*Step*) with 15% mol TEOS added in the 2nd step (Fig. 4.10(a) and 4.10(d)) show linear to step-shaped uptakes at partial pressures between 0.1 and 0.5. These features indicate the presence of mesopore in framework.

All the products exhibited type IV isotherms with apparent hysteresis loop, indicating the existence of defined mesopores in the frameworks [9, 10, 66, 67]. When modified with MPTMS, the adsorbed amount at the saturated pressure (see in axis Y from graph) decreased, revealing lower porosity of the products. The more content of MPTMS was incorporated, the lower porosity might be obtained. If the adsorbent has smaller pore diameter, the result from the nitrogen condensation step will shift to lower vapor pressure.

From the results, the nitrogen condensation step (see in axis X from graph) gradually shifted to lower vapor pressure in the modified MCM-41, which associates with the decreasing of the mesopore diameter. The degree of decrease observed in adsorbents depends on the synthesis type, as following: MP-MCM-41 (*Graft-step*) > MP-MCM-41(*Step*) > MCM-41 (*Step*) and MP-MCM-41 (*Graft-con*) > MP-MCM-41(*Con*) > MCM-41 (*Con*).

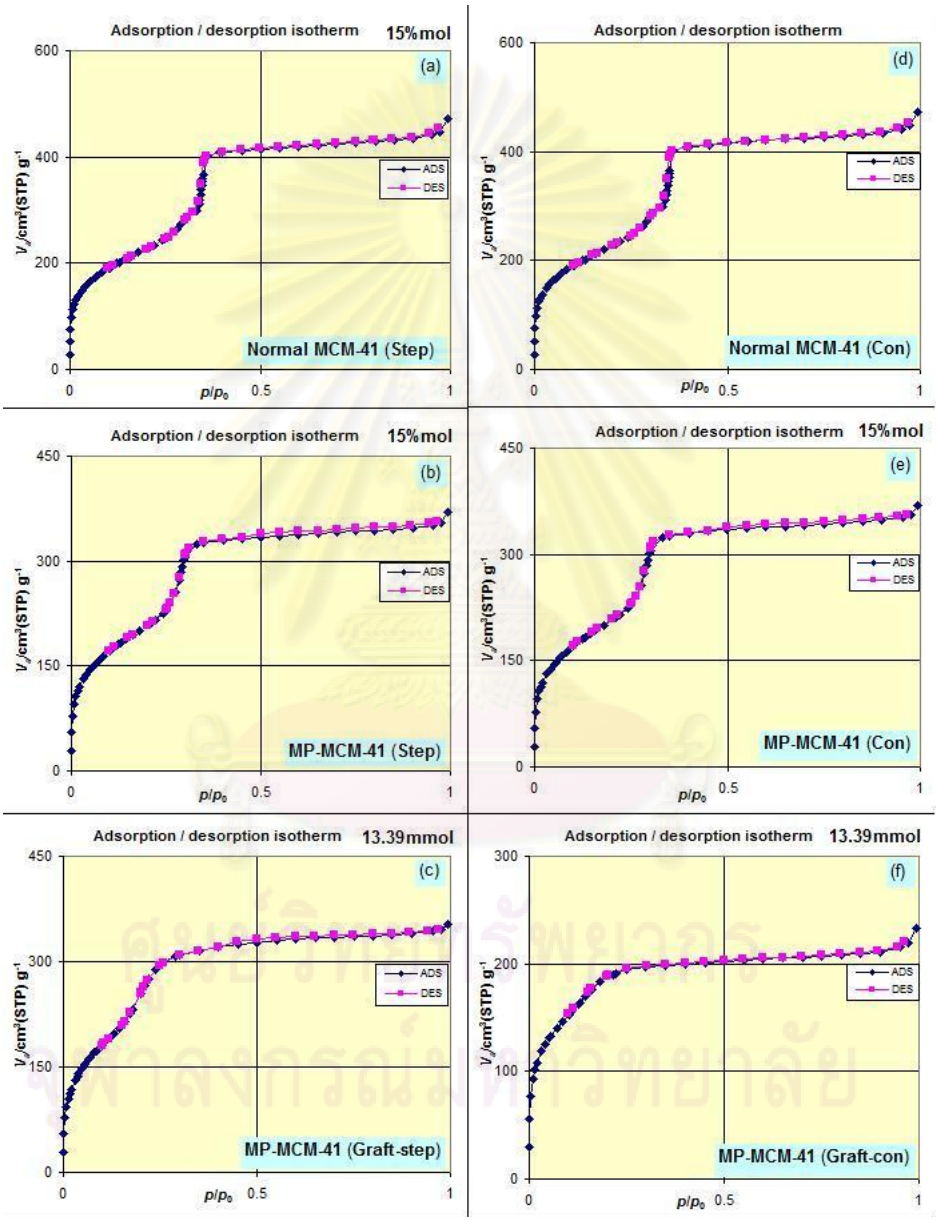


Figure 4.10 Nitrogen adsorption-desorption isotherm of (a) MCM-41(*Step*), (b) MP-MCM-41(*Step*) 15%mol, (c) MP-MCM-41 (*Graft-step*) 13.39 mmol/g, (d) MCM-41(*Con*), (e) MP-MCM-41(*Con*) 15%mol, and (f) MP-MCM-41(*Graft-con*) 13.39 mmol/g.

From the experimental results, the nitrogen condensation step of the products shifted to near low vapor pressure when adding amount of MPTMS increased, indicating that the product had higher MPTMS content and then the pore diameter was lower. Nonetheless, specific surface area and porosities of the obtained adsorbents still remained in the range of the hexagonal mesoporous structures after 3-mercaptopropyl modification.

4.1.2.4 Thermogravimetric analysis

The amount of 3-mercaptopropyl groups attached on MP-MCM-41 was determined by thermo gravimetric analysis (TGA). The TGA profiles are shown in Fig. 4.11 and the appendix. For the normal MCM-41 materials, a weight loss of about 2 % was observed at a temperature lower than 180 °C, due to the evaporation of adsorbed water and a further weight loss of about 0.9 – 2.4 % was observed at temperatures higher than 210 °C. When the surfactant was not removed by reflux, the significant weight loss (about 29.4 %) due to the residual surfactant decomposition was observed at temperatures higher than 180 °C (Fig. A2–A3, appendix). Therefore, reflux treatment is necessary and was applied to remove the surfactants for all MCM-41 products.

The functionalized products showed weight loss in three steps: first step at temperature lower than 180 °C, which was due to the evaporation of adsorbed water, second step at 300-450 °C (approximately 4–13%), which could be attributed to the loss of 3-mercaptopropyl groups, and the last step at temperature between 500–650 °C (approximately 2.5–8.3%), which was due to the breaking of the siloxane bridges (Si-O-Si bonds) [10, 11]. The increase in the extent of weight loss due to the 3-mercaptopropyl groups on the adsorbents was observed when used higher adding amount of MPTMS.

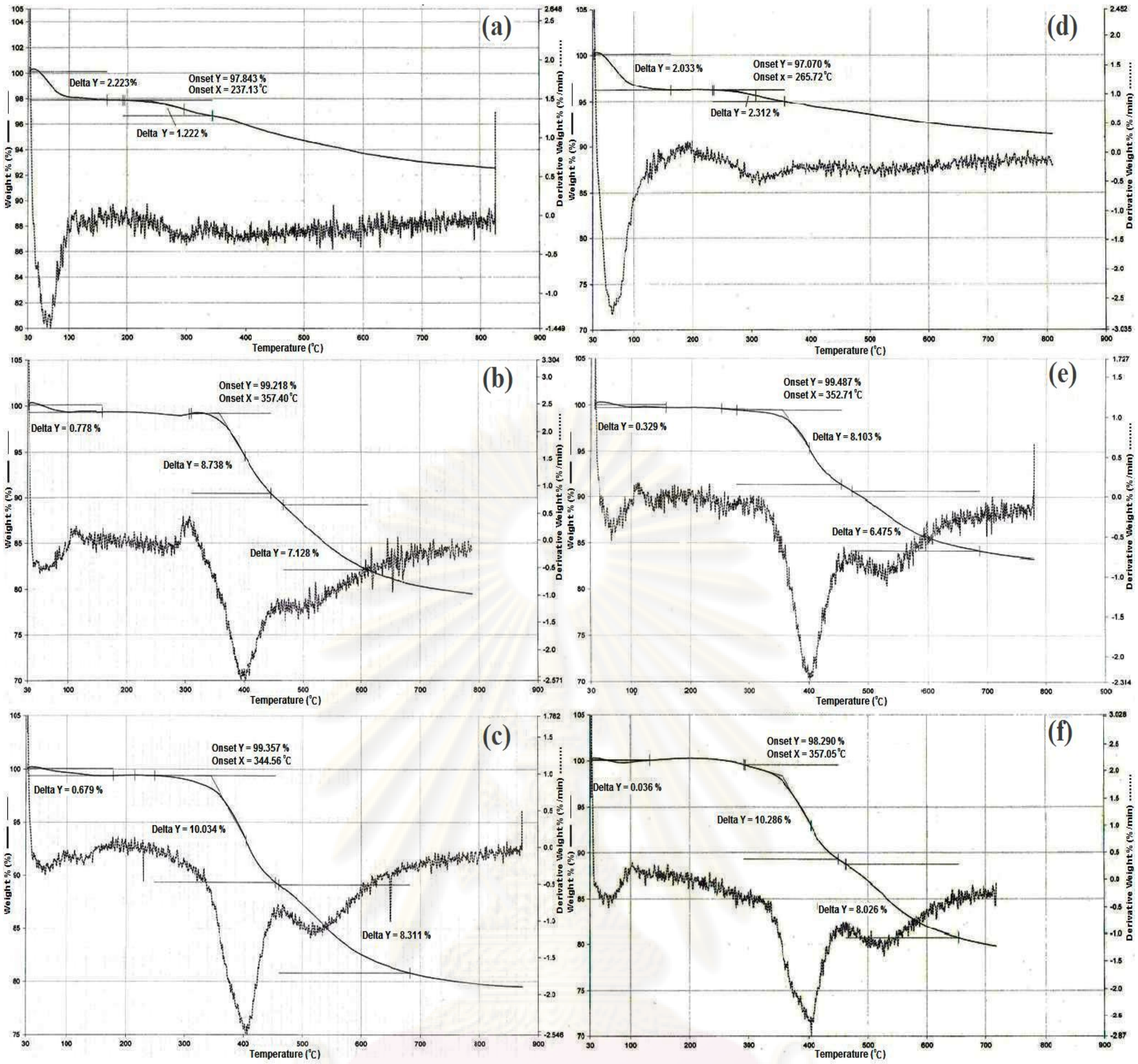


Figure 4.11 TGA curves of (a) MCM-41(*Con*), (b) MP-MCM-41(*Con*), (c) MP-MCM-41 (*Graft-con*), (d) MCM-41(*Step*), (e) MP-MCM-41(*Step*) and (f) MP-MCM-41(*Graft-step*).

The overall loading of 3-mercaptopropyl on the adsorbents was calculated using weight loss data from TGA curves of MCM-41 and MP-MCM-41 (Fig. A4–A36) and the equation 4.1 [10, 11, 70].

$$\textbf{Loading capacity}\ (\text{mmol Ligand/g adsorbent}) = \frac{\text{Ligand (g)}}{\text{100 g adsorbent}} \times \frac{\text{1 mol Ligand}}{\text{M.W. ligand (g)}} \times \frac{\text{1000 mmol Ligand}}{\text{1 mol Ligand}}$$

$$\textbf{Loading capacity}\ (\text{mmol MP/g adsorbent}) = \frac{\text{Ligand (\% g)} \times 10}{\text{M.W. ligand (g)}} \qquad (4.1)$$

3-mercaptopropyl trimethoxysilane

$(CH_2)_3SH$ M.W. = 75 g/mol

The calculated loading capacity of 3-mercaptopropyl on the adsorbents are shown in Table 4.6. In every method of synthesis, the results from TGA show an increasing trend of 3-mercaptopropyl amount attached on MP-MCM-41 when increased the adding amount of the ligand. The loading capacity represents the amount of ligand (mmol) modified on one gram of the final products obtained from each synthesis method.

Table 4.6 Calculated loading capacity of the adsorbents

Adding amount of MPTMS	**Loading capacity** (mmol MP/g adsorbent) [a]			
	MP-MCM-41 (*Step*)	**MP-MCM-41 (*Con*)**	**MP-MCM-41 (*Graft-step*)**	**MP-MCM-41 (*Graft-con*)**
5 % mol	0.5187 ± 0.003	0.5968 ± 0.030		
10 % mol	0.8876 ± 0.017	0.9730 ± 0.004		
15 % mol	1.0807 ± 0.002	1.1647 ± 0.004		
20 % mol	1.0864 ± 0.004	1.1683 ± 0.005		
4.46 mmol/g			0.5193 ± 0.009	0.4153 ± 0.004
8.93 mmol/g			0.8708 ± 0.007	0.7761 ± 0.003
13.39 mmol/g			1.0628 ± 0.003	1.0135 ± 0.004
17.86 mmol/g			1.0947 ± 0.007	1.0037 ± 0.003

[a] Mean ± S.D. (n=3)

The loading capacities of the final products were compared when used the same range of starting amount of MPTMS in the synthesis (Fig. 4.12). It should be noted that the starting amount of MPTMS used in every method is practically in the same range of quantity but presented in different unit depending on the method of synthesis.

The loading amount MP ligand on the obtained products increased when the adding amount increased. The results show that the adsorbents having highest loading capacity could be prepared when used adding amount higher than 15% mol MPTMS for *Con* method and *Step* method and higher than 13.39 mmol MPTMS/g MCM-41 for *Graft* method. From the XRD results previously discussed, a high adding amount of MPTMS resulted in less ordered structure. To continue to add the MPTMS may eventually result in disordered structure.

The suitable starting amount of ligand MPTMS, in respect to the highest loading capacity and the good crystalline mesoporous structure of the adsorbents, is 15% mol MPTMS for *Con* method and *Step* method and 13.39 mmol MPTMS/g MCM-41 for *Graft* method.

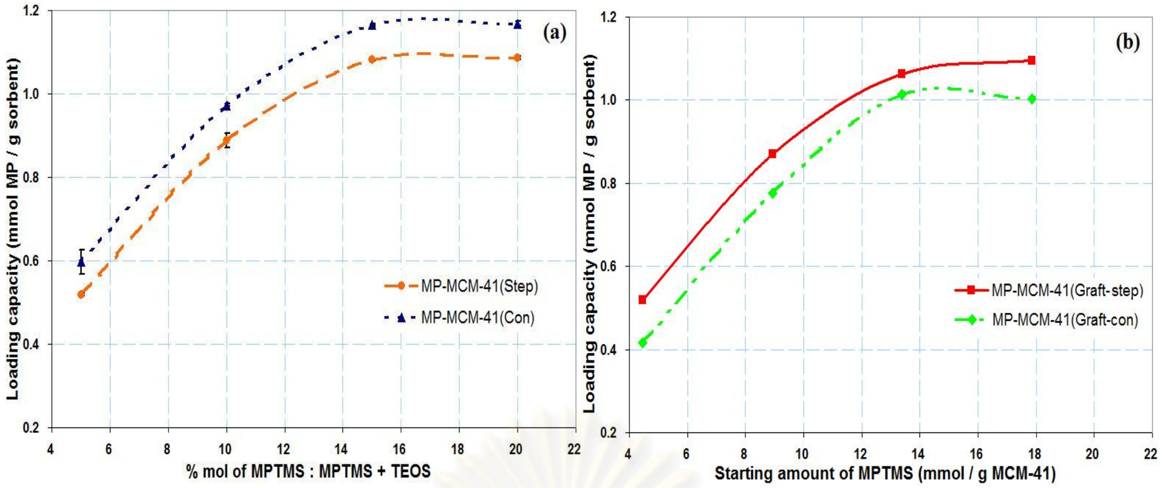


Figure 4.12 Loading capacity calculated from TGA of the adsorbents obtained from (a) *Con* and *Step* method, (b) *Graft* method using MCM-41 (*Con*) and MCM-41 (*Step*).

The ligand loading efficiency of the synthesis method could be compared by comparing the ligand loading capacity of the adsorbents obtained when used the same adding amount of ligand. The efficiency of the method in ligand loading is in the following order: *Con* method > *Graft* method using MCM-41 (*Step*) > *Step* method > *Graft* method using MCM-41 (*Con*).

From the results in Fig. 4.12 and data fitting, the equations describing the relationship between the adding amount of ligand and the ligand loading capacity of the adsorbent were obtained as shown in Table 4.7.

Table 4.7 Relationship between loading capacity of the adsorbents (y) and the adding amount of ligand (x)

Synthesis method	**Mathematic equation** [a]	**Correlation coefficient** (R^2)	**Equation no.**
Con	$y = -0.0037x^2 + 0.1316x + 0.0313$	1	(4.2)
Step	$y = -0.0036x^2 + 0.129x - 0.0368$	1	(4.3)
Graft-step	$y = -0.004x^2 + 0.1323x + 0.0088$	1	(4.4)
Graft-con	$y = -0.0046x^2 + 0.1485x - 0.1607$	0.9968	(4.5)

[a] The unit of y is mmol MP/g MP-MCM-41 and the unit of x is % mol MPTMS for *Con* and *Step* method and mmol MPTMS/g MCM-41 for *Graft* method.

The limit of use of the equation (4.2) – (4.5) is that they are valid only for the calculation of the adding amount of ligand (x) less than or equal 20 % mol MPTMS for *Con* and *Step* method and 17.86 mmol MPTMS/g MCM-41 for *Graft* method. However, the adding amount higher than the limits may results in disordered structure which is undesirable for the use as adsorbents.

Furthermore, to choose the suitable synthesis method of adsorbents, the adsorption efficiency of the obtained products need to be evaluated and compared. The adsorption efficiency might increase in increasing the ligand loading on the products. Therefore, to correctly compare adsorption efficiency of the adsorbents prepared by *Con*, *Step* and *Graft* method, the adsorbents containing equal amount of ligand were prepared.

4.2 Synthesis of MP-MCM-41 containing equal amount of 3-mercaptopropyl

MP-MCM-41 adsorbents which had the equal loading amount of 3-mercaptopropyl were prepared by three synthesis methods using adding amount of MPTMS calculated from equation (4.2) – (4.5). To obtain 1 mmol MP/g MP-MCM-41, the amount of MPTMS to be added in the synthesis was 10.40 % mol for *Con* method, 12.17 % mol for *Step* method, 11.47 mmol and 13.28 mmol for *Graft* method using MCM-41 (*Step*) and MCM-41 (*Con*) as starting material, respectively.

4.2.1 Characterization of MP-MCM-41 containing equal amount of 3-mercapto propyl

The MP-MCM-41 adsorbents which were prepared to have 1 mmol 3-mercapto propyl were characterized by different techniques as followed.

4.2.1.1 Thermogravimetric analysis

Loading capacity or the amount of 3-mercaptopropyl per gram adsorbent was calculated from TGA curves (Fig. A25–A30 in appendix) and shown in Table 4.8. The results show that MP-MCM-41 adsorbents containing 1 mmol MP/g could be successfully prepared using the adding amount calculated from equation (4.2) – (4.5).

Table 4.8 Loading capacity of the adsorbents prepared to have equal loading amount of MP measured by TGA

Adsorbents	**Adding amount of MPTMS**	**Loading capacity** [a] (mmol MP / g adsorbent)
MP-MCM-41 (*Con*)	10.40 % mol (MPTMS : MPTMS + TEOS)	1.0032 ± 0.030
MP-MCM-41 (*Step*)	12.17 % mol (MPTMS : MPTMS + TEOS)	1.0105 ± 0.036
MP-MCM-41 (*Graft-step*)	11.47 mmol MPTMS / g MCM-41	1.0209 ± 0.034
MP-MCM-41 (*Graft-con*)	13.28 mmol MPTMS / g MCM-41	1.0633 ± 0.031

[a] *Mean ± S.D. (n=3)*

To prove the validity of the obtained equations in the synthesis of modified MCM-41, another organic molecule was used in the modification. MCM-41 were functionalized with triethoxyoctylsilane, which is aliphatic hydrocarbon, by three synthesis methods and using the equation (4.2) – (4.5) for calculation of the adding amount of triethoxyoctylsilane (TEOTS). To obtain 1 mmol OT/g OT-MCM-41, the amount of TEOTS to be added in the synthesis was 10.40 % mol for *Con* method, 12.17 % mol for *Step* method, 11.47 mmol and 13.28 mmol for *Graft-step* method and *Graft-con* method, respectively.

The obtained products (OT-MCM-41) were characterized by TGA for determination of the loading amount of octyl per gram adsorbent by using the percentage of weight loss in TGA curves (Fig. A31–A36 in appendix) and equation (4.1). Loading amounts of octyl per gram adsorbent are shown in Table 4.9.

Table 4.9 Loading capacity of OT-MCM-41 adsorbents prepared by different synthesis methods

Adsorbents	**Adding amount of TEOTS**	**Loading capacity** [a] (mmol OT / g adsorbent)
OT-MCM-41 (*Con*)	10.40 % mol (TEOTS : TEOTS + TEOS)	0.9360 ± 0.095
OT-MCM-41 (*Step*)	12.17 % mol (TEOTS : TEOTS + TEOS)	1.1204 ± 0.110
OT-MCM-41 (*Graft-step*)	11.47 mmol TEOTS /g MCM-41	1.0059 ± 0.134
OT-MCM-41 (*Graft-con*)	13.28 mmol TEOTS /g MCM-41	0.9727 ± 0.036

[a] *Mean ± S.D. (n=3)*

The TGA results from Fig. 4.13 (or Fig. A33 – A36 in appendix) show that the loss of octyl group was observed at very high temperature (500-650 °C) in the analysis of OT-MCM-41 (*Con*) and OT-MCM-41 (*Step*). This is probably due to the attachment of the long length molecules inside the pore or in the core structure of OT-MCM-41. Therefore, the octyl group and/or the residual of decomposed octyl group would be burned out at the temperature near the temperature that cause the breaking of siloxane bridges (Si-O-Si bonds) in the core structure at 500 – 650 °C [10, 11].

The loading capacities of the obtained adsorbents are close to 1.0 mmol octyl/g adsorbent. The results indicate that the equation (4.2) – (4.5) could be used for calculation of the adding amount of functional group for the preparation of modified MCM-41 by these three synthesis methods.

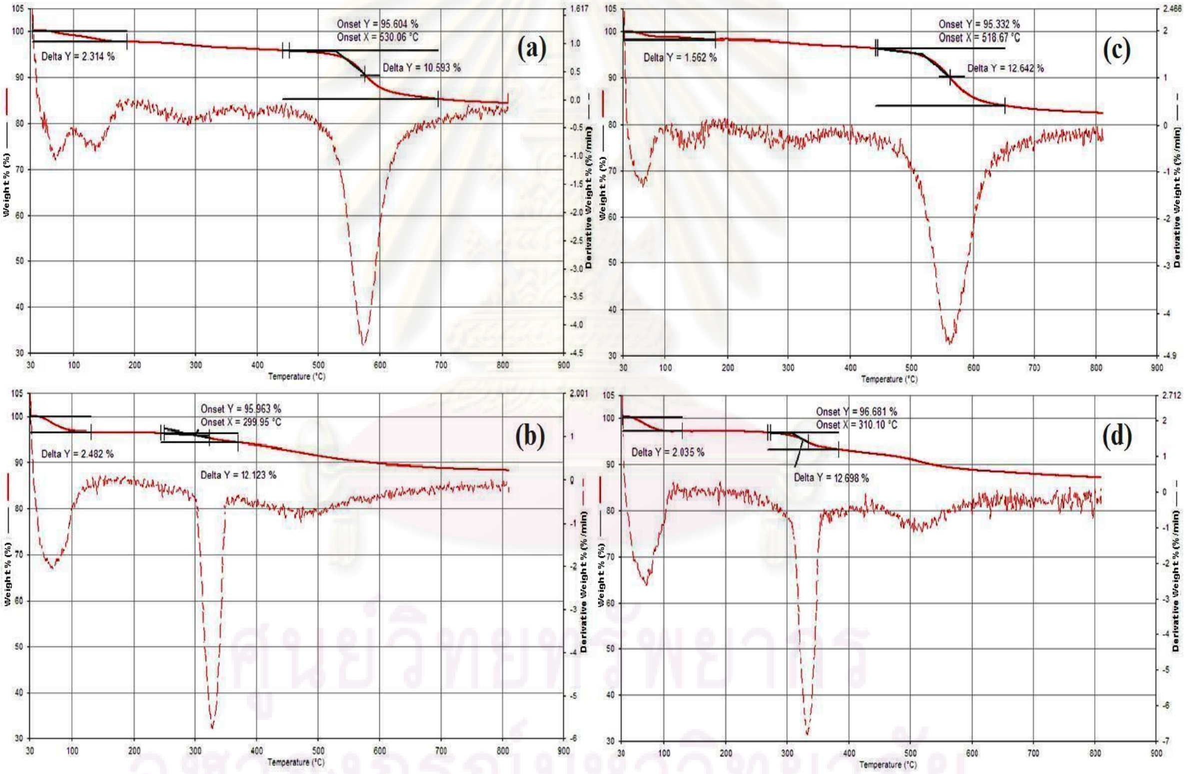


Figure 4.13 TGA curves of (a) OT-MCM-41 (*Con*), (b) OT-MCM-41 (*Graft-con*), (c) OT-MCM-41 (*Step*) and (d) OT-MCM-41(*Graft-step*).

4.2.1.2 X-ray diffraction technique

MP-MCM-41 adsorbents which contained the equal loading amount of 3-mercaptopropyl were characterized by X-ray diffractometer (XRD) to confirm the hexagonal mesoporous structure of adsorbents as shown in Fig. 4.14.

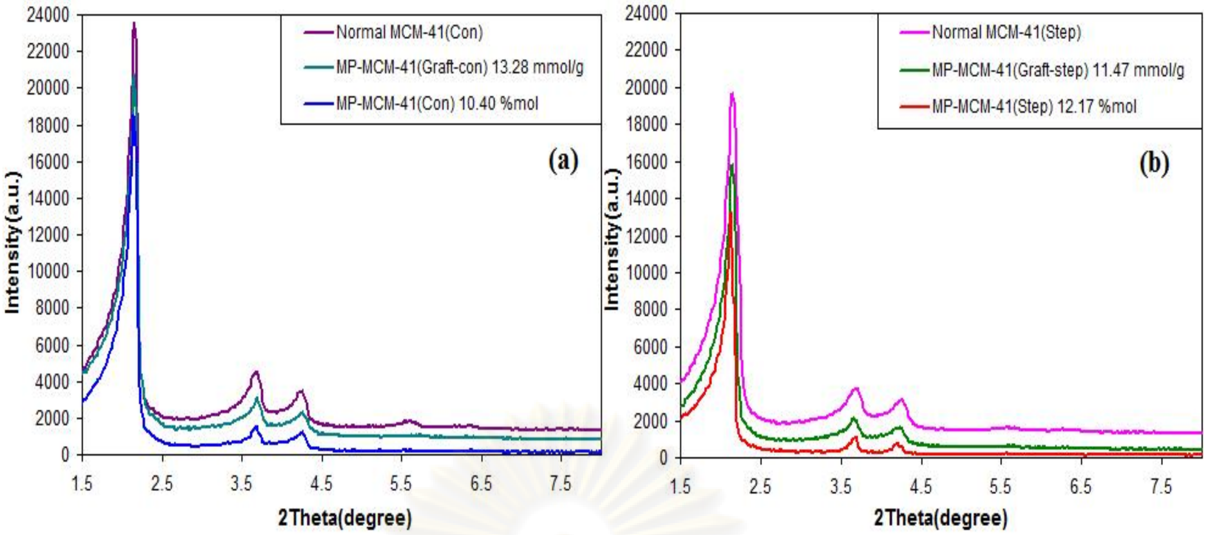


Figure 4.14 XRD patterns of MCM-41 and MP-MCM-41 from (a) *Con* method and *Graft* method using MCM-41 (*Con*), (b) *Step* method and *Graft* method using MCM-41 (*Step*).

No change in the XRD pattern was observed after modification of MCM-41 with MPTMS. Furthermore, the decrease in peak intensity and also the peak broadening of the modified products indicate a slight disorder of crystalline structure of MCM-41. The results are in agreement with those observed previously in topic 4.1.2.1.

4.2.1.3 Fourier transform infrared spectroscopy

The FT-IR spectra of MP-MCM-41 adsorbents containing equal amount of 3-mercaptopropyl were shown in Fig. 4.15 – 4.16.

FT-IR spectra of MP-MCM-41 obtained from *Con* method, *Step* method and *Graft* method (Fig. 4.16– 4.17) showed new peaks corresponding to (1) vibrations of CH_2 at 2925 and 2859 cm^{-1}, (2) stretching of SH at 2571 cm^{-1}, and (3) CH_2 rocking vibrations of Si–CH_2R at 690 cm^{-1}. This indicates that the obtained adsorbents are successfully synthesized with MPTMS and the results are in agreement with those observed previously.

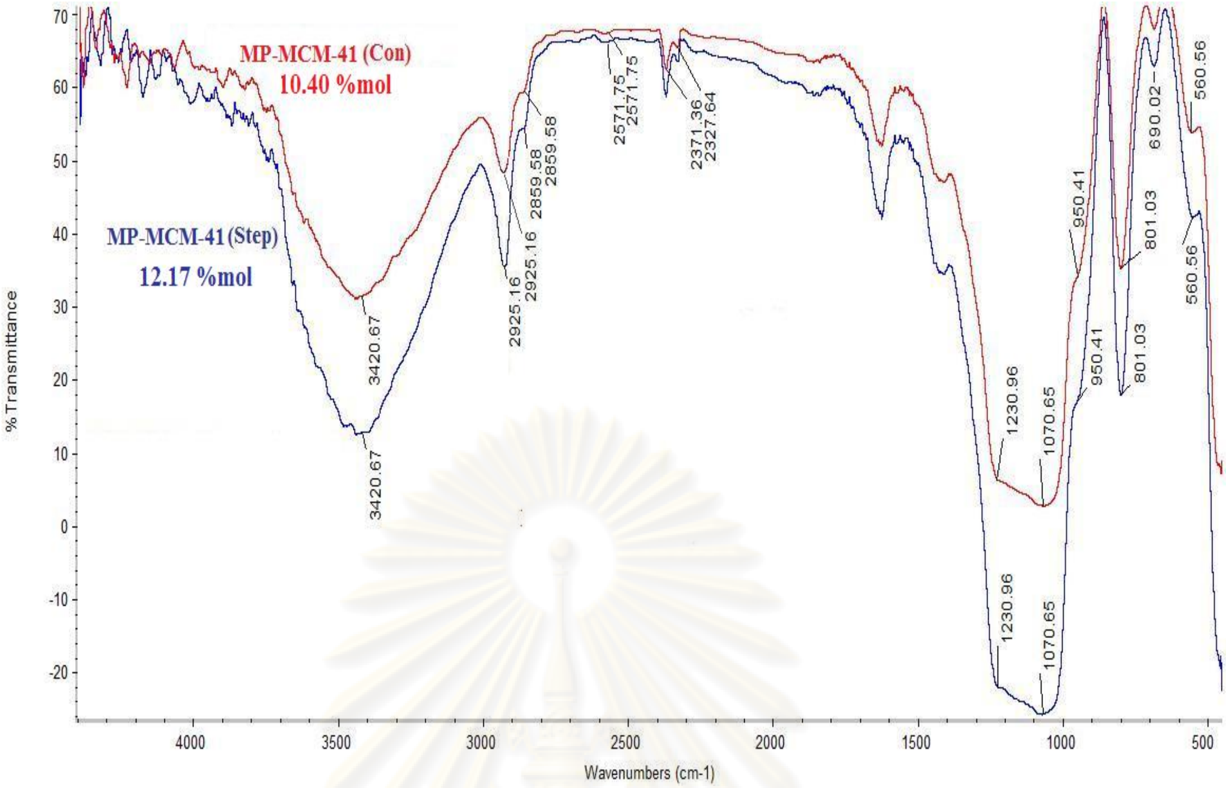


Figure 4.15 FT-IR spectra of **MP-MCM-41** (*Con*) and **MP-MCM-41** (*Step*) containing approximately 1.0 mmol MP/g.

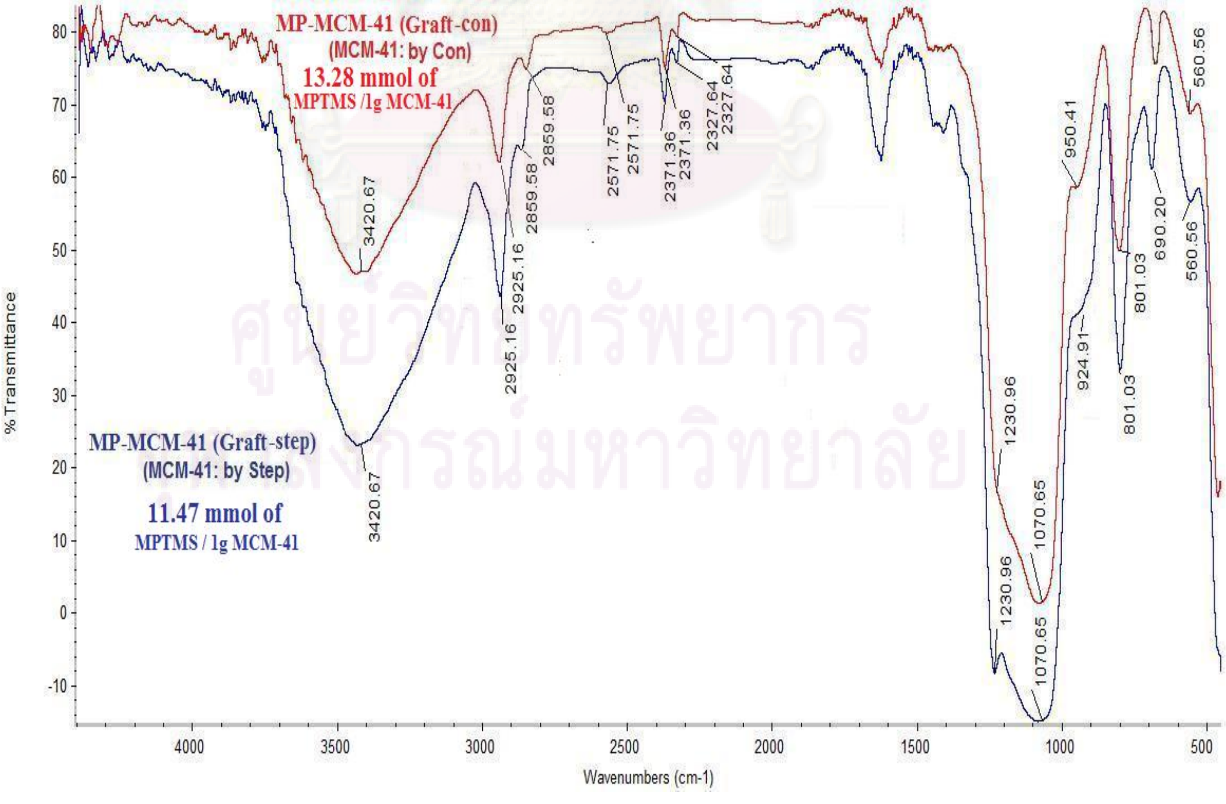


Figure 4.16 FT-IR spectra of **MP-MCM-41** (*Graft-con*) and **MP-MCM-41** (*Graft-step*) containing approximately 1.0 mmol MP/g.

4.2.1.4 Surface area analysis (Brunauer-Emmett-Teller method (BET))

MP-MCM-41 adsorbents which contained approximately 1.0 mmol MP/g were analyzed for the surface area, pore volume and pore diameter by surface area analyzer using BET method (Table 4.10).

Table 4.10 Physical parameters of the adsorbents containing approximately 1.0 mmol MP/g MP-MCM-41

Sample	**Adding amount of MPTMS**	**BET result** [a]		
		Surface area (BET) (m^2/g)	**Total Pore volume** (cm^3/g)	**Pore diameter** (nm)
Normal MCM-41 (*Con*)	–	914	0.73	3.4
Normal MCM-41 (*Step*)	–	939	0.73	3.5
MP-MCM-41 (*Con*)	10.40 %mol	897	0.62	3.2
MP-MCM-41 (*Step*)	12.17 %mol	854	0.54	2.9
MP-MCM-41(*Graft-con*)	13.28 mmol/g	831	0.53	2.9
MP-MCM-41(*Graft-step*)	11.47 mmol/g	735	0.53	2.6

[a] *Mean (n=2)*

The results from surface analysis show a decrease in surface area from 914 to 897 m^2/g and 939 to 854 m^2/g when MCM-41 was modified with MPTMS by *Con* method and *Step* method, respectively. A reduction in surface area from 914 to 831 m^2/g and 939 to 735 m^2/g were also observed when used *Graft* method to modify MCM-41 (*Con*) and MCM-41 (*Step*), respectively. The decrease in surface area, pore diameter and pore volume could be attributed to the occupation of functionalized molecules on surface and inside pores of adsorbents. The diameter of the pores of the obtained products in the range of 2.6 – 3.5 nm indicates the presence of mesoporous channels.

The results from characterization confirm the success of the preparation of the MP-MCM-41 adsorbents containing approximately 1.0 mmol MP/g. To evaluate the adsorption efficiency of the adsorbents prepared by different methods, MP-MCM-41 containing equal amount of ligand were further used in the adsorption of mercury(II) ions. The suitable adsorbents for mercury removal should provide high adsorption efficiency with reasonable amount of ligand loading. Then the suitable synthesis method will be chosen.

4.3 Comparison of adsorption efficiency of the MP-MCM-41 prepared by different methods

MP-MCM-41 adsorbents were used in the adsorption of mercury(II) ions in aqueous solutions by batch method. The adsorption experiments were carried out using 0.01 g adsorbents, 10 mL solution (pH 6) and stirring time of 2 h. The adsorption efficiency of all adsorbents was determined. The mercury(II) ions adsorption efficiency is presented in term of adsorption capacity and percentage adsorption, calculated from equation (4.6) and (4.7), respectively.

$$\text{Adsorption capacity (q)} = \left(\frac{C_i - C_e}{100} \times V\right) \times \frac{1}{m} \qquad (4.6)$$

$$\text{Adsorption (\%)} = \frac{C_i - C_e}{C_e} \times V \qquad (4.7)$$

where C_i = initial concentration of mercury(II) ions in aqueous solution (mg/L)

C_e = equilibrium concentration of mercury(II) ions in aqueous solution (mg/L)

q = adsorption capacity of the obtained adsorbents (mg/g)

V = volume of mercury(II) ions aqueous solution (mL)

m = weight of adsorbent (g)

Mercury (II) ions adsorption efficiency of MP-MCM-41 was studied as following:

4.3.1 Comparison of mercury(II) ions adsorption efficiency of MP-MCM-41 prepared by three synthesis methods using different adding amount of MPTMS

MP-MCM-41 adsorbents were prepared by using 5 – 20 % mol MPTMS for *Con* and *Step* method and 4.46 – 17.86 mmol MPTMS/g MCM-41 for *Graft* method as discussed previously. The adsorption capacity of the adsorbents was evaluated using batch method. The initial concentration of mercury (II) solution was 210 mg/L. Mercury(II) ions adsorption capacity of MP-MCM-41 adsorbents are shown in Table 4.11.

Table 4.11 Mercury(II) ions adsorption capacity of MP-MCM-41 prepared by different synthesis methods with variation of the adding amount of MPTMS

Adsorbents	**Adding amount**	**Loading amount** [a] (mmol MP/g adsorbent)	**Adsorption capacity** [a] (mg/g)
MP-MCM-41 (*Con*)	5 % mol MPTMS	0.5968 ± 0.030	66.14 ± 1.35
	10 % mol MPTMS	0.9730 ± 0.004	120.65 ± 0.74
	15 % mol MPTMS	1.1647 ± 0.004	153.75 ± 0.57
	20 % mol MPTMS	1.1683 ± 0.005	159.38 ± 0.52
MP-MCM-41 (*Step*)	5 % mol MPTMS	0.5187 ± 0.003	144.81 ± 2.28
	10 % mol MPTMS	0.8876 ± 0.017	151.25 ± 2.14
	15 % mol MPTMS	1.0807 ± 0.002	175.53 ± 0.20
	20 % mol MPTMS	1.0864 ± 0.004	178.24 ± 0.46
MP-MCM-41 (*Graft-con*)	4.46 mmol MPTMS /g MCM-41	0.4153 ± 0.004	158.82 ± 0.19
	8.93 mmol MPTMS /g MCM-41	0.7761 ± 0.003	179.56 ± 0.48
	13.39 mmol MPTMS /g MCM-41	1.0135 ± 0.004	192.12 ± 0.08
	17.86 mmol MPTMS /g MCM-41	1.0037 ± 0.003	196.01 ± 0.16
MP-MCM-41 (*Graft-step*)	4.46 mmol MPTMS /g MCM-41	0.5193 ± 0.009	181.06 ± 0.01
	8.93 mmol MPTMS /g MCM-41	0.8708 ± 0.007	209.98 ± 0.11
	13.39 mmol MPTMS /g MCM-41	1.0628 ± 0.003	209.13 ± 0.39
	17.86 mmol MPTMS /g MCM-41	1.0947 ± 0.007	209.01 ± 0.28

[a] *Mean ± S.D. (n=3)*

Furthermore, the adsorption efficiency of the products prepared from different synthesis methods was also compared in function of loading capacity as shown in Fig. 4.17. The optimum condition in the synthesis will be chosen based on the loading amount of ligand and the adsorption capacity for mercury(II) ions of the obtained products (Table 4.11and Fig. 4.17).

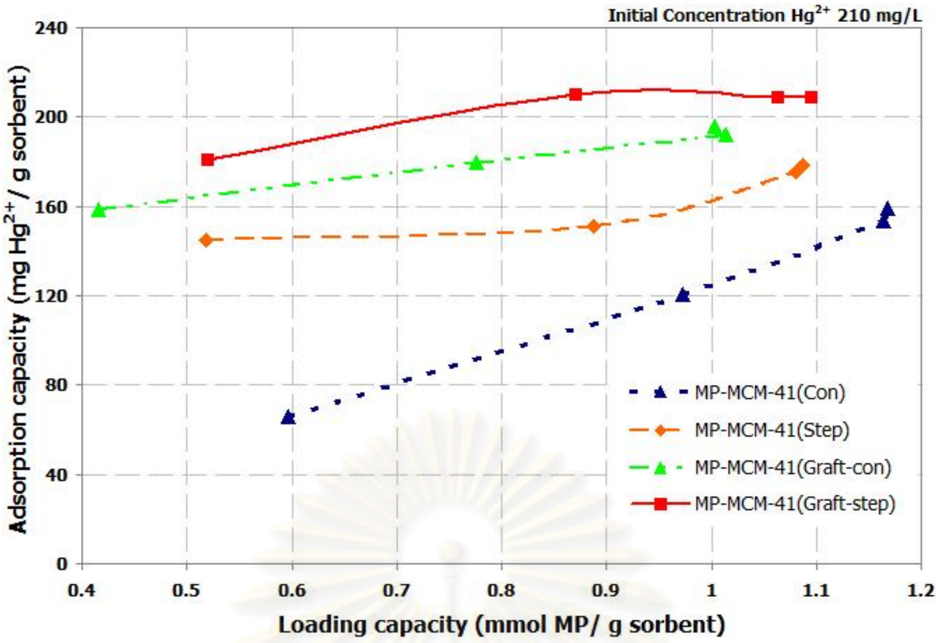


Figure 4.17 Mercury(II) ions adsorption capacity of MP-MCM-41 by each loading capacity of MP from each synthesis methods.

From Fig. 4.17, the results show an increase in adsorption capacity for mercury(II) ions of the obtained adsorbents when the ligand loading capacity of the adsorbents increased. The adsorption efficiency of MP-MCM-41 is in the order: MP-MCM-41(*Graft-step*) > MP-MCM-41(*Graft-con*) > MP-MCM-41(*Step*) > MP-MCM-41(*Con*), respectively. The highest adsorption efficiency was achieved by using MP-MCM-41 prepared by *Graft* method using MCM-41(*Step*), despite of lower ligand loading capacity compared to adsorbents prepared by other methods. This is probably due to the presence of MP molecules mainly on the surface of MCM-41 which is highly active for adsorption of ions from solution. The significant reduction in surface area and pore size of MP-MCM-41 (*Graft-step*) also confirm the modification of the ligand molecules on the surface of MCM-41. On the other hand, the ligand modified on solid by *Con* method and *Step* method may be present on the surface and also in the core structure of MP-MCM-41 which are “inactive” for adsorption. From Fig. 4.17, the suitable adsorbent was MP-MCM-41 (*Graft-step*) prepared by adding MPTMS 8.93 mmol MPTMS /g MCM-41. It was chosen after consideration of its high adsorption capacity and less amount of ligand added, compared to MP-MCM-41(*Graft-step*) prepared by adding 13.39 and 17.86 mmol MPTMS/g MCM-41. It also maintained the good order of crystalline structure of MCM-41.

The most suitable synthesis method of adsorbents for mercury(II) ions adsorption in solution is *Graft* method using MCM-41(*Step*). For better comparison of the adsorption efficiency of the products, MP-MCM-41 containing equal amount of ligand loading were prepared.

4.3.2 Comparison of mercury(II) ions adsorption efficiency of MP-MCM-41 containing equal loading amount of 3-mercaptopropyl

The MP-MCM-41 containing approximately 1.0 mmol MP/g were prepared and characterized as discussed previously. The adsorption experiments were carried out using mercury(II) solution (210 mg/L) at pH 6. The results are shown in Table 4.12 and Fig. 4.18.

Table 4.12 Adsorption efficiency of MP-MCM-41 adsorbents containing approximately 1.0 mmol MP/g

Adsorbents	Adsorption capacity (mg/g)	Removal (%)
Normal MCM-41 (*Step*)	0.38 ± 0.10	0.18 ± 0.05
Normal MCM-41 (*Con*)	0.24 ± 0.12	0.12 ± 0.06
MP-MCM-41 (*Step*)	163.80 ± 1.70	78.75 ± 0.09
MP-MCM-41 (*Con*)	121.22 ± 0.49	57.90 ± 0.56
MP-MCM-41(*Graft-step*)	209.30 ± 1.20	99.97 ± 0.01
MP-MCM-41 (*Graft-con*)	186.63 ± 1.11	88.85 ± 0.53

Mean ± S.D. (n=3)

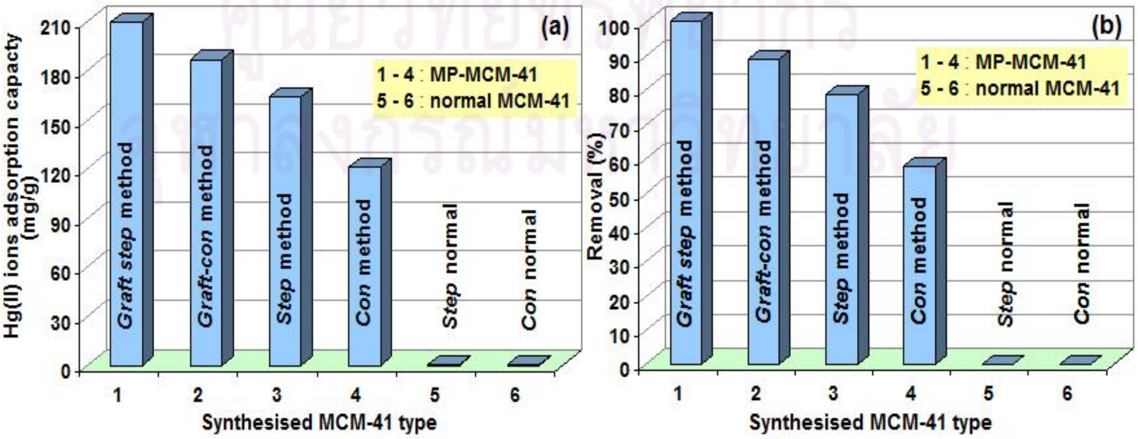


Figure 4.18 Mercury(II) ions adsorption of MP-MCM-41 containing approximately 1.0 mmol MP/g (a) mercury adsorption capacity, (b) % removal.

The adsorption efficiency of adsorbents was correctly compared when the adsorbents had the equal amount of functional group. When the ligand content is the same, the adsorption capacity of the MP-MCM-41 adsorbents and the percentage of mercury(II) ions removal is in the order of MP-MCM-41 (*Graft-step*) > MP-MCM-41 (*Graft-con*) > MP-MCM-41 (*Step*) > MP-MCM-41 (*Con*). This result supports the results from topic 4.3.1.

In conclusion, the most suitable method for synthesis of the adsorbent is chosen based on the following features: (i) the method should yield the adsorbents that have high adsorption capacity with reasonable amount of ligand loading and (ii) its crystalline structure is still preserved. The order of adsorption efficiency and loading efficiency are presented below;

Ligand loading efficiency: *Con* method > *Graft* method using MCM-41 (*Step*) > *Step* method > *Graft* method using MCM-41(*Con*)

Mercury(II) ions adsorption efficiency: *Graft* method using MCM-41 (*Step*) > *Graft* method using MCM-41(*Con*) > *Step* method > *Con* method

Thus, the most suitable method for synthesis the adsorbents for mercury(II) ions adsorption in solution is *Graft* method using MCM-41 (*Step*).

4.4 Adsorption study

The effect of various parameters (i.e. pH, contact time, interfering ions) was studied. The MP-MCM-41 (*Graft-step*) prepared by adding of 11.47 mmol MPTMS/g MCM-41 and containing 1.0 mmol MP/g final product was chosen and used in this study.

4.4.1 Effect of pH of mercury(II) ions solution

The pH of solution could have strong influence on adsorption due to the presence of different species of mercury in solution at different pH (i.e. metal ions and/or metal hydroxide precipitate). The effect of pH on the mercury(II) ions adsorption on MP-MCM-41 is shown in Table 4.13 and Fig. 4.19.

Table 4.13 Effect of pH on the mercury(II) ions adsorption by MP-MCM-41

Initial pH	**Adsorption capacity** (mg/g)	**Removal** (%)	**pH at equilibrium**
1	126.01 ± 1.25	60.53 ± 0.01	3.18 ± 0.27
2	143.26 ± 1.67	69.05 ± 0.41	4.67 ± 0.27
3	173.54 ± 2.63	82.81 ± 0.01	6.48 ± 0.14
4	192.63 ± 1.33	92.54 ± 0.01	6.89 ± 0.04
5	204.39 ± 0.98	96.57 ± 0.83	7.35 ± 0.11
6	210.13 ± 0.01	99.95 ± 0.10	7.55 ± 0.09
7	209.48 ± 1.20	99.97 ± 0.01	7.66 ± 0.06
8	210.20 ± 0.01	99.98 ± 0.01	8.06 ± 0.07

Mean ± S.D. (n=3)

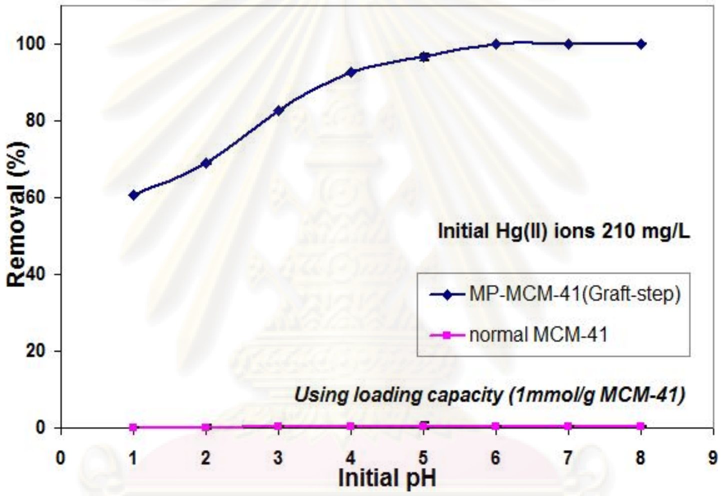


Figure 4.19 Effect of initial pH on mercury(II) ions removal (%) by MP-MCM-41.

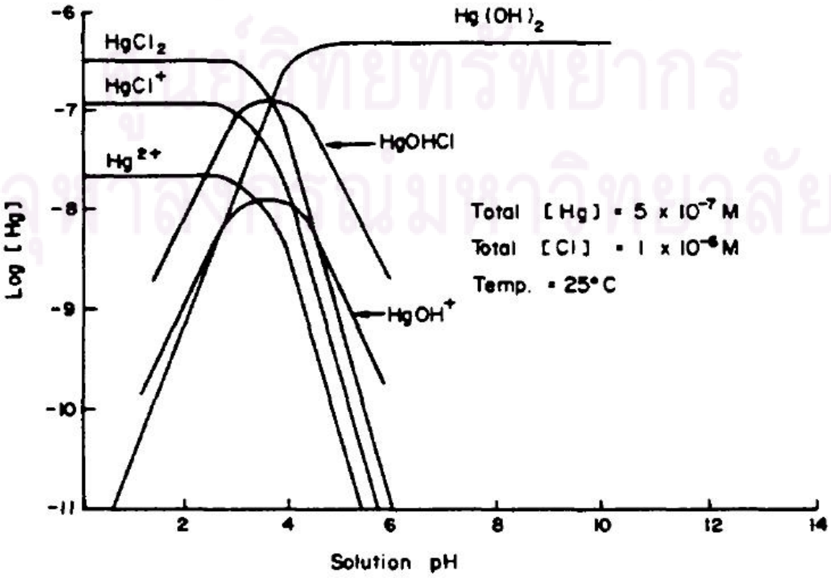


Figure 4.20 Mercury speciation diagram [90].

The adsorption capacity of MP-MCM-41 and the percentage of mercury removal increased when the pH of solutions increased. Regarding the speciation of Hg, in solution at pH less than 4, the major species of mercury(II) ions are Hg^{2+} cations, while $Hg(OH)_2$ species dominate at pH higher than 4 as shown in Fig. 4.20 [90]. The mixture of cation and hydrolyzed species may be found at pH 4 to 6.

When the pH of the solution is lower than the pK_a value of the ligand ($pK_a = 10.6$, [91]), the –SH groups on mercaptopropyl will be in neutral from (–SH) and will not dissociate to yield $–S^-$ groups. In the experiments, pH value of all solution was less than 8. Thus, the end group of the functionalized molecules was in form of –SH. Different species of metallic complexes may occur when mercury(II) speciation was changed. The forms of mercury which are likely to interact with –SH groups are Hg^{2+}, $HgOH^+$, and $Hg(OH)_2$. In this study, the following complexation reactions are proposed.

$$\equiv Si{-}C_3H_6{-}SH + Hg^{2+} + 2NO_3^- \rightarrow \equiv Si{-}C_3H_6{-}\overset{H}{S}\rightarrow Hg^{2+}\ 2(NO_3^-) \qquad (4.8)$$

$$\equiv Si{-}C_3H_6{-}SH + HgOH^+ + NO_3^- \rightarrow \equiv Si{-}C_3H_6\left[\overset{H}{S}\rightarrow HgOH\right]^+ (NO_3^-) \qquad (4.9)$$

$$\equiv Si{-}C_3H_6{-}SH + Hg(OH)_2 \rightarrow \equiv Si{-}C_3H_6{-}\overset{H}{S}\rightarrow Hg(OH)_2 \qquad (4.10)$$

When pH of solution is lower than pH 6 and the mercury(II) ions are in the forms of the Hg^{2+}cations or $HgOH^+$, their complexation with –SH groups may lead to the formation of positively charged complexes (eq.4.8 and 4.9), which require anions as counter ions. On the other hand, when the pH of solution is higher than 6, the complexation of the $Hg(OH)_2$ involves the formation of a neutral complex (eq.(4.10)). The formation of positively charged complexes inside the mesoporous adsorbents could prevent its complete filling by mercury(II) ions. The obtained positively charged complexes located on the inside walls of the porous materials may act as an electrostatic barrier and limit the passage of positively charged species such as Hg^{2+} through the pores. Thus, the mercury (II) ions adsorption capacity at pH less than 6 could be lower than that observed at pH higher than 6.

Regarding the speciation of mercury ions, when the initial pH was 1 and 2, the equilibrium pH could raise to pH 4.7 and the dominate species in the solution were Hg^{2+} cations and $HgOH^+$. Mercury(II) ions adsorption capacity increased when the initial pH was higher than 3 due to the presence of $Hg(OH)_2$ forms at equilibrium which are better adsorbed on MP-MCM-41. In conclusion, the suitable pH for mercury(II) ions adsorption were the initial pH of 5 – 8 and the equilibrium pH of 7.55.

4.4.2 Effect of contact time

The adsorption, which occurs between liquid (solute) and solid (adsorbent) phase, have three main mechanisms as following: (i) bulk transport, (ii) film transport and (iii) intraparticle transport. The bulk transport usually occurs rapidly and the process of film and/or intraparticle transport is often the rate determining step for adsorption equilibrium. In this experiment, the effect of contact time was studied and the equilibrium time for the adsorption process was determined for the further experiments. The results of mercury(II) ions adsorption by MP-MCM-41 as a function of stirring time was shown in Fig. 4.21.

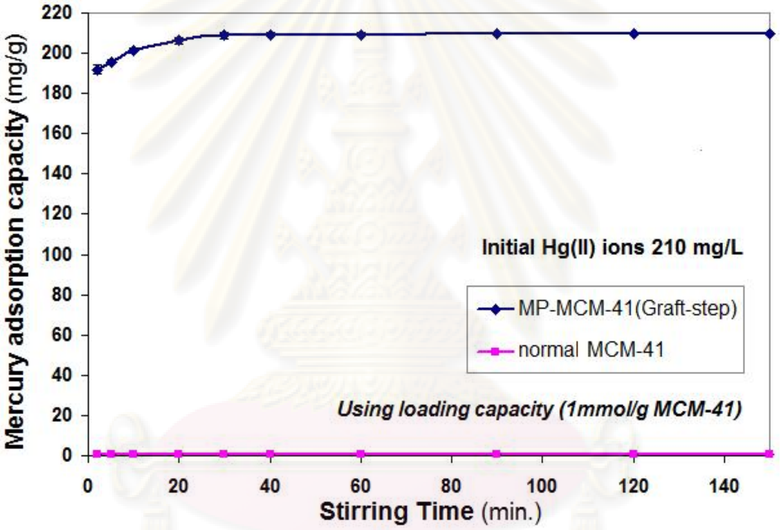


Figure 4.21 Effect of stirring time on the mercury(II) ions adsorption capacity by MP-MCM-41 (*Graft-step*).

The adsorption efficiency increased with the increasing of contact time and reached the equilibrium after 20 min. The adsorption time of 120 min was chosen for the adsorption experiments to ensure the adsorption equilibrium.

4.4.3 Effect of foreign ions

The presence of ions other than mercury (II) ions may affect the adsorption of mercury(II) ions by the adsorbents due to the complex formation and/or the formation of insoluble compounds of mercury(II) ions with other ions especially. To evaluate the selectivity of adsorbents toward mercury(II) ions, the adsorption of mercury(II) ions was performed in the presence of anions such as NO_3^-, SO_4^{2-} and especially Cl^- that more appeared in petrochemical wastewater. The sodium salt of those anions was added to the mercury(II) ion solutions with a concentration of 0.1 or 1.0 M. The results are shown in Table 4.14.

Table 4.14 Effect of foreign ions on the mercury(II) ions adsorption by MP-MCM-41

Salts	**Adsorption capacity** (mg/g)	**Removal** (%)
$NaNO_3$ 0.1 M	199.25 ± 0.78	96.04 ± 0.20
$NaNO_3$ 1.0 M	192.45 ± 1.15	91.85 ± 0.02
Na_2SO_4 0.1 M	195.06 ± 1.10	94.02 ± 0.13
Na_2SO_4 1.0 M	193.95 ± 0.75	92.26 ± 0.36
NaCl 0.1 M	157.90 ± 0.98	75.61 ± 0.23
NaCl 1.0 M	123.18 ± 0.64	58.79 ± 0.11

Mean ± S.D. (n=3)

The results show that the presence of NO_3^- and SO_4^{2-} did not affect the mercury(II) ions adsorption capacity of adsorbent significantly, using pair t-Test. An increase in NO_3^- concentrations reduced the mercury(II) ions adsorption capacity significantly. Furthermore, the presence of Cl^- (0.1 and 1.0 M) obviously reduced the mercury adsorption efficiency. It could be explained that Cl^- in mercury(II) solution might form complex with mercury(II), giving different Hg-Cl species. Anions (NO_3^-, SO_4^{2-} and Cl^-) can act as ligands to form different mercury(II) complexes species in solution with formation constants shown in Table 4.15.

Table 4.15 Aqueous speciation reactions and equilibrium constants of Hg(II) ions [92,93]

Reaction	**log *K***
$Hg^{2+} + 2\,H_2O \rightleftharpoons Hg(OH)_2 + 2H^+$	−6.19
$Hg^{2+} + H_2O \rightleftharpoons HgOH^+ + H^+$	−2.70
$Hg^{2+} + NO_3^- \rightleftharpoons HgNO_3^+$	0.45
$Hg^{2+} + Cl^- + H_2O \rightleftharpoons HgClOH + H^+$	3.23
$Hg^{2+} + Cl^- \rightleftharpoons HgCl^+$	6.74

Reaction	**log *K***
$Hg^{2+} + 2Cl^{-} \rightleftharpoons HgCl_2$	13.22
$Hg^{2+} + 3Cl^{-} \rightleftharpoons HgCl_3^{-}$	14.07
$HgCl_3^{-} + Cl^{-} \rightleftharpoons HgCl_4^{2-}$	15.07
$Hg^{2+} + SO_4^{2-} \rightleftharpoons HgSO_4$	1.39
$Hg^{2+} + SO_4^{2-} + 2H_2O \rightleftharpoons Hg(OH)_2SO_4^{2-} + 2H^{+}$	−4.83[a]

[a] Conditional equilibrium constant (log *K*, ionic strength = 0.1) optimized by using the Hg(II)–SO_4–quartz and Hg(II)–PO_4–quartz system data.

The presence of Cl^{-} affected the removal efficiency of mercury(II) ions by MP-MCM-41 significantly. It was found that the adsorption efficiency decreased by increasing the Cl^{-} concentration from 0.1 to 1.0 M. The dominant mercuric species were also different in the solutions containing different concentration of Cl^{-}. By calculation using the equilibrium constants in Table 4.15, the dominant mercuric species in 0.1 M NaCl solution were $HgCl_2$, $HgCl_3^{-}$ and $HgCl_4^{2-}$ while the major species found in the 1.0 M NaCl solution was only $HgCl_4^{2-}$ [17]. The reduction of mercury adsorption efficiency in 0.1 M and 1.0 M NaCl solution reveals that the interaction of the species $HgCl_2$, $HgCl_3^{-}$ and $HgCl_4^{2-}$ with the ligand is less favorable than the other species (i.e. $Hg(OH)_2$, Hg^{2+}).

4.4.4 Adsorption isotherms

The adsorption equilibrium between mercury(II) ions in aqueous phase and the obtained adsorbent in solid phase can be described by adsorption isotherms. The earliest and simplest adsorption isotherms are Langmuir and Freundlish isotherms. In this study, the adsorption behavior of the obtained MP-MCM-41 was described by using their isotherms.

The Langmuir sorption isotherm is widely used to describe monolayer adsorption, when the adsorption occurs at specific homogeneous sites on the adsorbent and the adsorption can not further occur at that sites. In consequence, the adsorption capacity of the adsorbent is limited for the analytes. The equation of Langmuir isotherm is shown in equation 4.11 [94, 95].

$$\frac{C_e}{q} = \frac{1}{bq_m} + \frac{C_e}{q_m} \tag{4.11}$$

where C_e = equilibrium concentration of the analyte 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 the affinity of binding sites (L/mg or L/mol)

The value of q_m and b were obtained by the slope and intercept of the relation of linear plot of $\frac{C_e}{q}$ with C_e, respectively. In addition, the essential characteristics of Langmuir isotherm could be explained in terms of dimensionless constant separation factor of equilibrium parameter, R_L as shown in equation 4.12 [95, 96]. The parameter R_L indicated the type of isotherm as presented in Table 4.16.

$$R_L = \frac{1}{1 + bC_i} \tag{4.12}$$

where b = Langmuir constant related to the affinity of binding sites (L/mg or L/mol)

C_i = initial concentration of mercury(II) ions in aqueous solution (mg/L or mol/L)

Table 4.16 R_L value that associates with the type of isotherm

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

The Freundlich isotherm is a model to predict the adsorption behavior of adsorbent based on adsorption on heterogeneous surface. The Freundlich isotherm is presented by the following equation [97].

$$\log q = \log K_f + \tfrac{1}{n} \log C_e \tag{4.13}$$

where K_f = Freundlich constant related to adsorption capacity (mg/g or mol/g)

n = the numerical value of Freundlich constant

K_f and n can be determined from the intercept and slope relation of linear plot of log q with log C_e, respectively.

In adsorption isotherms study, the tested adsorbent was chosen from MP-MCM-41 (*Graft-step*) prepared by using adding amount of 13.39 mmol MPTMS/g MCM-41. After that, the maximum adsorption capacity of the MP-MCM-41 was compared to the other materials reported by researchers. Then, it was also used in the study of reusability of MP-MCM-41, and tested with real wastewater samples.

In this study, the adsorption experiments were performed using the mercury(II) ions solutions of concentration 40 – 420 mg/L having initial pH of 6.0 and a fixed amount of MP-MCM-41 (0.01 g/10 mL of mercury solution) at 25.0 ± 0.5 ^{o}C. The equilibrium had to be attained and the residual concentration of mercury(II) ions in solution was determined using CVAAS. The results are shown in Fig. 4.22 – 4.24.

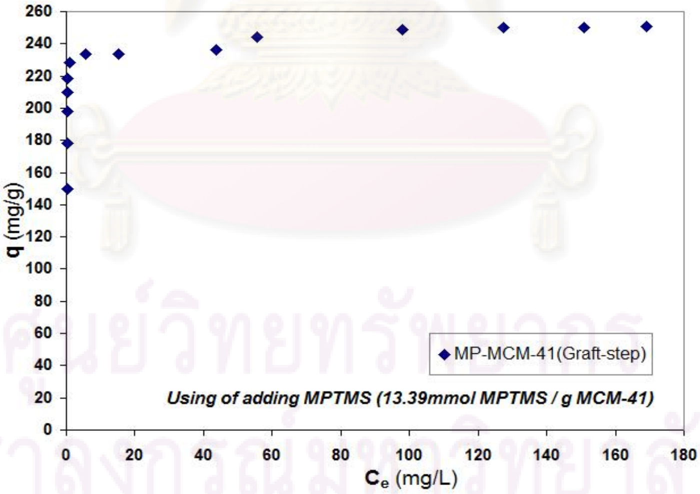


Figure 4.22 Adsorption isotherm of mercury(II) ions by MP-MCM-41(*Graft-step*) prepared with adding amount of 13.39 mmol MPTMS/g MCM-41.

The results from Fig. 4.22 show that adsorption capacity (q) increased rapidly at low equilibrium concentration of mercury and reached a constant value. Then, the experimental data of mercury(II) ions adsorption were taken for linear plotting using Langmuir and Freundlich models (Fig. 4.23 and 4.24).

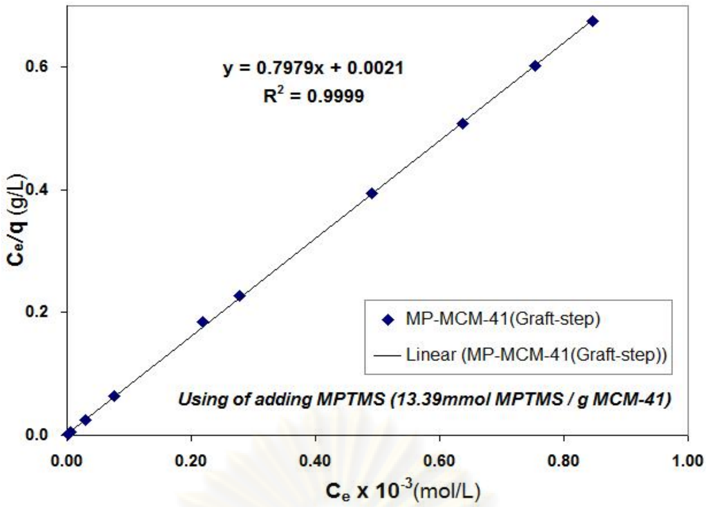


Figure 4.23 Langmuir isotherm plot of adsorption of mercury(II) ions by MP-MCM-41(*Graft-step*) prepared with adding amount of 13.39 mmol MPTMS/g MCM-41.

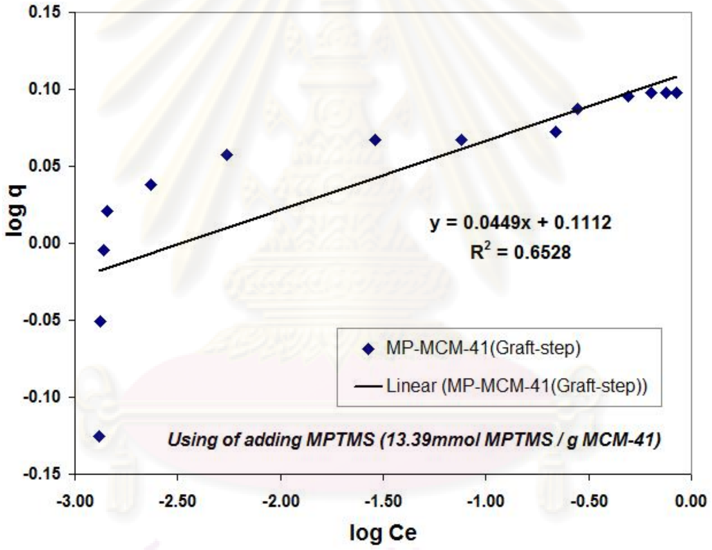


Figure 4.24 Freundlich isotherm plots of adsorption of mercury(II) ions by MP-MCM-41 (*Graft-step*) prepared with adding amount of 13.39 mmol MPTMS/g MCM-41.

The data obtained from Langmuir and Freundlich equations are shown in Table 4.17 – 4.18, respectively.

Table 4.17 Langmuir isotherm parameters at 25.0 ± 0.5 °C of MP-MCM-41(*Graft-step*)

Linear equation	**R^2**	**b x 10^5** (L/mol)	**$q_{m,cal}$** (mmol/g)^a	**$q_{m,cal}$** (mg/g)^a	**$q_{m,exp}$** (mg/g)^b	**R_L**
Y = 797.94x + 0.0021	0.999	3.799	1.25	251	250	0.00125 - 0.00349

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

[b] The maximum adsorption capacity obtained by the experimental.

Table 4.18 Freundlich isotherm parameters at 25.0 ± 0.5 °C of MP-MCM-41(*Graft-step*)

Linear equation	**R^2**	K_f (mol/g)	K_f (mg/g)	$\frac{1}{n}$	**n**
Y = 0.0449x + 0.1112	0.6528	1.29	258400	0.0449	22.27

The correlation coefficients (r^2) of the linear regression line of Langmuir isotherm was higher than 0.99 while that of Freundlich isotherm was 0.6528. This indicates that the adsorption of mercury(II) ions onto MP-MCM-41 fits to Langmuir model better than the Freundlich one. From the linear regression line fitted with Langmuir isotherm and reaching the saturation of adsorption capacity as shown in Fig. 4.22, those indicate the monolayer coverage and no further adsorption could occur [17, 64, 94, 95].

The calculated R_L values (see in Table 4.17) was between 0.0013 and 0.0035, in range of $0< R_L <1$, indicating highly favorable adsorption of mercury(II) ions on MP-MCM-41 [95, 96]. By the results corresponding to Langmuir relation, it could be assumed that the adsorption mechanism of mercury(II) on MP-MCM-41 are the chemisorption by coordination of MP group on MP-MCM-41 with mercury(II) ions and monolayer coverage on surface occurred [94, 95].

The maximum adsorption capacity of mercury(II) ions of MP-MCM-41(*Graft-step*) in this thesis was 1.25 mmol/g. The maximum adsorption capacity of mercury(II) ions of the modified MCM-41 and SBA-15, and the other modified materials are shown in Table 4.19 and Table 4.20.

Table 4.19 The adsorption capacity of the modified MCM-41and SBA-15 for mercury(II) ions removal

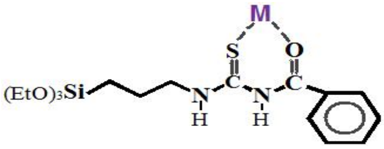
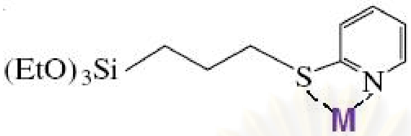
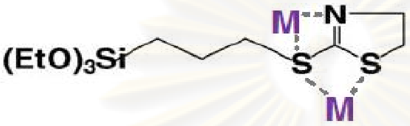
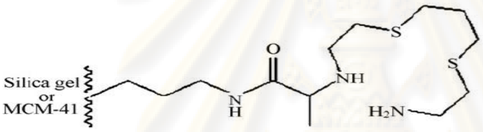
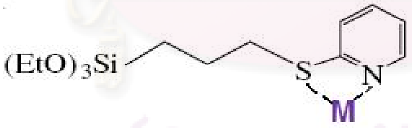
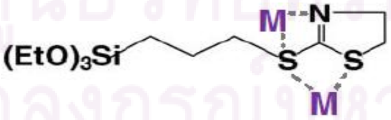
Adsorbents	**Type of organofunctionalized**	**Adsorption condition**			**Ref.**
		pH	**Time** (min)	**Adsorption capacity** (mmol / g)	
MCM-41 (Jaroniec, 2003)	benzoylthiourea  	Not shown	40	**5**	[9]

Table 4.19 The adsorption capacity of the modified MCM-41and SBA-15 for mercury(II) ions removal (continued)

Adsorbents	**Type of organofunctionalized**	**Adsorption condition**			**Ref.**
		pH	**Time** (min)	**Adsorption capacity** (mmol / g)	
MCM-41 (Sierra , 2006)	2-mercaptopyridine (MP) 	6	240	(Homo) **0.12** (Hetero) **0.09**	[10]
MCM-41 (Sierra , 2006)	2-mercaptothiazoline (MP) 	6	240	(Homo) **0.70** (Hetero) **0.25**	[11]
MCM-41 (Unob , 2008)	2-(3-(2-aminoethylthio)propylthio) ethanamine (AEPE) 	3	60	(Hetero) **0.70**	[17]
SBA-15 (Luan , 2005)	3-mercaptopropyltrimethoxysilane (MPTMS) 	Not shown	Not shown	**0.40**	[98]
SBA-15 (Sierra , 2006)	2-mercaptopyridine (MP) 	6	240	(Homo) **0.16** (Hetero) **0.08**	[10]
SBA-15 (Sierra , 2006)	2-mercaptothiazoline (MP) 	6	240	(Homo) **1.10** (Hetero) **0.12**	[11]
MCM-41	3-mercaptopropyltrimethoxysilane (MPTMS) 	6	120	**1.25**	**This work**

Homo = Synthesis by *Graft* method (homogeneous type)

Hetero = Synthesis by *Graft* method (heterogeneous type)

Table 4.20 The maximum adsorption capacity of the other modified materials

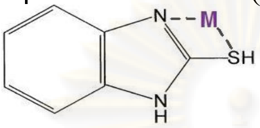
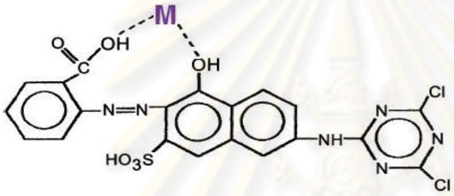
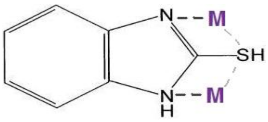
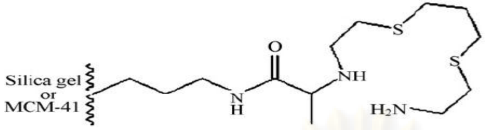
Adsorbents	**Type of organofunctionalized**	**Adsorption condition**			**Ref.**
		pH	**Time** (min)	**Adsorption capacity** (mmol / g)	
Fluorohectorite clay (Mercier, 1998)	3-mercaptopropyltrimethoxysilane (MPTMS) 	Not shown	1,080	**0.74**	[76]
Clay (Anirudhan, 2002)	2-mercaptobenzimidazole(MBI) 	4 - 8	360	**0.145-0.178**	[8]
Composite membranes (Bektas, 2002)	Procion Brown MX 5BR 	2 - 6	45	**0.34**	[14]
Silica gel (Cestari,1997)	3-mercaptopropyltrimethoxysilane (MPTMS) 	7	480	**0.70**	[78]
Silica gel (Vieira,1997)	3-mercaptopropyltrimethoxysilane (MPTMS) 	Not shown	Not shown	**0.40**	[79]
Silica gel (Cestari,2004)	dithizone 	6	30	**0.32**	[12]
Silica gel (Alcantara, 2007)	2-mercaptobenzimidazole(MBI) 	Not shown	Not shown	(Homo) **1.42** (Hetero) **1.35**	[13]

Table 4.20 The maximum adsorption capacity of the other modified materials (continued)

Adsorbents	**Type of organofunctionalized**	**Adsorption condition**			**Ref.**
		pH	**Time** (min)	**Adsorption capacity** (mmol / g)	
Silica gel (Unob, 2008)	2-(3-(2-aminoethylthio)propylthio) ethanamine (AEPE)  	3	60	(Hetero) **0.79**	[17]

When compared the adsorption capacity of MP-MCM-41(*Graft-step*) to the other materials reported by other authors, the adsorbents prepared in this work has fairly good capacities for mercury(II) ions. Furthermore, the adsorption capacity of the MP-MCM-41 (*Graft-step*) is higher than those of activated carbon (0.17 – 1.12 mmol/g) [77, 78, 79, 99], clay (0.32 – 0.62 mmol / g) [73, 74, 84, 86, 93, 100] and close to some of chelating resins (1 – 3.60 mmol / g) [54, 80, 81, 101].

4.5 Study of reusability of 3-mercaptopropyl functionalized MCM-41

The step of regeneration of MP-MCM-41(*Graft-step*) was shown in Fig. 4.25. The experimental conditions for mercury(II) ions adsorption and desorption on 10 mg of MP-MCM-41 were as followed; adsorption performed by using 10 mL of Hg^{2+} solution (210 mg/L) at pH 6 with contact time of 2h and elution by 10 mL of 4% thiourea (v/v) in 0.1 M HCl for 1 h [102,103].

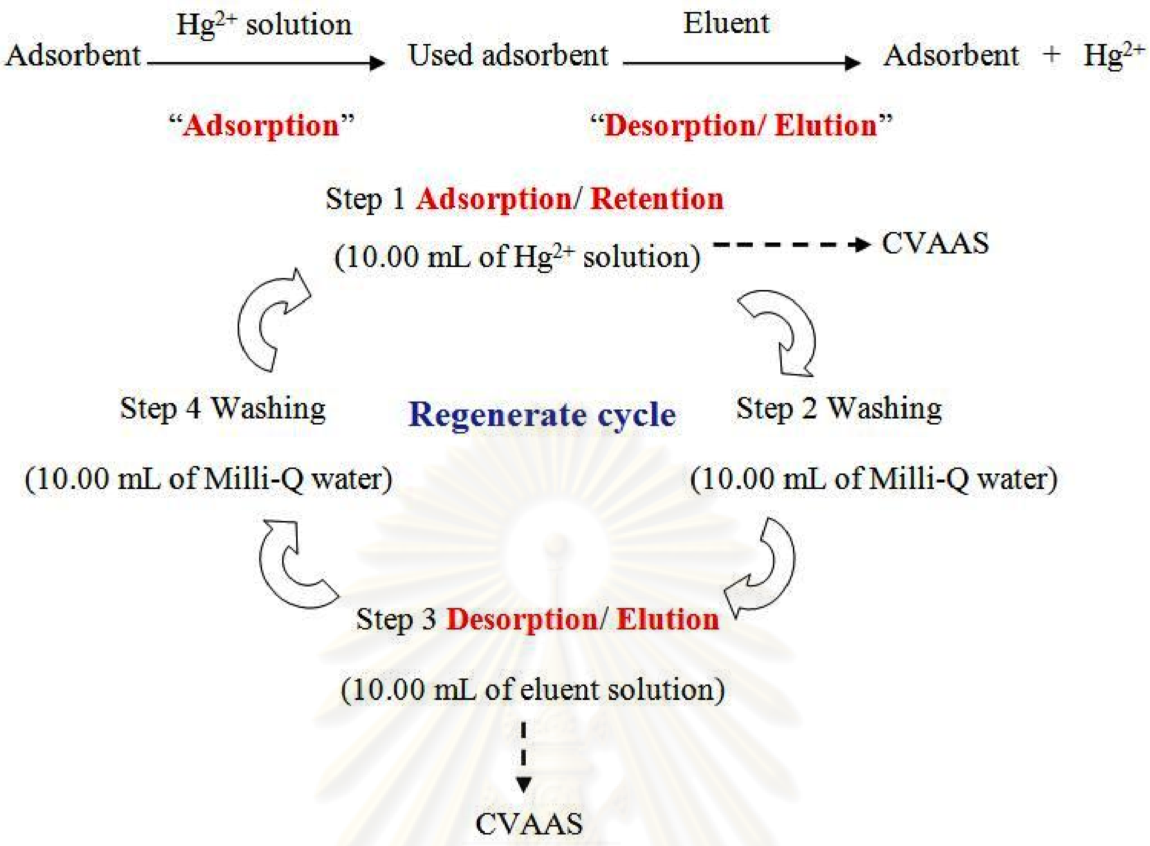


Figure 4.25 Mercury(II) ions adsorption- desorption cycle diagram.

The experimental results were reported in terms of the percentage adsorption and desorption which were calculated by equation 4.14 and 4.15.

$$\text{Adsorption (\%)} = \frac{N_a}{N_s} \times 100 \qquad (4.14)$$

where N_a = the adsorbed amount of metal ion from adsorbent (mg)

N_s = the starting amount of metal ion (mg)

$$\text{Desorption (\%)} = \frac{N_e}{N_a} \times 100 \qquad (4.15)$$

where N_e = the eluted amount of metal ion from adsorbent (mg)

N_a = the adsorbed amount of metal ion on adsorbent (mg)

N_a = (the adsorbed amount of metal ion) + (the residual amount of metal ion)
in each retention cycle on adsorbent in those cycle

To evaluate the reusability of the MP-MCM-41, the percentage of adsorption and desorption in each cycle were calculated and shown in Table 4.21.

Table 4.21 The percentage of adsorption and desorption of mercury in each cycle

Cycle	**Adsorption** (%)	**Desorption** (%)
1	99.77 ± 0.01	98.55 ± 0.04
2	98.23 ± 0.02	94.00 ± 0.04
3	93.65 ± 0.29	83.44 ± 0.16
4	83.18 ± 0.30	63.93 ± 0.26
5	63.66 ± 0.48	35.30 ± 0.13
6	35.16 ± 0.28	13.40 ± 0.05

Mean ± S.D. (n=3)

(MP-MCM-41 prepared from *Graft-step* method by adding MPTMS 13.39 mmol/1g MCM-41.)

In the first cycle, the spent MP-MCM-41 was regenerated and about 98.5% of the adsorbed mercury(II) ions was removed when it was treated with 4% thiourea (v/v) in 0.1 M HCl for 60 min. It was observed that more than 80% of the adsorbed mercury(II) ions were desorbed within the first 20 min.

The results from Table 4.21 show that the adsorption efficiency of MP-MCM-41 decreased upon the successive adsorption-desorption steps. It decreased more than 50% at the 6th cycle. The desorption of mercury(II) ions as a function of cycle number was shown in Fig. 4.26.

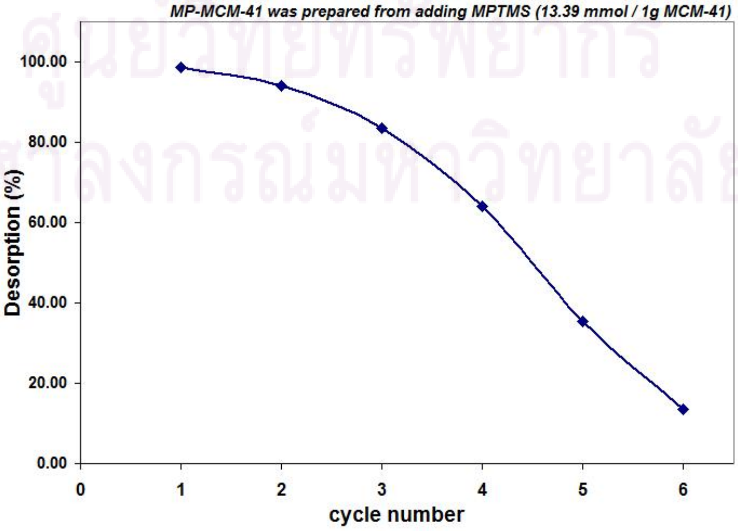


Figure 4.26 Reusability of MP-MCM-41 in mercury(II) ions removal.

From Table 4.21 and Fig. 4.26, the percentage adsorption of MP-MCM-41 was 64% at cycle 5 while the percentage desorption was 35%. The adsorbent could be used up to 4 cycles before the adsorption capacity reduced to less than 50%.

Despite of this dramatic capacity loss after 4th cycle of use, the MP-MCM-41 was still able remove mercury from solution and to reduce the mercury concentration in water to the acceptable concentration; it requires the addition of much larger amounts of solid particles in the medium to compensate the capacity loss.

4.6 Application to real wastewater samples from refinery process

Finally, MP-MCM-41 prepared by *Graft-step* method with adding amount of MPTMS of 13.39 mmol/1g MCM-41 was applied to remove mercury(II) ions in real wastewater samples from refineries. In this work, the wastewater and mud wash water from crude distillation units of refineries were collected, analyzed and used in the experiment of mercury(II) ions removal.

The wastewater and mud wash water were filtered and the pH of sample solutions was measured. The concentration of mercury(II) ions in samples was analyzed by using CVAAS. The samples were digested as suggested in ASTM D3223-02 [87], USEPA 7470A [88], and ASTM F885-88 [89] before the determination of the concentration of mercury. The results are shown in Table 4.22.

Table 4.22 Mercury(II) ions adsorption of real wastewater by MP-MCM-41

Sample source	**Sample**	**pH**	**Initial mercury concentration** (μg/L)	**Final mercury concentration** (μg/L)
Refinery 1	Plant 2 wastewater	8.91	89.2	ND
	Plant 3 wastewater	8.30	54.7	ND
Refinery 2	Plant 2 wastewater	8.45	47.1	ND
	Plant 3 wastewater	6.86	50.4	ND
Refinery 3	Plant 1 wastewater	7.24	46.1	ND
	Plant 2 wastewater	7.52	100.7	ND
Refinery 1	Mud wash water	7.65	1817.4	ND
Refinery 2	Mud wash water	7.35	1578.4	ND

Mean (n=2)

ND = Non detectable, Limit of detection for mercury was 0.003 μg/mL or 0.003 ppm.

Limit of detection (LOD) was determined by measuring ten samples of blank and calculated from:

$$\text{signal}_{\text{LOD}} = \text{signal}_{\text{blank}} + 3\ (\text{S.D. of signal blank})$$

Then the signal of LOD was compared to working standard curve. Limit of detection for mercury in our experiments was 0.003 μg/mL or 0.003 ppm.

The result of mercury adsorption show the high percentage of mercury removal and the concentration of mercury(II) ions after completed adsorption had lower than the limit of detection in all sample. The results confirms that MP-MCM-41 could be applied to remove mercury(II) ions in the real wastewater from refinery.

CHAPTER V

CONCLUSION

3-mercaptopropyl modified MCM-41 (MP-MCM-41) were successfully synthesized by three synthesis methods; (i) Conventional hydrothermal templated sol-gel method, (ii) Original stepped template sol-gel method, and (iii) Grafting method that was divided into *Graft-con* method and *Graft-step* method. The adding amount of ligand 3-mercaptopropyl trimethoxysilane (MPTMS) was varied. The efficiency of the method in ligand loading on the adsorbents was evaluated and compared using loading capacity of the obtained MP-MCM-41. In the same range of adding amount of MPTMS, the efficiency of the method in ligand loading followed the order *Con* method > *Graft* method using MCM-41 (*Step*) > *Step* method > *Graft* method using MCM-41 (*Con*).

All the obtained MP-MCM-41 were characterized by X-ray diffraction spectroscopy, fourier transform infrared spectroscopy, surface area analysis and thermal analysis. The results from all techniques confirmed that MCM-41 could be modified with MPTMS and the hexagonal ordered structure was preserved. The adsorption efficiency of the obtained products were evaluated and compared. The order of adsorption efficiency of products followed MP-MCM-41 (*Graft-step*) > MP-MCM-41 (*Graft-con*) > MP-MCM-41 (*Step*) > MP-MCM-41 (*Con*).

The most suitable method for synthesis of the adsorbent was chosen based on the following features: (i) the method should yield the adsorbents that have high adsorption capacity with reasonable amount of ligand loading and (ii) its crystalline structure is still preserved. Thus, the most suitable method for synthesis the adsorbents for mercury(II) ions adsorption in solution is *Graft* method using MCM-41 (*Step*)

The suitable condition for mercury(II) ions adsorption of MP-MCM-41 using batch system were pH of solution at 5 – 8. The adsorption equilibrium could be obtained after 20 min of contact time. The adsorption behavior of mercury on MP-MCM-41 at equilibrium could be described as monolayer adsorption according to Langmuir isotherm model. MP-MCM-41 prepared by (*Graft-step*) method with adding amount of 13.39 mmol MPTMS/MCM-41 had the maximum adsorption capacity of 1.25 mmol/g. By comparison with the other researches, the adsorption capacity of the MP-MCM-41 (*Graft-step*) in this thesis is higher than those of SBA-15 [10, 11, 98], activated carbon [77, 78, 79, 99], clay [73, 74, 84, 86, 93, 100] and close to some of chelating resins [54, 80, 81, 101].

Furthermore, the presence of Cl^- (0.1 and 1.0 M) obviously reduced the mercury(II) removal efficiency of MP-MCM-41while NO_3^- and SO_4^{2-} had less affected. This material could be reused at lease 4 cycles with good adsorption efficiency for mercury(II) ions. Finally, the obtained MP-MCM-41 was successfully applied to remove mercury from wastewater collected from refinery processes.

Suggestions for future work

- MP-MCM-41 from (*Graft-step*) synthesis method which is proved to be the best synthesis method in this thesis should be applied to remove other metal ions (i.e. Pd^{2+}, Cd^{2+}, Cr^{2+}, Fe^{2+}, Ag^{2+}) from wastewater.
- MP-MCM-41 should be used in the removal of metal ions from other wastewater sources (such as pharmaceutical wastewater, metal fused industrial wastewater, paper and paint industrial wastewater, tap water, etc.) and the effect of heavy metal ions and cations on metal adsorption should be further studied.
- MP-MCM-41 has high affinity towards mercury(II) ions. Then, it may be applied to prepare the sensor for mercury(II) ions detection.

REFERENCES

[1] Information analyzed division, Information service department, Food institute, Hazardous in Food. May (2004): 44–46.

[2] Berglund F. and Bertin M. Chemical Fallout. Thomas Publishers, Springfield (1969).

[3] Autumphurgpon W. Bangkok field survey 1997: Total explolation and production Thailand. Environmental Field Survey, Marine Environmental Mercury Expert Panel, (1997).

[4] Pollution from sea division, The ministry of science technology and environment, The report meeting of management for following after and verify of mercury problem. 3rd ed. Quality water management division, Pollution control department, Bangkok, (2002).

[5] Wastewater quality standards[Online]. Pollution control Department, Ministry of Natural Resources and Environment. Available from: http://www.pcd.go.th/info_serv /reg_ std_water04.html [2008, August 8]

[6] Drinking water quality standards[Online]. Pollution control Department, Ministry of Natural Resources and Environment. Available from: http://www.pcd.go.th/info_serv/reg_ std_water01.html [2008, August 8]

[7] Murphy J., Jones P. and Hill S.J. Determination of total mercury in environmental and biological samples by flow injection cold vapour atomic absorption spectrometry. Spectrochimica Acta Part B 51 (1996): 1867–1873.

[8] Manohar D.M., Anoop Krishnan, K., and Anirudhan T.S. Removal of mercury(II) from aqueous solutions and chlor-alkali industry wastewater using 2-mercapto benzimidazole-clay. Water Res. 36 (2002): 1609–1619.

[9] Antochshuk J.V., Jaroniec M., Olkhovyk O., Park I.S. and Ryoo R. Benzoyl thiourea-modified mesoporous silica for mercury(II) removal. Langmuir 19 (2003**):** 3031–3034.

[10] Sierra I., Perez Q. D., and Hierro I.D. Mesoporous silica functionalized with 2-mercaptopyridine: synthesis, characterization and employment for Hg(II) adsorption. J. Micropor. Mesopor. Mater. 89 (2006): 58–68.

[11] Sierra I., Perez Q.D., Hierro I.D., and Fajardo M. 2-Mercaptothiazoline modified mesoporous silica for mercury removal from aqueous media. J. Hazard. Mater. B. 134 (2006): 245–256.

[12] Cestari A. R., Vieira E. F.S., and Lopes E.C.N. Kinetics and equilibrium parameters of Hg(II) adsorption on silica–dithizone. J. Colloid Interface Sci. 272 (2004): 271–276.

[13] Alcantara E.F.C., Rodrigues D.V., and Evangelista S.M. Modification of silica gel by attachment of 2-mercaptobenzimidazole for use in removing Hg(II) from aqueous media: A thermodynamic approach. J. Colloid Interface Sci. 311 (2007): 1–7.

[14] Bektas S., Genc O., Arpa C., Bayramoglu G., and Arıca M.Y. Selective recovery of mercury by Procion Brown MX 5BR immobilized poly(hydroxyethyl methacrylate/ chitosan) composite membranes. Hydrometallurgy 67 (2002): 53–62.

[15] Beck J.S., Vartuli J.C., Roth W.J., and Leonowicz M.E. A new family of mesoporous molecular sieves prepared with liquid crystal templates. J. Am. Chem. Soc. 114 (1992): 10834–10843.

[16] Zhang C., Zhou W., and Liu S. Synthesis and characterization of organo functionalized MCM-41 by the original stepped templated sol-gel technology. J. Phys. Chem. 109 (2005): 24319–24325.

[17] Puanngam M. and Unob F. Preparation and use of chemically modified MCM-41 and silica gel as selective adsorbents for Hg(II) ions. J. Hazard. Mater. 154 (2008): 578–587.

[18] Chen H. and Wang Y. Preparation of MCM-41 with high thermal stability and complementary textural porosity. J. Ceramics Inter. 28 (2002): 541–547.

[19] Nie Z., Wei Q., Hao Y., Chen Z., Zou J. and Wang W. Direct synthesis of thiol-ligands-functionalized SBA-15: Effect of 3-mercaptopropyltrimethoxysilane concentration on pore structure. Mater. Lett. 59 (2005): 3611–3615.

[20] Kresge C.T., Leonowicz M.E., Roth W.J., Vartuli J.C. and Beck J.S. Ordered mesoporous molecular sieves synthesized by a liquid-crystal template mechanism. Nature. 359 (1992): 710–712.

[21] Molecule of the month MCM-41[Online]. Available from: www.chm.bris.ac.uk/motm/mcm41mcm41.html [2008, October 31]

[22] Rogerio A.A., Marcus V., Joao R. and Ernesto A. MCM-41 ordered mesoporous molecular sieves synthesis and characterization. Mat. Res. 2(1999): 1516–1439.

[23] Ciesla U. and Schuth F. Ordered mesoporous materials. J. Micropor. Mesopor. Mater. 27 (1999): 131–149.

[24] Hagen J. Industrial Catalysis. New York, Weinheim Wiley, 1999.

[25] Vartuli J.C., Kresge C.T., Roth W.J., McCullen S.B., Beck J.S., Schmitt K.D., Leonowicz M.E., Lutner J.D. and Sheppard E.W. Designed Synthesis of Mesoporous Molecular Sieve Systems Using Surfactant-Directing Agents. Advan. Cat. & Nano. Mater. Mobil Research and Development Corporation Central Research Laboratory, Princeton, New Jersey.

[26] Soler-Illia G.J.A.A., Sanchez C., Lebeau B. and Patarin J. Chemical strategies to design textured materials : from microporous and mesoporous oxides to nanonetworks and hierarchical structures. Chem. Rev. 102 (2002): 4093.

[27] Tanev P.T. and Pinnavania T.J. Mesoporous silica molecular sieves prepared by ionic and neutral surfactant templating: a comparison of physical properties. Chem. Mater. 8 (1996): 2068–2079.

[28] Simulations of sol gel materials[Online]. Gelb research group, Washington University, St. Louis. Available from: www.chemistry.wustl.edu/~gelb/solgel.html [2009, June 18]

[29] Lin H.P., Kao C.P. and Mou C.Y. Counterion and alcohol effect in the formation of mesoporous silica. J. Micropor. Mesopor. Mater. 48 (2001): 135–141.

[30] Ying J.Y., Mehnert C.P. and Wong M.S. Synthesis and applications of supramolecular-templated mesoporous materials. Angew. Chem. Int. Ed. 38 (1999): 56.

[31] Igarashi N., Hashimoto K. And Tatsumi T. Studies on the structural stability of mesoporous molecular sieves organically functionalized by a direct method. J. Mater. Chem. 12 (2002): 3631–3636.

[32] Lu X.B. Removal of the template molecules from MCM-41 with supercritical fluid in a flow apparatus. Ind. Eng. Chem. Res. 42 (2003): 653–656.

[33] Zhao D., Feng J., Hua Q., Malosh N., Fredrickson G.H., Chmelka B.F. and Stucky G.D. Triblock copolymer syntheses of mesoporous silica with periodic 50 to 300 angstrom pores. Science 279 (1998): 548.

[34] Ying J. and Mehnert C. Palladium grafted mesoporous MCM-41 material as heterogeneous catalyst for Heck reactions. Chem. Commun. (1997): 2215.

[35] Lim M.H., Blanford C.F. and Stein A. Synthesis of ordered microporous silicates with organosulfur surface groups and their applications as solid acid catalysts. Chem. Mater. 10 (1998): 467–470.

[36] Yoshitake H., Yokoi T. and Tatsumi T. Adsorption behavior of arsenate at transition metal cations captured by amino-functionalized mesoporous silicas. Chem. Mater. 15 (2003): 1713–1721.

[37] Zhang H.J., Li H.R., Lin J., Fu L.S., Guo J.F., Meng Q.G. and Liu F.Y. Phenanthroline-functionalized MCM-41 doped with europium ions. Micropor. Mesopor. Mater. 55 (2002): 103–107.

[38] Huang L., Xiao H. and Ni Y. Cationic MCM-41: synthesis, characterization and sorption behavior towards aromatic compounds. Colloid and Surf. A. Phys. Eng. 247 (2004): 129–136.

[39] Mark Wilhelm S., Liang L. and Kirchgessner D. Identification and properties of mercury species in crude oil. Energy & Fuels 20 (2006): 180–186.

[40] Lenihan J.W. and Fletcher W.W. The chemical environmental. Environ. & Man. 6 (1977).

[41] Mercury element[Online] The free encyclopedia, Wikipedia. Available from: http://en.wikipedia.org/wiki/Mercury_(element) [2009, June 20]

[42] Yan T.Y. Method for removing mercury from hydrocarbon oil by high temperature reactive adsorption. U.S. Patent. 4909926 (1990).

[43] Sarrazin P. Processes prevent detrimental effects from As and Hg in feed stocks. J. Oil Gas 4 (1993): 86–90.

[44] Yan T.Y. Use of dilute aqueous solutions of alkali polysulfides to remove trace amounts of mercury from liquid hydrocarbons. U.S. Patent. 4915818 (1990).

[45] Wilhelm S.M., Liang L., Cussen D. and Kirchgessner D.A. Mercury in crude oil processed in the united states (2004). Environ. Sci. Technol. 41 (2007): 4509–4514.

[46] Wilhelm S.M. and Bloom N. Mercury in petroleum. Fuel pro. tech. 63 (2000): 1–27.

[47] Audeh C.A. Process for the removal of mercury from natural gas condensate. U.S. Patent 4985137. (1991).

[48] Leeper J.E. Mercury-LNG plant’s problem. Hydrocarbon pro. 59 (1980): 237–240.

[49] Using Gas Geochemistry to Assess Mercury Risk[Online] Oil tracers L.L.C. Available from: http://www.gaschem.com/mercur.html [2009, June 18]

[50] National risk management research laboratory, Research triangle park, Mercury in petroleum and natural gas estimation of emissions from production, processing and combustion. EPA Res. and develop. September 2001.

[51] Hazardous waste[Online]. U.S. Environmental Protection Agency. Available from: http://www.epa.gov/epawaste/hazard/index.html [2007, August 14]

[52] Duisters H.A.M. and Van G.C. Process for removing mercury from a non-polar organic medium. U.S. Patent. 4950408. (1990).

[53] Ho T.L. Hard and Soft Acids and Bases Principle in Organic Chemistry. New York, USA. : Academic Press, Inc., (1977).

[54] Asem A.A., Ahmed M.D. and Khalid Z.E. Selective separation of mercury (II) using a synthetic resin containing amine and mercaptan as chelating groups. Reac. & Func. Poly. 65 (2005): 267–275.

[55] Patterson J.W. Wastewater treatment technology. USA. : Ann Arbor Science Inc., (1977).

[56] Yan T.Y. Processing for removing mercury from water and hydrocarbon condensate. U.S.Patent 4962276 (1990).

[57] Bouveng H.O. Control of mercury in effluents from chlorine plants. J. Pure Appl. Chem. 29 (1979): 75–91.

[58] Perry R. Mercury recovery from contaminated wastewater and sludge. U.S. EPA-660/2-74-086 (1974).

[59] Roesmer J. Radiochemistry of mercury. NAS-NS-3026(Rev.), National academy of science-national research council, U.S. Atomic Energy Commission, (1970).

[60] Bradl H.R. Heavy metals in the environment. New York, USA. : Elsevier Academic Press, Inc., (2005).

[61] Eckenfelder W.W. Application of adsorption in wastewater treatment. Tenessee. : Enviro Press., (1981).

[62] Bohn H.L., McNeal B.L. and O'Connor G.A. Soil Chemistry. 3rd ed. New York, USA. : John Wiley & Sons. Inc., (2001).

[63] Eckenfelder W.W. Industrial water pollution control. 3rd ed. Singapore : Mc Graw-Hill book Co., (2000).

[64] Goldberg S., Criscenti L.J., Turner D.R., Davis J.A. and Cantrell K.J. Adsorption-desorption process in subsurface reactive transport modeling. Vadose Zone J. 6 (2007): 407–435.

[65] Moore D.M. and Reynolds Jr.R.C. X-Ray Diffraction and the Identification and Analysis of Clay Minerals. New York : Oxford University Press, (1989).

[66] Basic operating principles of the sorptomatic[Online] Available from: http://www.saf.chem.ox.ac.uk/Instruments/BET/sorpoptprin.html [2009, April 10]

[67] Analysis software user's manual, BELSORP, BEL Japan, Inc.

[68] Fourier transform infrared spectroscopy[Online] West coast analytical service. Available from: http://www.wcaslab.com/tech/tbftir.html [2009, May 18]

[69] Li Y.S., Wang Y., Tran T. and Perkins A. Vibrational spectroscopic studies of (3-mercaptopropyl)trimethoxylsilane sol–gel and its coating. Spectrochimica Acta Part A 61 (2005): 3032–3037.

[70] Quintanilla D.P., Sanchez A., Hierro I.D., Fajardo M. and Sierra I. Preparation, characterization, and Zn^{2+} adsorption behavior of chemically modified MCM-41 with 5-mercapto-1-methyltetrazole. J. Colloid Interface Sci. 313 (2007): 551–562.

[71] Pyris 1 TGA Thermogravimetric analyzer[Online] PerkinElmer. Available from: http://las.perkinelmer.com/Content/RelatedMaterials/ProductNotes/PRD_Pyris1TGAThermogravimetricAnalyzer [2008, December 2]

[72] Thermal gravimetric analysis[Online] Orton. Available from: http://www.simex.cm.mx [2008, December 16]

[73] Dias Filho N.L., Polito W.L. and Gushikem Y. Sorption and preconcentration of some heavy metals by 2-mercaptobenzothiazole-clay. Talanta 41 (1995): 1031-1036.

[74] Sun C., Qu R., Ji C. and Wang Q. A chelating resin containing S, N and O atoms: Synthesis and adsorption properties for Hg(II). J. Euro. Poly. 42 (2006): 188–194.

[75] Mercier L. and Detellier C. Preparation, characterization and application as heavy metals sorbents of covalently grafted thiol functionalities on the interlamellar surface of montmorillonite. Environ. Sci. Technol. 29 (1995): 1318–1323.

[76] Mercier L. and Pinnavaia T.J. A functionalized porous clay heterostructure for heavy metal ion (Hg^{2+}) trapping. J. Micropor. Mesopor. Mater. 20 (1998): 101–106.

[77] Tonle I.K., Ngameni E. Njopwouo D. and Walcarius A. Functionalization of natural smectite-type clays by grafting with organosilanes: physico-chemical characterization and application to mercury(II) uptake. Phys. Chem. 5 (2003): 4951–4961.

[78] Cestari A.R. and Airoldi C. Chemisorption on Thiol–Silicas: Divalent Cations as a Function of pH and Primary Amines on Thiol–Mercury Adsorbed. J. Colloid Surf. Sci. 195 (1997): 338–342.

[79] Vieira E.F.S., Simony J.A. and Airoldi C. Interaction of cations with SH-modified silica gel: thermochemical study through calorimetric titration and direct extent of reaction determination**.** J. Mater. Chem. **7** (1997): 2249–2252.

[80] Nam K.H., Gomez-salazar S. and Tavlarides L.L. Mercury (II) adsorption from waste waters using a thiol functional adsorption. Ind. Eng. Chem. Res. 42 (2003): 1955–1964.

[81] Krishnan K.A. and Anirudhan T.S. Removal of mercury(II) from aqueous solution and chlor-alkali industry effluent by stream activated and sulphurised activated carbons prepared from bagasse pith: kinetics and equilibrium studies. J. Hazard. Mater. 92 (2002): 161–183.

[82] Yardim M.P., Budinova T., Ekinci E., Petrov N., Razvigorova M. and Minkova V. Removal of mercury (II) from aqueous solution by activated carbon obtained from furfural. Chemosphere. 52 (2003): 835–841.

[83] Budinova T., Savova D., Petrov N., Razvigorova M., Minkova V., Ciliz N., Apak E. and Ekinci E. Mercury adsorption by different modifications of furfural adsorbent. Ind. Eng. Chem. Res. 42 (2003): 2223–2229.

[84] Denizli A., Senel S., Alsancak G., Tuzmen N. and Say R. Mercury removal from synthetic solutions using poly(2-hydroxyethylmethacrylate) gel beads modified with poly(ethyleneimine). Reat. Funct. Polym. 55 (2003): 121–130.

[85] Khan A., Mahmood F. and Ahmed S. Functional sol-gel material for extraction of mercury(II). Reac. and Func. Polym. 66 (2006): 1014–1020.

[86] Evangelista S.M., DeOliveira E., Castro G.R., Zara L.F. and Prado A.G.S. Hexagonal mesoporous silica modified with 2-mercaptothiazoline for removing mercury from water solution. Surf. Sci. 601(2007): 2194–2202.

[87] ASTM D3223-02, Standard test method for total mercury in water. ASTM International. (2002).

[88] Method 7470A. Mercury in liquid waste (manual cold-vapor technique). US EPA. (1994).

[89] ASTM F885-88, Standard test method for analyses of metals in refuse-derived fuel by atomic adsorption spectroscopy. ASTM International. (2002).

[90] Knocke W.R. and Hemphili L.H. Mercury(II) sorption by waste rubber. Water Res. 15 (1981): 275–282.

[91] Horak J. and Lindner W. Contribution of sulfonyl–aromatic and sulfonic acid–aromatic interactions in novel sulfonyl/sulfonic acid-embedded reversed phase materials. J. Chromatogr. A, 1191 (2008): 141–156.

[92] Dean J.A. Lange's Handbook of Chemistry. 13th ed. Singapore : McGraw-Hill Book Co., (1987).

[93] Sarkar D., Essington M.E. and Misra K.C. Adsorption of mercury(II) by kaolinite. Soil Sci. Soc. Am. J. 64 (2000): 1968–1975.

[94] Langmuir I. The adsorption of gases on plane surfaces of glass, mica and platinum. J. Am. Chem. Soc. 40 (1918) 1361–1403.

[95] Hall K.R., Eagleton L.C., Acrivos A., and Vermeulen T. Pore- and solid-diffusion kinetics in fixed-bed adsorption under constant-pattern conditions. Ind. Eng. Chem. Fundam. 5 (1966): 212–223.

[96] Vadivelan V. and Vasanth Kumar K. Equilibrium, kinetics, mechanism, and process design for the sorption of methylene blue onto rice husk. J. Colloid Interface Sci. 286 (2005): 90–100.

[97] Freundlich H.M.F. Over the adsorption in solution. J. Phys. Chem. 57 (1906): 385–470.

[98] Luan Z., Fournier J. A., Wooten J. B., Miser D. E. and Chang M. J. Functionalized mesoporous SBA-15 silica molecular sieves with mercaptopropyl groups: Preparation, characterization and application as adsorbents. Surf. Sci. and Cat. 156 (2005): 897–906.

[99] Kadirvelu K. and Rajagopal C. Sorption of lead, mercury and cadmium ions in multi-component system using carbon aerogel as adsorbent. J. Hazard. Mater. 153 (2008): 502–507.

[100] Hameed B.H. Equilibrium and kinetics studies of 2,4,6-trichlorophenol adsorption onto activated clay. Colloid and Surf. A. Phys. Eng. 307 (2007): 45–52.

[101] Sonmez H.B. and Bicak N. An alternative approach for grafting of acrylate esters from crosslinked polystyrene beads by ATRP and their modification for selective mercury extraction. React. Func. Polym. 61 (2004): 33–41.

[102] Zheng F. and Hu B. MPTS-silica coated capillary microextraction on line hyphenated with inductively coupled plasma atomic emission spectrometry for the determination of Cu, Hg and Pb in biological samples. Talanta 73 (2007) 372–379.

[103] Huang C. and Hu B. Silica-coated magnetic nanoparticles modified with γ-mercaptopropyltrimethoxysilane for fast and selective solid phase extraction of trace amounts of Cd, Cu, Hg, and Pb in environmental and biological samples prior to their determination by inductively coupled plasma mass spectrometry. Spectro. Acta B. 63 (2008): 437–444.

APPENDIX

Experimental Data

Table A1 Physical parameters of MCM-41 and MP-MCM-41 adsorbents measured by N_2 adsorption-desorption isotherms

		BET result		
Sample	**Adding reagent**	**Surface area** (BET) (m^2/g)	**Total Pore volume** (cm^3/g)	**Pore diameter** (nm)
normal MCM-41 (*Step*)		1296	1.16	4.1
MP-MCM-41 (*Step*)	5 %mol TEOS	831	0.64	3.3
MP-MCM-41 (*Graft-step*)	4.46 mmol MPTMS/g	815	0.61	3.2
normal MCM-41 (*Con*)		906	0.80	3.7
MP-MCM-41 (*Con*)	5 %mol TEOS	843	0.71	3.5
MP-MCM-41 (*Graft-con*)	4.46 mmol MPTMS/g	842	0.70	3.4
normal MCM-41 (*Step*)		1251	0.99	3.9
MP-MCM-41 (*Step*)	10 %mol TEOS	759	0.57	2.9
MP-MCM-41 (*Graft-step*)	8.93 mmol MPTMS/g	750	0.55	2.9
normal MCM-41 (*Con*)		887	0.78	3.6
MP-MCM-41 (*Con*)	10 %mol TEOS	794	0.60	3.0
MP-MCM-41 (*Graft-con*)	8.93 mmol MPTMS/g	787	0.58	2.9
normal MCM-41 (*Step*)		1058	0.81	3.8
MP-MCM-41 (*Step*)	15 %mol TEOS	701	0.53	2.6
MP-MCM-41 (*Graft-step*)	13.93 mmol MPTMS/g	691	0.53	2.5
normal MCM-41 (*Con*)		858	0.76	3.6
MP-MCM-41 (*Con*)	15 %mol TEOS	728	0.54	2.7
MP-MCM-41 (*Graft-con*)	13.93 mmol MPTMS/g	713	0.53	2.6
normal MCM-41 (*Step*)		963	0.80	3.7
MP-MCM-41 (*Step*)	20 %mol TEOS	670	0.35	2.1
MP-MCM-41 (*Graft-step*)	17.86 mmol MPTMS/g	514	0.32	1.9
normal MCM-41 (*Con*)		857	0.73	3.5
MP-MCM-41 (*Con*)	20 %mol TEOS	690	0.43	2.2
MP-MCM-41 (*Graft-con*)	17.86 mmol MPTMS/g	685	0.36	2.1

Mean (n=2)

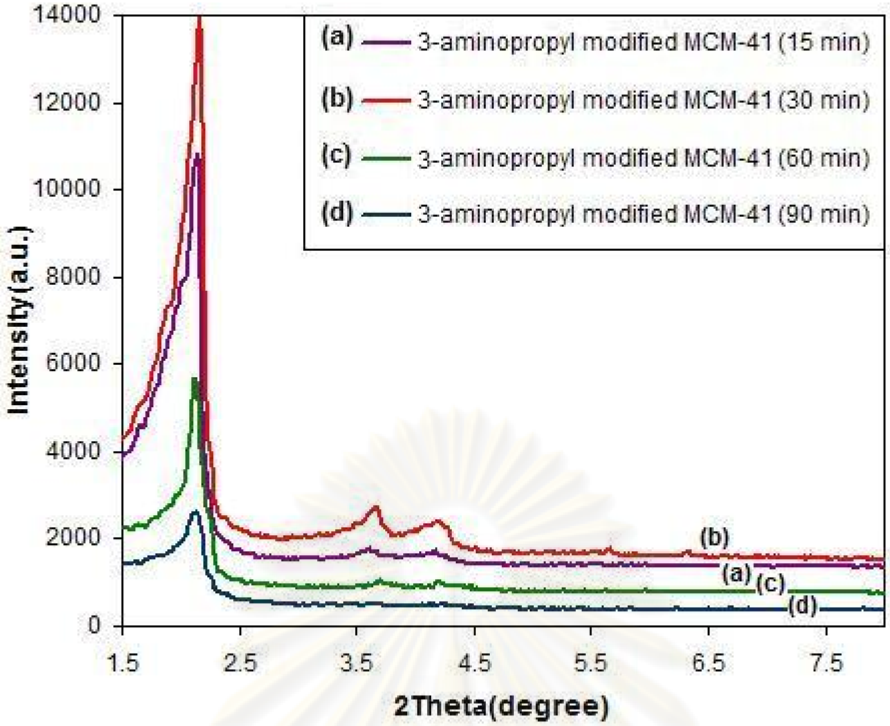


Figure A1 XRD patterns of 3-aminopropyl modified MCM-41 (*Step*) by variation of stirring time for gel formation (a) 15 min, (b) 30 min, (c) 60 min, and (d) 90 min.

In this study, 3-aminopropyl modified MCM-41 was synthesized by *Step* method and prepared by adding 3-aminopropyltriethoxysilane 10 %mol APTES/ APTES+TEOS. The stirring time for gel formation was varied (15, 30, 60, 90 min). The AP-MCM-41 prepared by using 30 min of the stirring time for gel formation showed the highest order of crystallinity of the product. Then, the stirring time for gel formation of 30 min was used for synthesis of the adsorbents by *Step* method in this thesis.

TGA curve of adsorbents which were varied the adding amount of MPTMS from three synthesis methods

Figure A2 TGA curves of normal MCM-41from ***Con*** method **when template was not removed**.

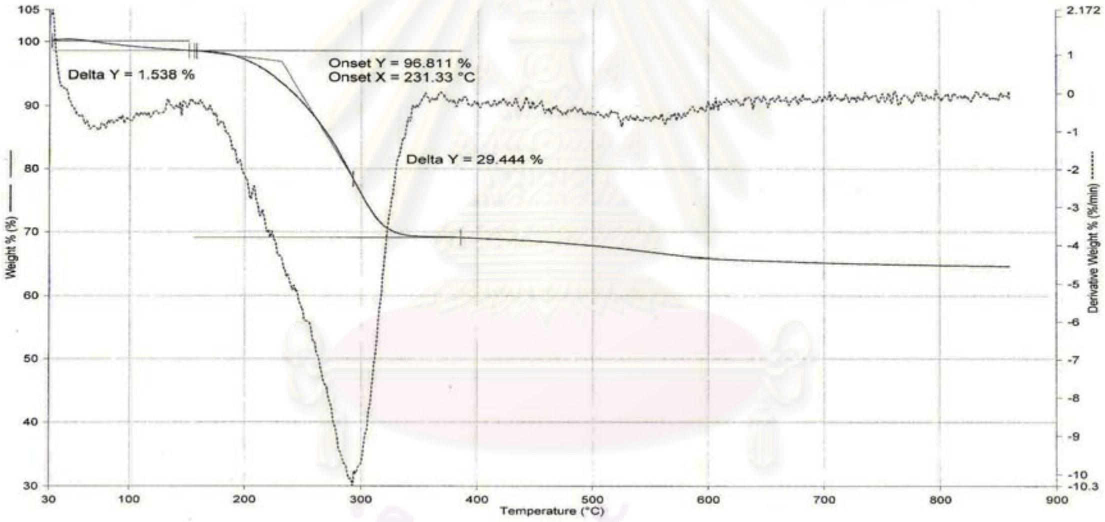


Figure A3 TGA curves of normal MCM-41 from ***Step*** method **when template was not removed**.

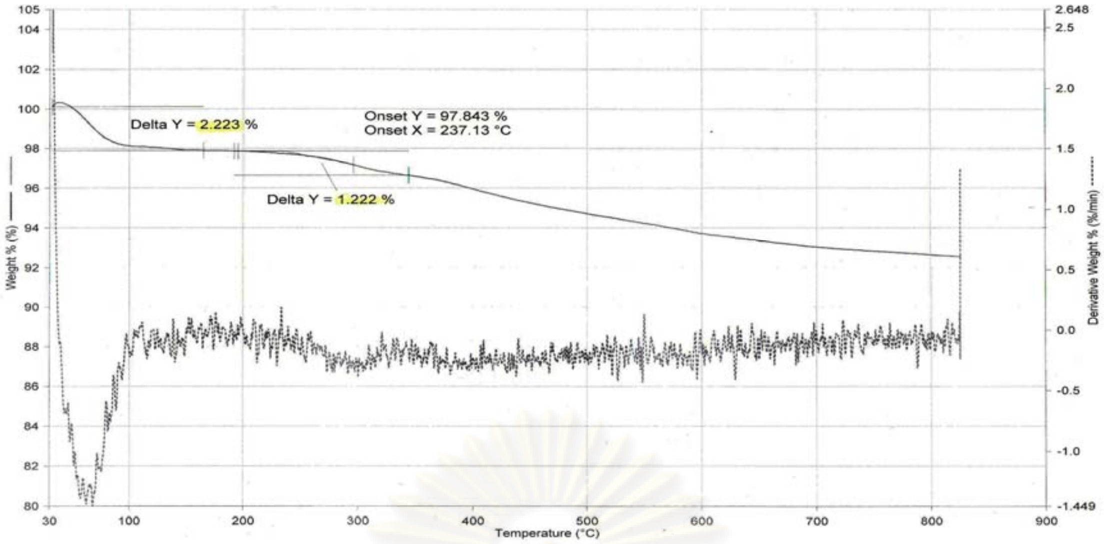


Figure A4 TGA curves of normal MCM-41 from ***Con*** method.

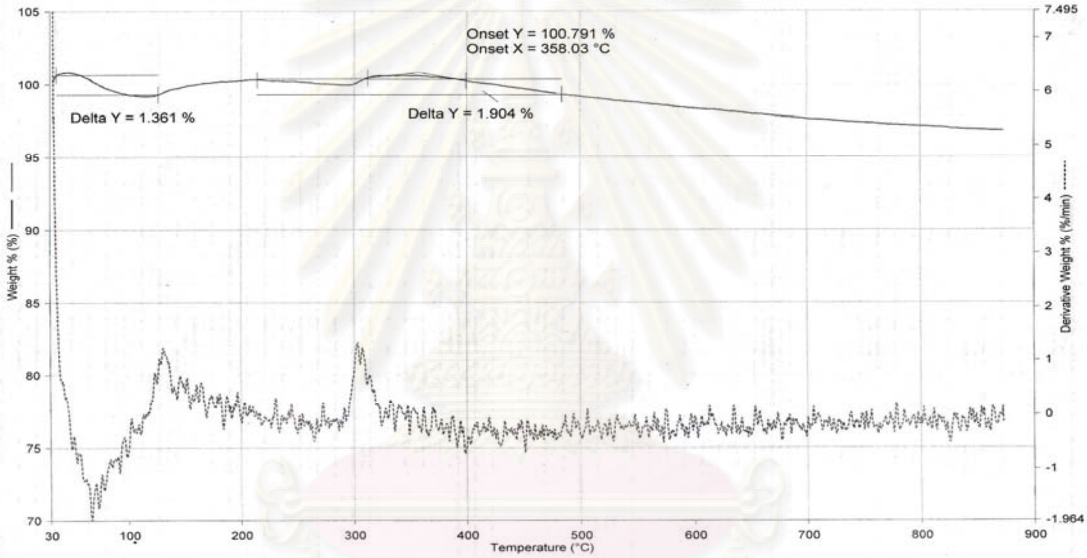


Figure A5 TGA curves of normal MCM-41 from ***Step*** method.
(TEOS adding = **5 %mol** of TEOS /MPTMS+TEOS)

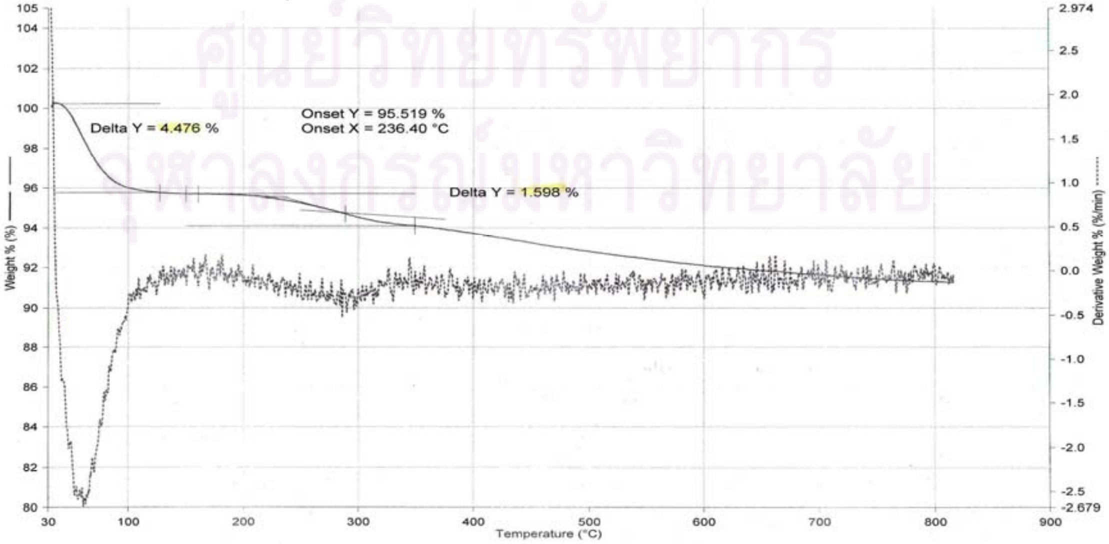


Figure A6 TGA curves of normal MCM-41 from ***Step*** method.
(TEOS adding = **10 %mol** of TEOS / MPTMS+TEOS)

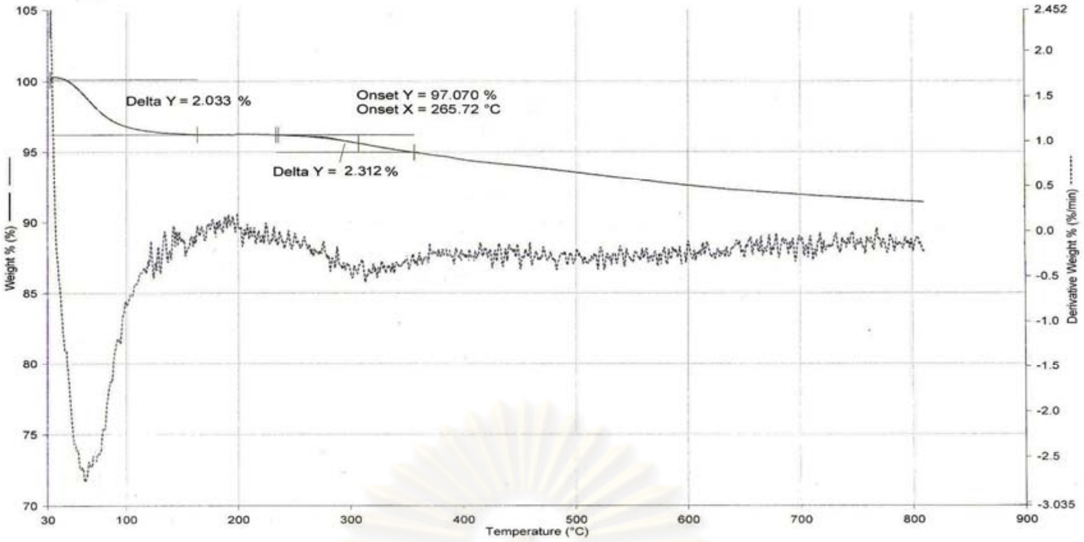


Figure A7 TGA curves of normal MCM-41 from ***Step*** method.
(TEOS adding = **15 %mol** of TEOS / MPTMS+TEOS)

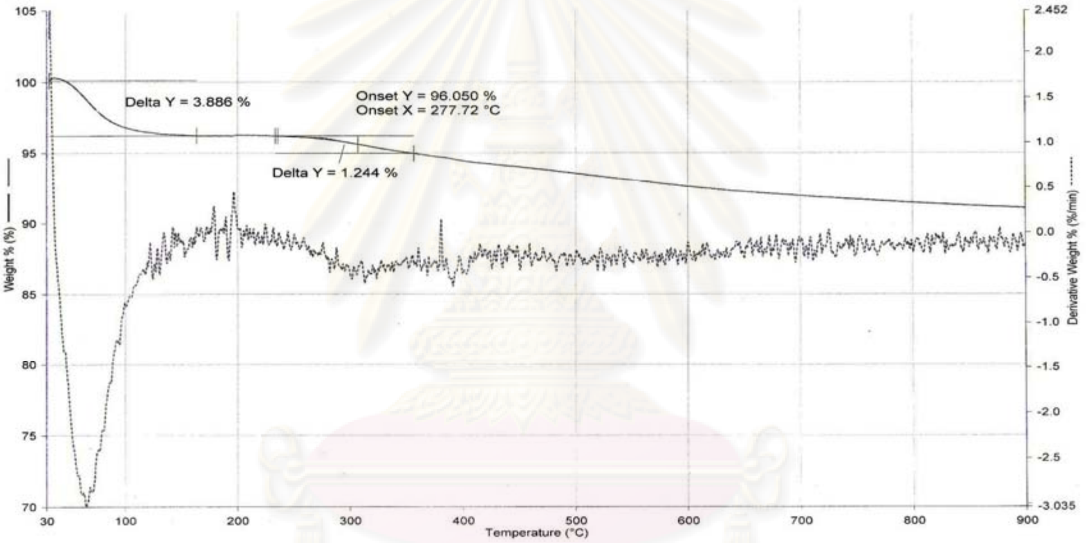


Figure A8 TGA curves of normal MCM-41 from ***Step*** method.
(TEOS adding = **20 %mol** of TEOS / MPTMS+TEOS)

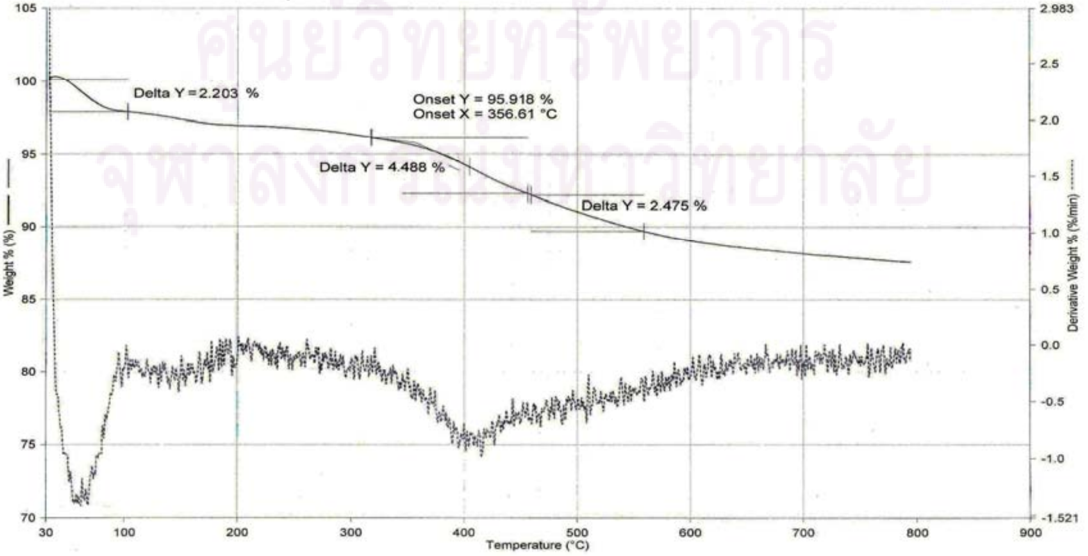


Figure A9 TGA curves of MP-MCM-41 from ***Con*** method.
(MPTMS adding = **5 %mol** of TEOS / MPTMS+TEOS)

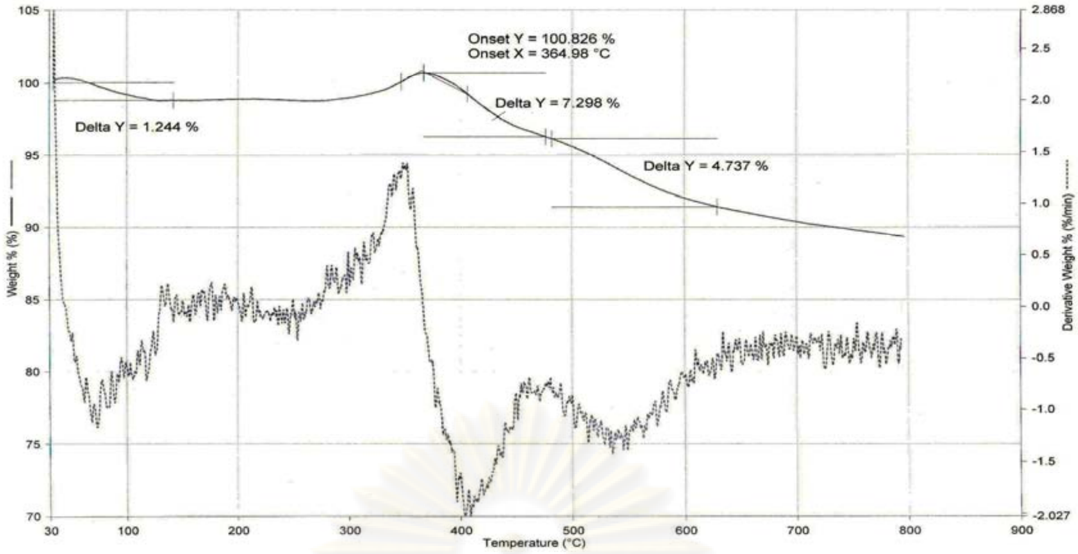


Figure A10 TGA curves of MP-MCM-41 from ***Con*** method.
(MPTMS adding = **10 %mol** of TEOS / MPTMS+TEOS)

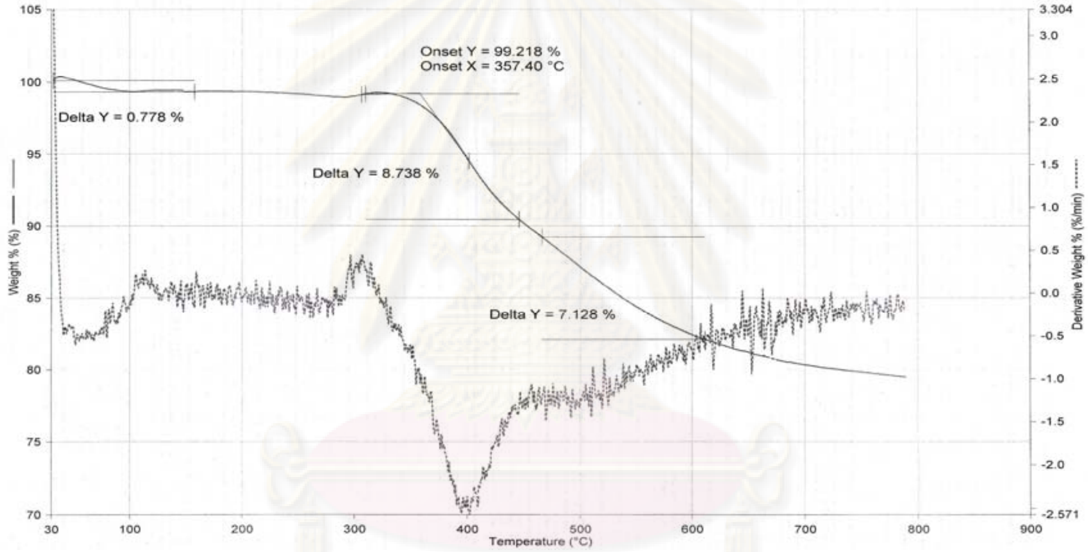


Figure A11 TGA curves of MP-MCM-41 from ***Con*** method.
(MPTMS adding = **15 %mol** of TEOS / MPTMS+TEOS)

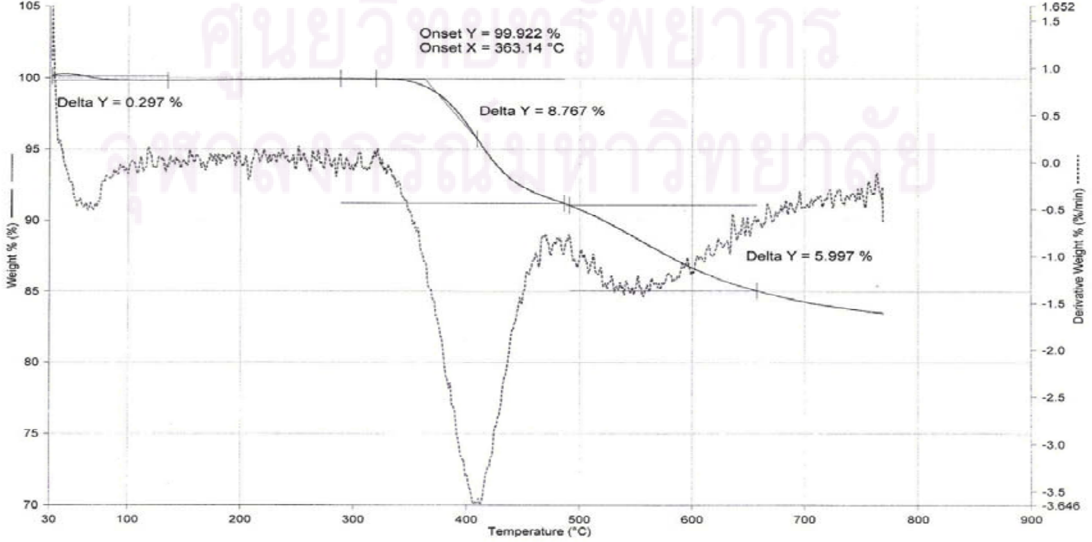


Figure A12 TGA curves of MP-MCM-41 from ***Con*** method.
(MPTMS adding = **20 %mol** of TEOS / MPTMS+TEOS)

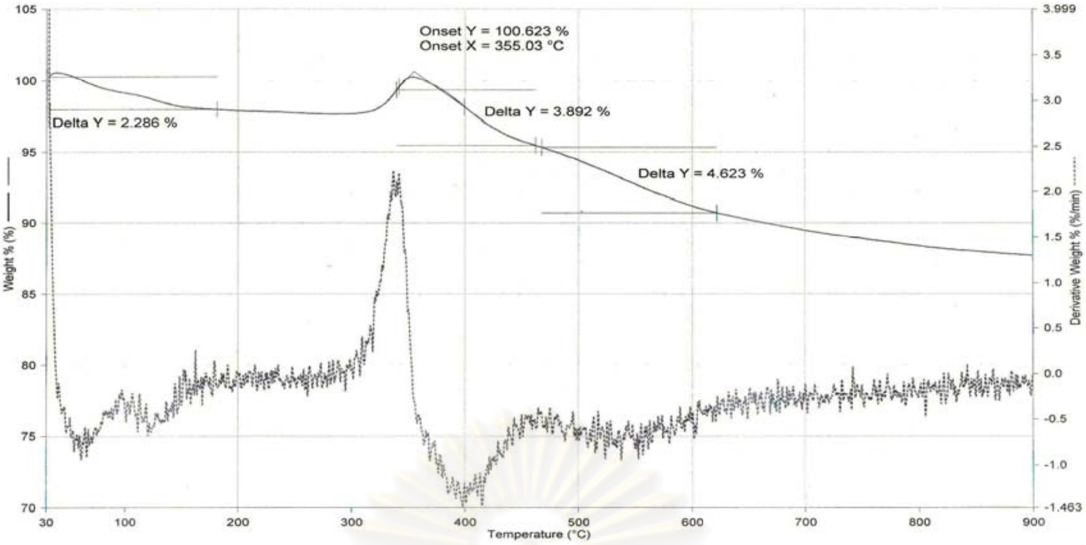


Figure A13 TGA curves of MP-MCM-41 from ***Step*** method.
(MPTMS adding = **5 %mol** of TEOS / MPTMS+TEOS)

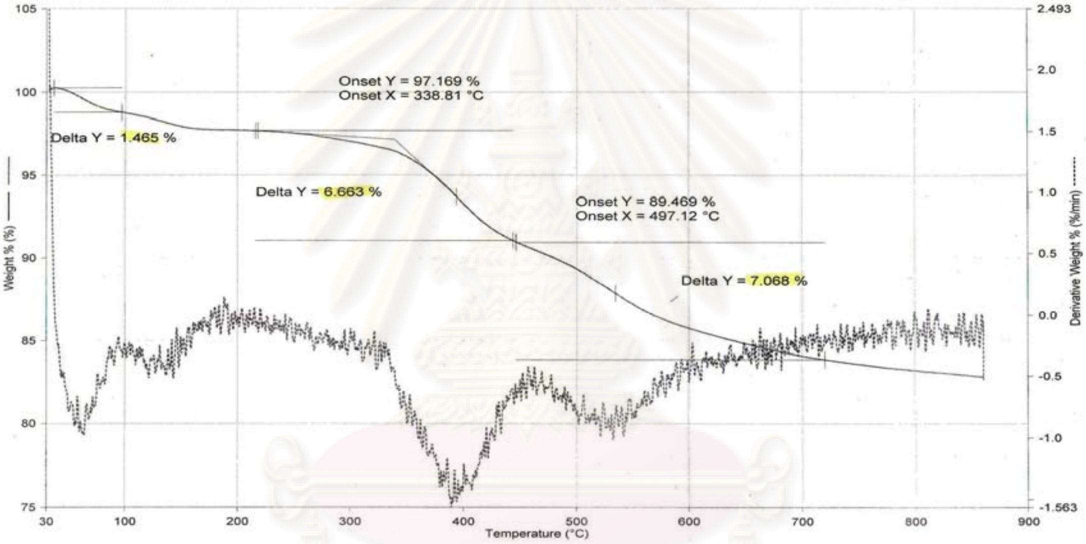


Figure A14 TGA curves of MP-MCM-41 from ***Step*** method.
(MPTMS adding = **10 %mol** of TEOS / MPTMS+TEOS)

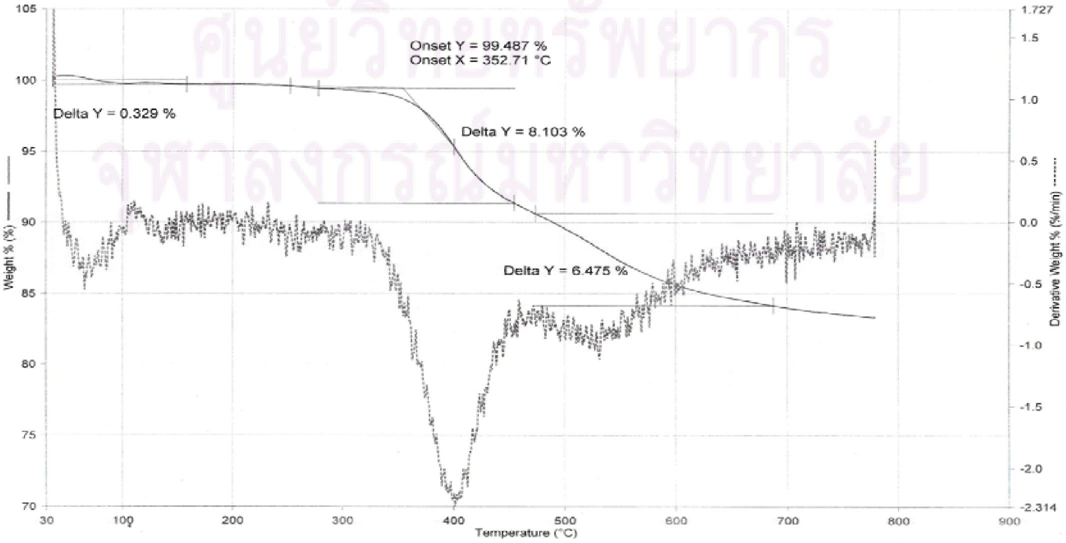


Figure A15 TGA curves of MP-MCM-41 from ***Step*** method.
(MPTMS adding = **15 %mol** of TEOS / MPTMS+TEOS)

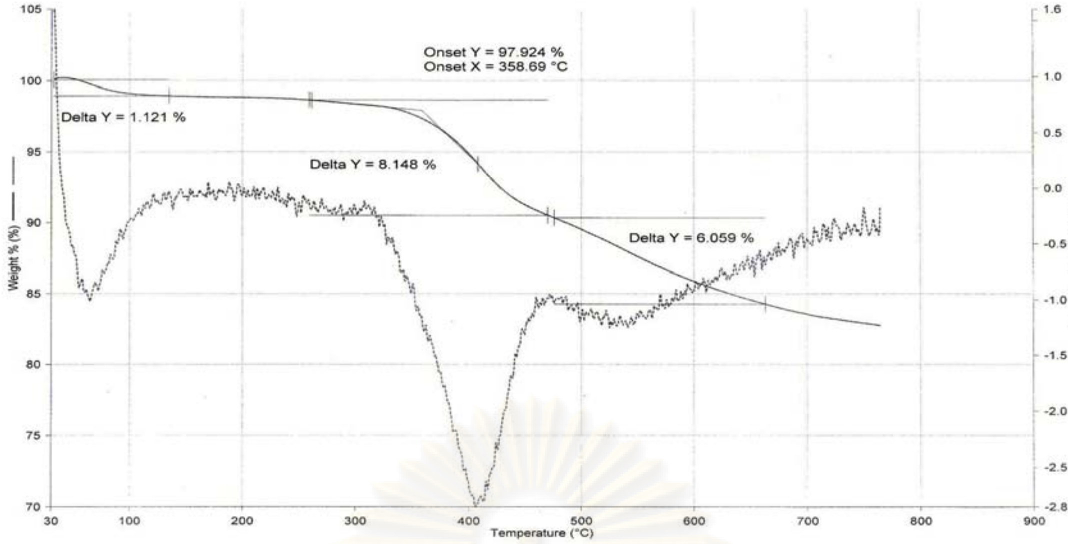


Figure A16 TGA curves of MP-MCM-41 from ***Step*** method.
(MPTMS adding = **20 %mol** of TEOS / MPTMS+TEOS)

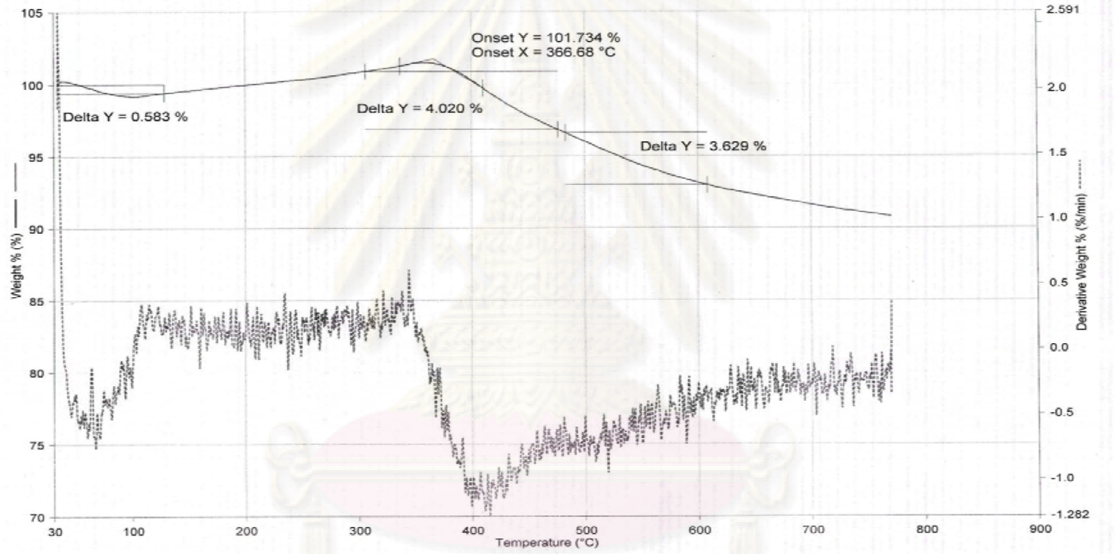


Figure A17 TGA curves of MP-MCM-41 from ***Graft-con*** method.
(MPTMS adding = **4.46 mmol** of MPTMS / 1 g MCM-41)

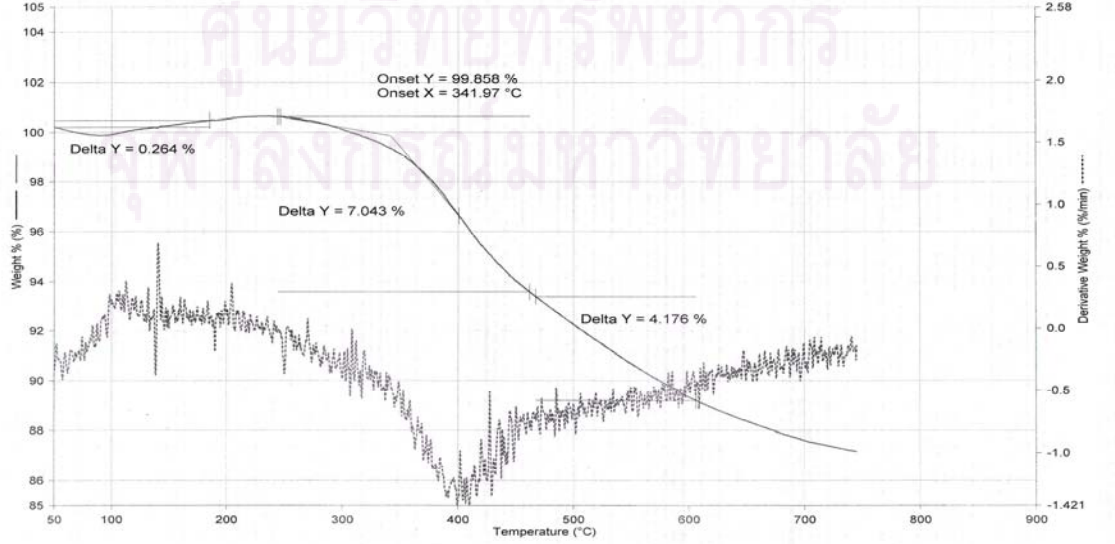


Figure A18 TGA curves of MP-MCM-41 from ***Graft-con*** method.
(MPTMS adding = **8.93 mmol** of MPTMS / 1 g MCM-41)

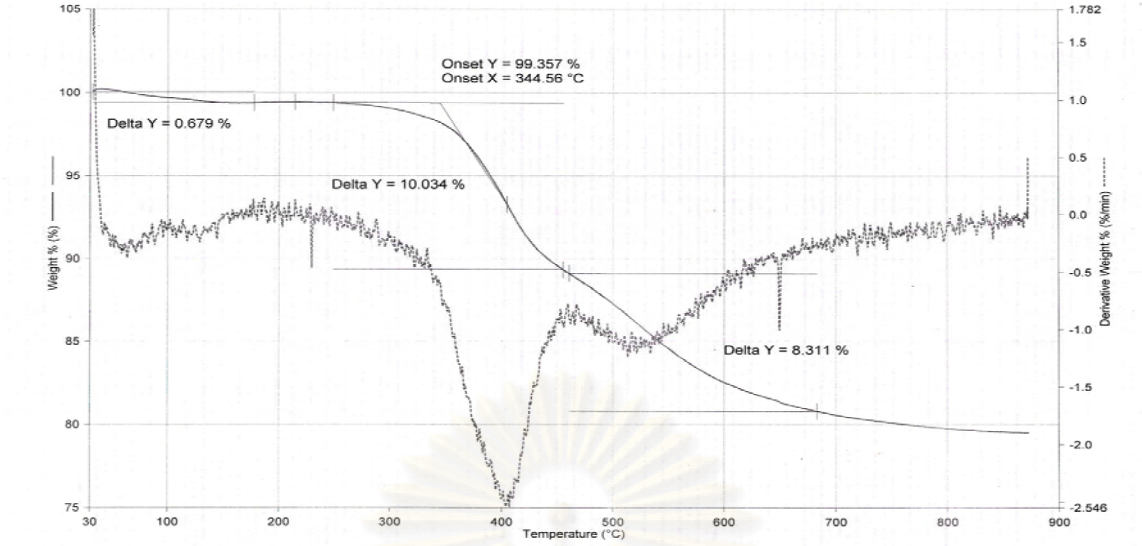


Figure A19 TGA curves of MP-MCM-41 from ***Graft-con*** method.
(MPTMS adding = **13.39 mmol** of MPTMS / 1 g MCM-41)

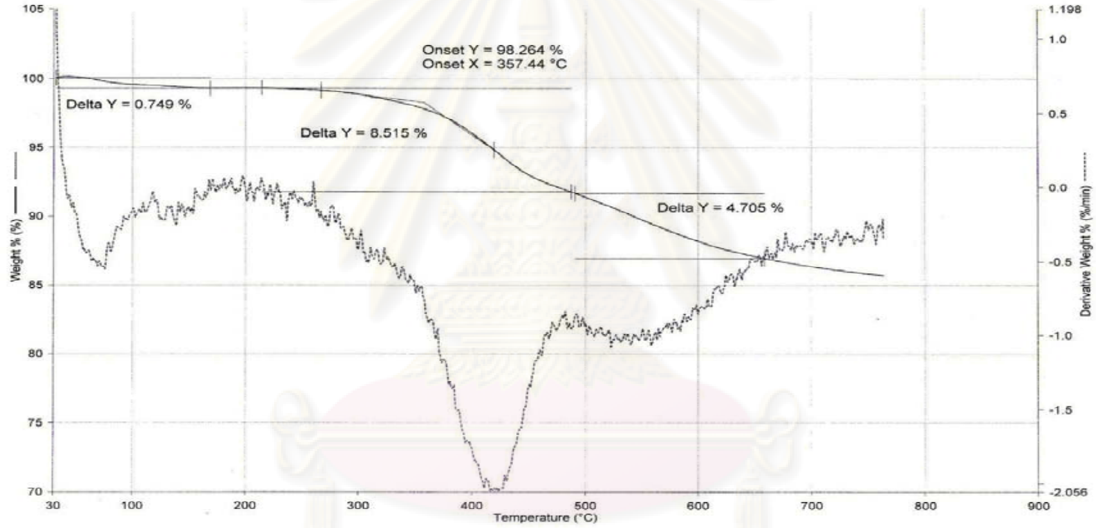


Figure A20 TGA curves of MP-MCM-41 from ***Graft-con*** method.
(MPTMS adding = **17.86 mmol** of MPTMS / 1 g MCM-41)

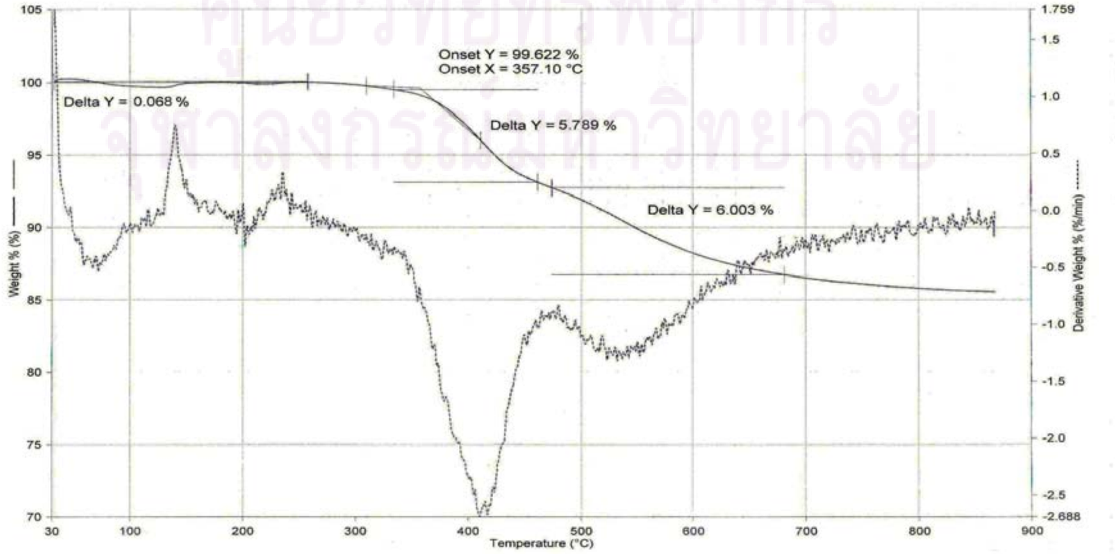


Figure A21 TGA curves of MP-MCM-41 from ***Graft-step*** method.
(MPTMS adding = **4.46 mmol** of MPTMS / 1 g MCM-41)

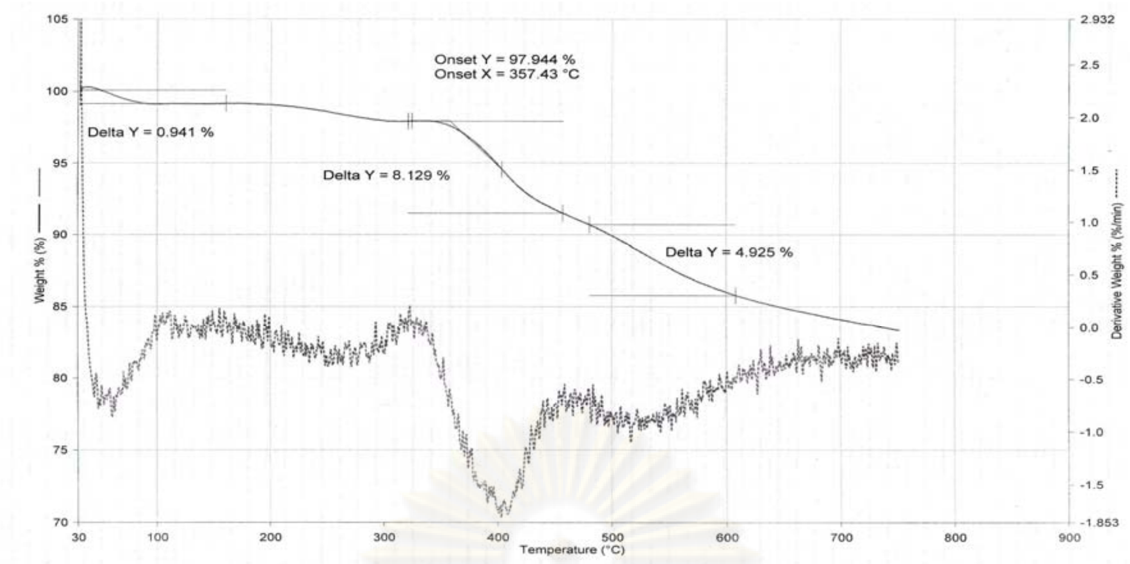


Figure A22 TGA curves of MP-MCM-41 from ***Graft-step*** method.
(MPTMS adding = **8.93 mmol** of MPTMS / 1 g MCM-41)

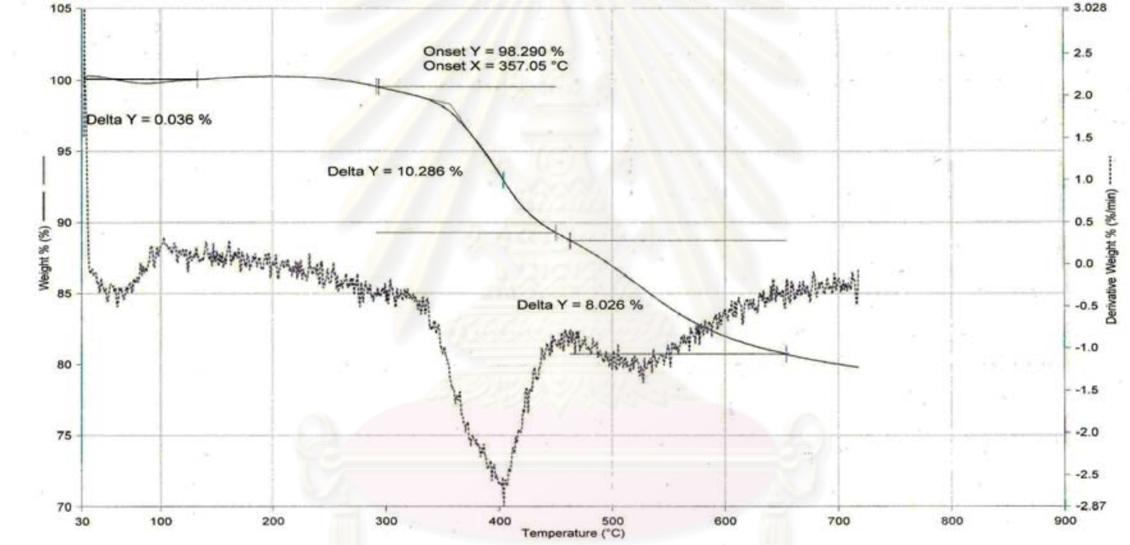


Figure A23 TGA curves of MP-MCM-41 from ***Graft-step*** method.
(MPTMS adding = **13.39 mmol** of MPTMS / 1 g MCM-41)

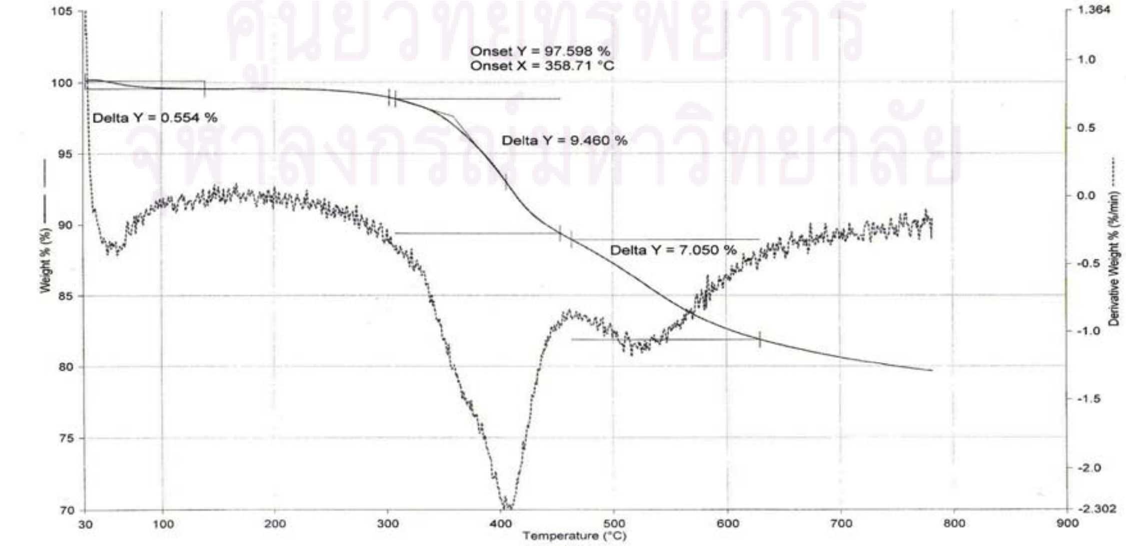


Figure A24 TGA curves of MP-MCM-41 from ***Graft-step*** method.
(MPTMS adding = **17.86 mmol** of MPTMS / 1 g MCM-41)

TGA curve of adsorbents which have the equal amount of MP on adsorbent from three synthesis methods

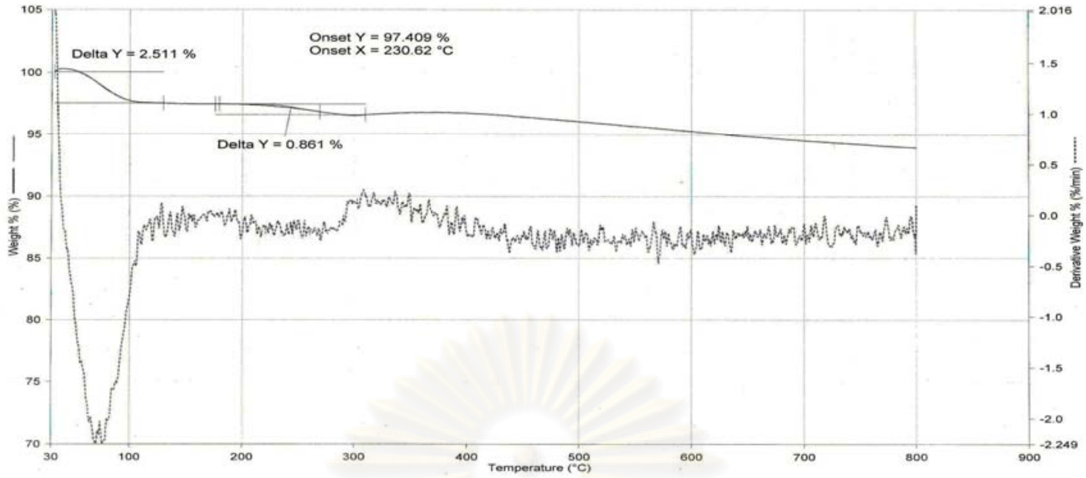


Figure A25 TGA curves of normal MCM-41 from ***Con*** method.
(TEOS adding = **10.40 %mol** of TEOS / MPTMS+TEOS)

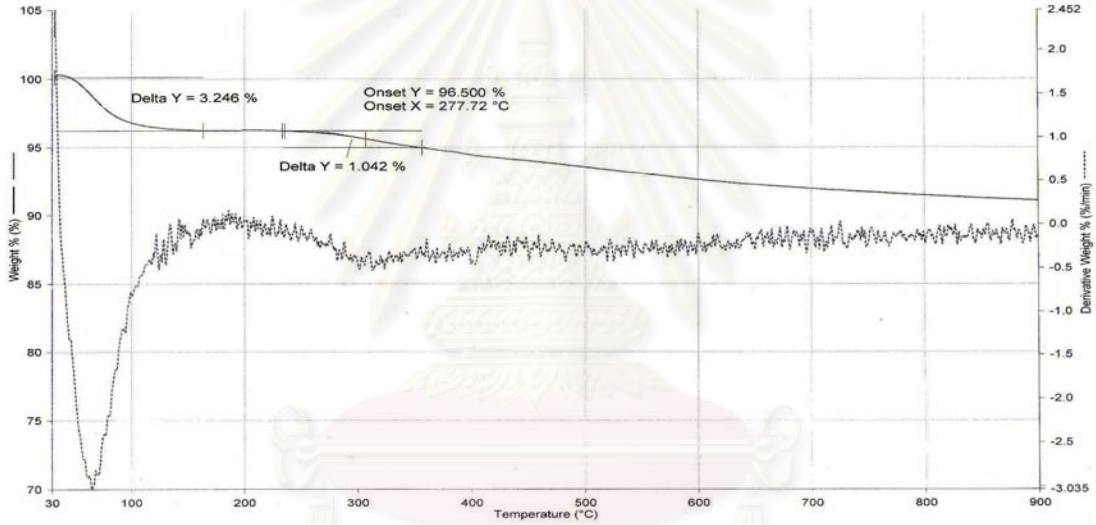


Figure A26 TGA curves of normal MCM-41 from ***Step*** method.
(TEOS adding = **12.17 %mol** of TEOS / MPTMS+TEOS)

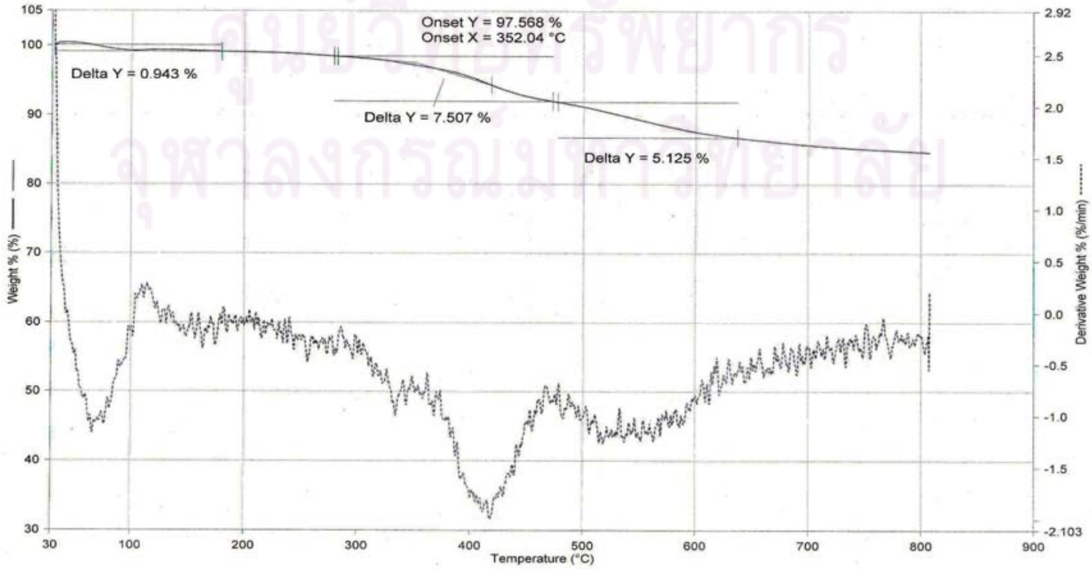


Figure A27 TGA curves of MP-MCM-41 from ***Con*** method.
(MPTMS adding = **10.40 %mol** of MPTMS / MPTMS+TEOS)

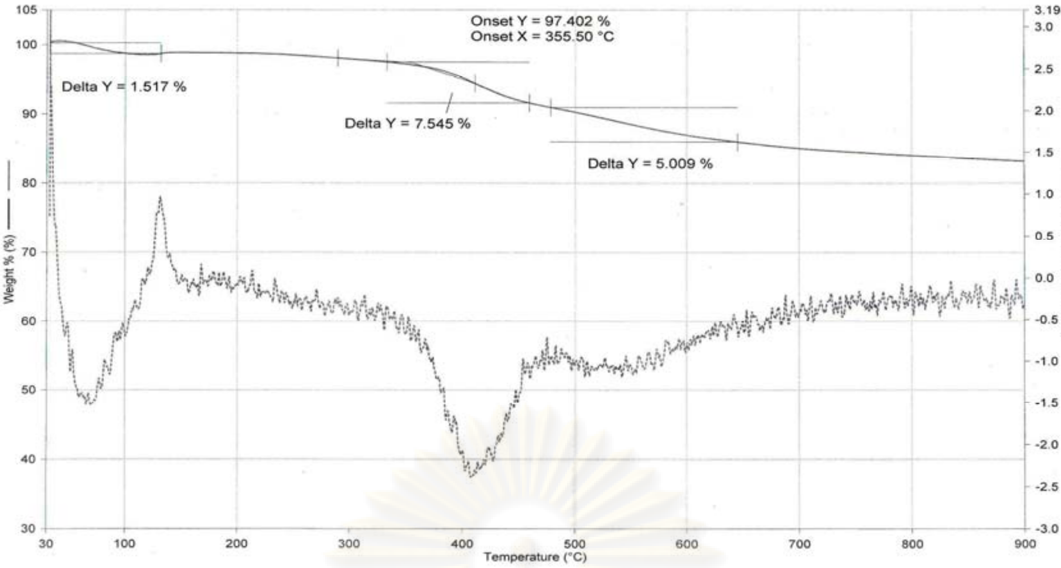


Figure A28 TGA curves of MP-MCM-41 from ***Step*** method.
(MPTMS adding = **12.17 %mol** of MPTMS / MPTMS+TEOS)

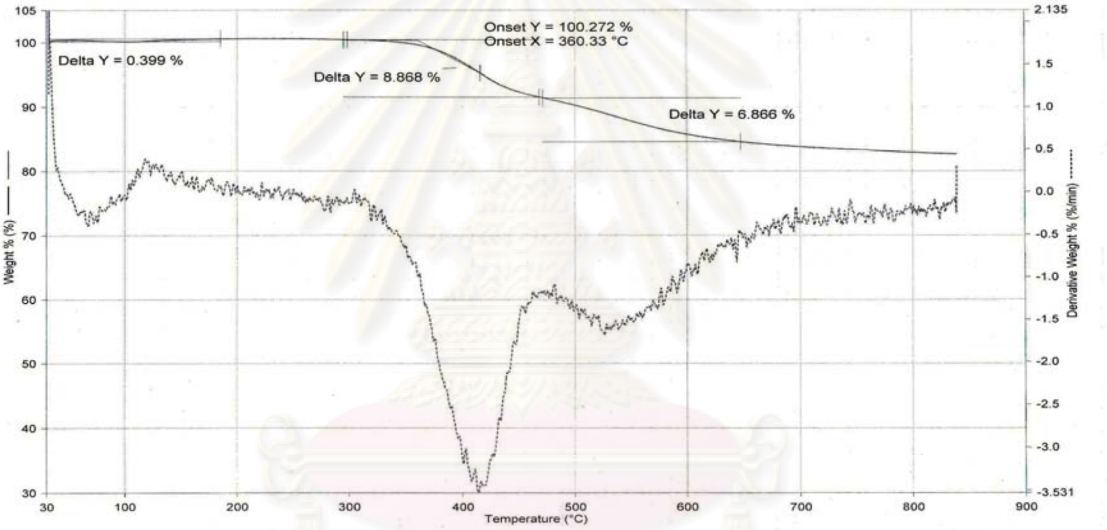


Figure A29 TGA curves of MP-MCM-41 from ***Graft-con*** method.
(MPTMS adding = **13.28 mmol** of MPTMS / 1 g MCM-41)

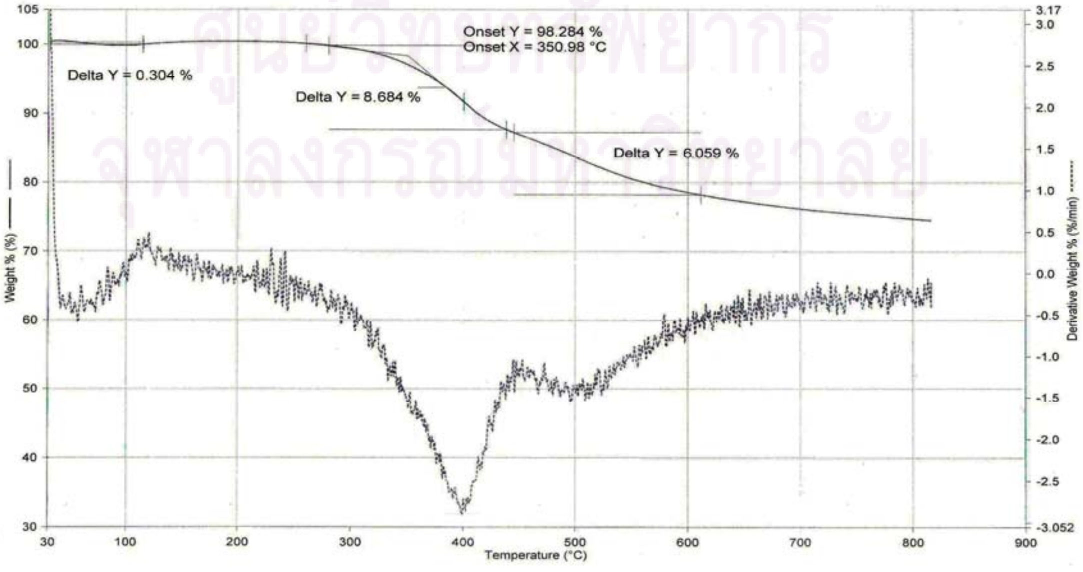


Figure A30 TGA curves of MP-MCM-41 from ***Graft-step*** method**.**
(MPTMS adding = **11.47 mmol** of MPTMS / 1 g MCM-41)

TGA curve of adsorbents which have the equal amount of octyl group on adsorbent from three synthesis methods

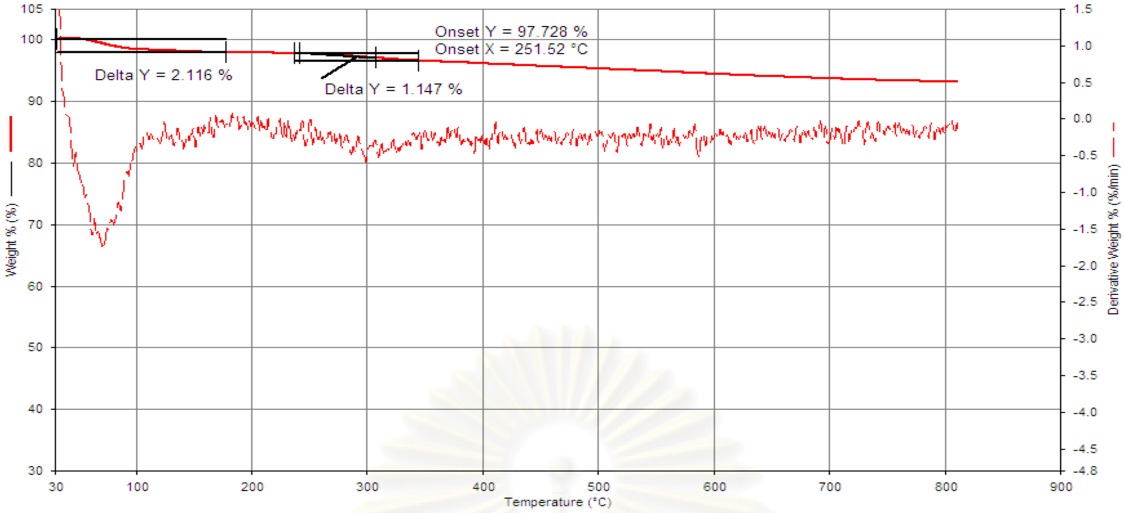


Figure A31 TGA curves of normal MCM-41 from ***Con*** method.
(TEOS adding = **10.40 %mol** of TEOS / Triethoxyoctylsilane +TEOS)

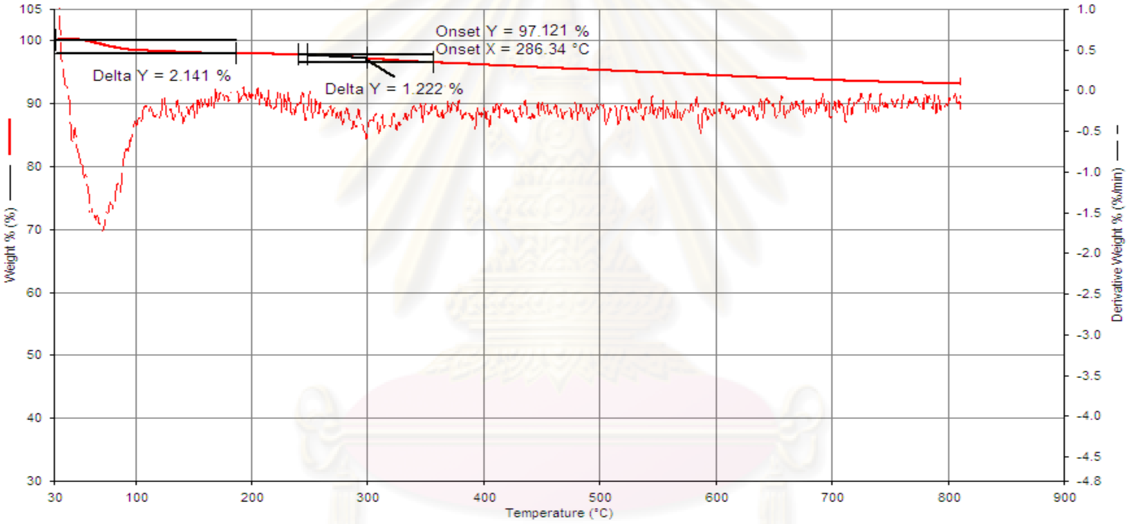


Figure A32 TGA curves of normal MCM-41 from ***Step*** method.
(TEOS adding = **12.17 %mol** of TEOS / Triethoxyoctylsilane +TEOS)

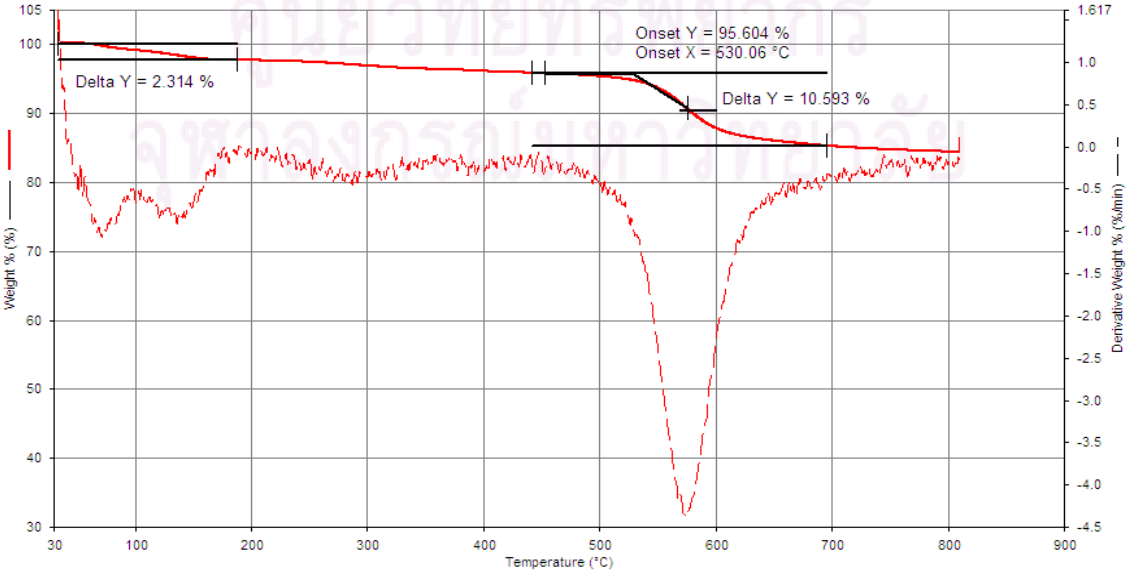


Figure A33 TGA curves of ($C_7H_2CH_3$)-MCM-41 from ***Con*** method.
(Ligand adding = **10.40 %mol** of Triethoxyoctylsilane / Triethoxyoctylsilane+TEOS)

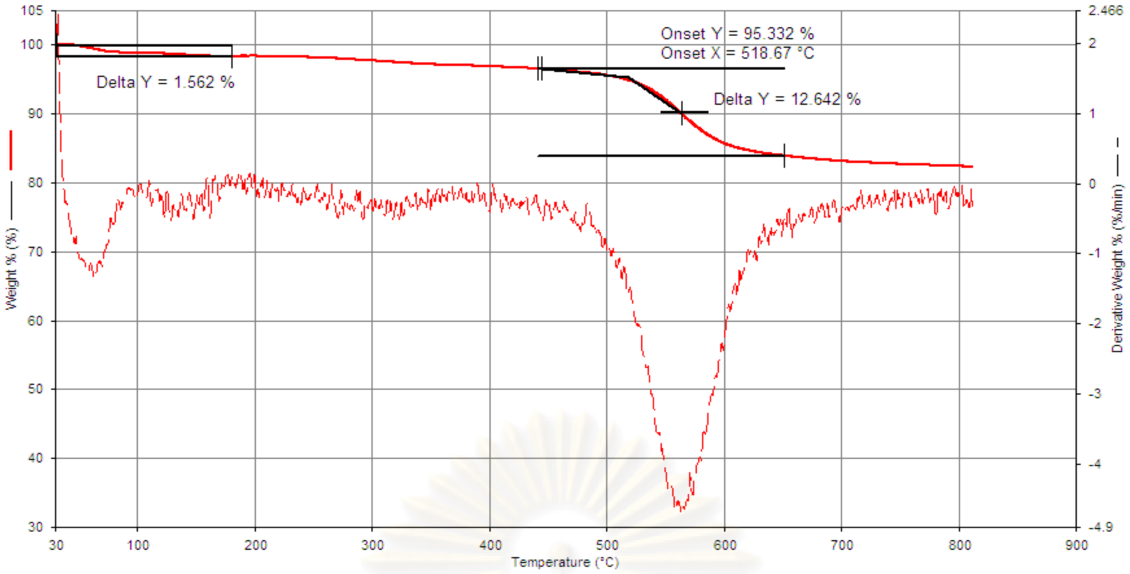


Figure A34 TGA curves of $(C_7H_2CH_3)$-MCM-41 from ***Step*** method.
(Ligand adding = **12.17 %mol** of Triethoxyoctylsilane / Triethoxyoctylsilane+TEOS)

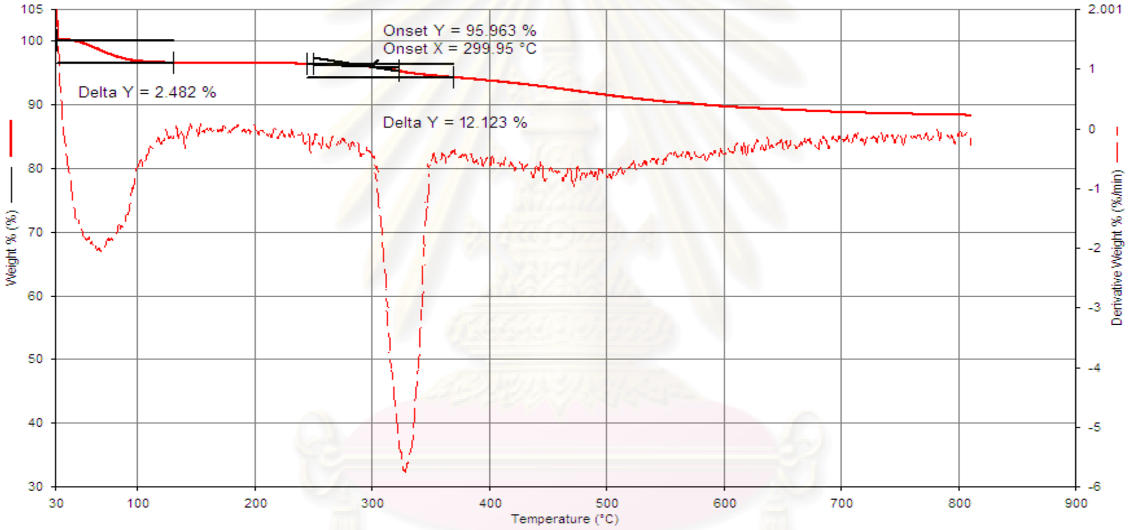


Figure A35 TGA curves of $(C_7H_2CH_3)$-MCM-41 from ***Graft-con*** method.
(Ligand adding = **13.28 mmol** of Triethoxyoctylsilane / 1 g MCM-41)

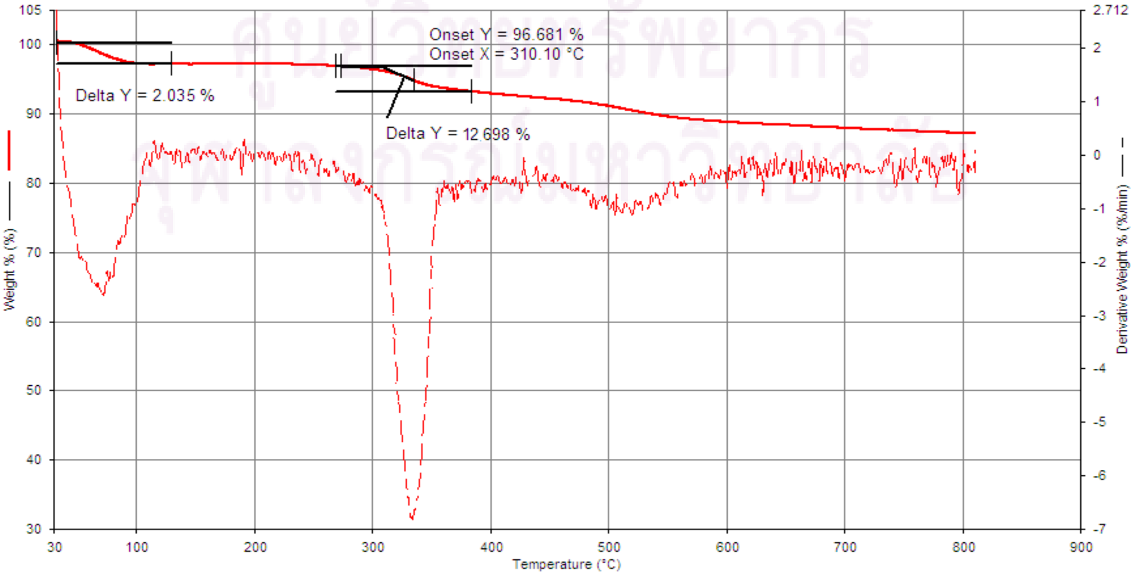


Figure A36 TGA curves of $(C_7H_2CH_3)$-MCM-41 from ***Graft-step*** method.
(Ligand adding = **11.47 mmol** of Triethoxyoctylsilane / 1 g MCM-41)

Table A2 Effect of stirring time in the mercury(II) ions adsorption by MP-MCM-41 (*Graft-step*)

Stirring Time (min)	**Adsorption capacity** (mg/g)	**Removal** (%)
2	192.02 ± 2.36	91.36 ± 0.02
5	195.88 ± 0.72	93.21 ± 0.03
10	201.57 ± 1.14	96.55 ± 0.03
20	206.23 ± 1.50	97.80 ± 0.03
30	208.76 ± 1.62	99.00 ± 0.03
40	209.13 ± 0.91	99.18 ± 0.08
60	209.26 ± 1.12	99.24 ± 0.12
90	209.64 ± 0.06	99.76 ± 0.03
120	209.66 ± 0.02	99.77 ± 0.01
150	209.69 ± 0.03	99.78 ± 0.01

Mean ± S.D. (n=3)

Table A3 Adsorption isotherm results for mercury(II) ions adsorption by MP-MCM-41(*Graft-step*) prepared with adding amount of 13.39 mmol MPTMS/g MCM-41

C_e (mg/L)	**Adsorption capacity** (mg/g)
0.26 ± 0.01	149.82 ± 0.01
0.27 ± 0.01	178.05 ± 0.01
0.28 ± 0.01	197.90 ± 0.01
0.29 ± 0.02	209.82 ± 0.02
0.47 ± 0.01	218.14 ± 1.25
1.10 ± 0.07	228.39 ± 1.38
5.79 ± 0.66	233.56 ± 0.68
15.13 ± 0.11	233.59 ± 1.24
43.82 ± 0.89	236.43 ± 0.89
55.71 ± 0.95	244.45 ± 0.95
98.01 ± 0.52	249.01 ± 1.29
127.23 ± 1.23	250.34 ± 0.40
150.78 ± 1.87	250.33 ± 1.24
169.19 ± 1.84	250.46 ± 0.39

Mean ± S.D. (n=3)

The initial concentration of mercury(II) ions solution was varied from 40 – 420 mg/L.

VITA

Miss Nattida Siriwong was born on September 8, 1982 in Chachoengsao, Thailand. She received her Bachelor degree of Engineering and Industrial Technology in the major of Petrochemical and Polymeric Material from Silapakorn University in 2003. After that, she worked as Technical Engineer at Zenith Power Corp., Ltd. in petrochemical field during 2004 – 2005. She worked as Engineering Engineer at ECHO Auto part (Thailand) Co., Ltd. in polymer field during 2006 – 2007. She has been a graduate student in the Program of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University and a member of Environmental Analysis Research Unit. In 14 – 16 January 2009, she attended Pure and Applied Chemistry International Conference in the title of “Synthesis of 3-mercaptopropyl functionalized MCM-41 for mercury removal” by poster presentation. In 21 – 22 May 2009, she attended the 2nd Polymer Graduate Conference of Thailand in the title of “Synthesis and use of 3-mercaptropropyl modified MCM-41 for mercury removal” by oral presentation. She has finished the Master degree of Science in 2009. Her present address is 30 moo 3, T. Bangkaew, A. Muang, Chachoengsao, Thailand, 2400. Contact number is 089-0986488.