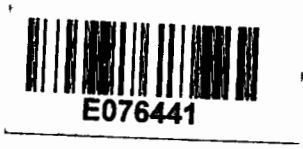
REMOVAL THIOPHENE FROM LIGHT HYDROCARBON USING TRANSITION METAL LOADING ZEOLITES



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ABSTRACT

Removal of thiophene from light hydrocarbon had been studied by adsorption on metal loading zeolites. Four different adsorbents, CuZSM-5, AgZSM-5, CuY and AgY, were studied. These zeolites were by ion-exchanged at 40°C with either copper(II) acetate or silver nitrate. XRD results showed that the adsorbents were well defined crystalline materials. From BET analysis, the adsorbents still had a high surface area as compared to the parent zeolites. AAS determined that 6% of copper content and 11% of silver content were loaded into the zeolites. The adsorptions were carried out at 30°C in a batch system with the following concentrations: 6.0, 4.5, 3.0, 1.5 and 0.5 wt%. Samples were analyzed with Gas Chromatography (GC). The adsorption profiles could be fit into first order reaction kinetic and silver metal loading zeolites possess faster rate of adsorption (~0.03 mol/L.min) as compared to copper (~0.015-0.18 mol/L.min). The adsorption isotherms of the adsorbents were obtained and fit well with Langmuir model. AgY possessed a maximum adsorption capacity (q_m) of 12.86 mmol/g, followed by CuY (11.84 mmol/g), CuZSM-5 (9.47 mmol/g) and AgZSM-5 (7.75 mmol/g). Since, the pore size of zeolite Y is larger than ZSM-5, the capacity of zeolite Y to adsorb thiophene was higher. On the other hand, adsorption constant (b) of ZSM-5 was higher than that of zeolite Y. This could be explained by short range interaction since the size of thiophene and the pore of ZSM-5 are similar. In addition, adsorption constants (b) of silver loaded adsorbents were large for both zeolite Y and ZSM-5, as compared to that of copper loaded adsorbents. Since thiophene is a soft base, it was able to interact strongly with silver cation that is a softer acid when compared with copper cation.

Keywords: Adsorption, Thiophene, Langmuir, Zeolite Y and ZSM-5

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CHAPTER 1

INTRODUCTION

1.1 Motivation

Combustion of fuels containing sulfur compound generates SO_X to atmosphere which causes air pollution, mainly acid rain and smog generation, must be minimized. In the petroleum industry, hydrodesulfurization (HDS) is a typical process to remove the sulfur species from hydrocarbons by transforming them into hydrogen sulfide (H_2S). H_2S, on one hand, is a useful product as it is the starting of sulfuric acid (H_2SO_4) production. However hydrodesulfurization is usually operated under severe condition, i.e. high temperature and pressure. It is also because hydrodesulfurization cannot lower the sulfur content to an ultra low level.

Environment regulations legislate very low concentration of sulfur in fuels. It was hence legalized that sulfurs should be reduced to an ultra-low level; below 10 ppm by the year 2010. Among this regulation, Ministry of Energy of Thailand has forced all the oil companies to produce gasoline with Euro 4 standard by 2012. This means that all the oil companies will have to limit the sulfur content to be lower than 50 ppm [3,4].

Over the past decades, many new technologies have been researched to find alternative methods to remove the sulfur species. Catalytic oxidation and extraction are being pursued as another alternative to sorptive sulfur removal. Ti-containing molecular sieve, particularly Ti-Beta and Ti-HMS, act as effective catalysts for oxidation of several types of sulfur-containing compounds in the presence of H_2O_2 [5,6]. Biological sulfur removal has also been demonstrated using several varieties of microorganisms [7] or even the pervaporation techniques with the advancement in membrane technology [8].

Zeolite is one of the examples that have found to be very optimistic and active adsorbent due to its high surface area and selectivity. Different types of zeolites have been researched over

the past decades with and without the transition metal including ZSM-5, zeolite-beta and zeolite-Y [2,9].

1.2 Objectives

1.2.1 To obtain zeolites containing copper and silver metal loading adsorbents for thiophene adsorption.

1.2.2 To understand the effect of copper and silver loading in zeolites.

1.3 Scope of study

1.3.1 Preparation of four different adsorbents: CuY, CuZSM-5, AgY, AgZSM-5.

1.3.2 Characterization of adsorbents before adsorption test with XRD, AAS and BET.

1.3.3 Investigation of copper loading zeolites (CuY and CuZSM-5) influencing the adsorption of thiophene.

1.3.4 Investigation of silver loading zeolites (AgY and AgZSM-5) influencing the adsorption of thiophene.

1.4 Expected Results

1.4.1 This research would provide appropriate adsorbents for thiophene adsorption.

CHAPTER 2

THEORY AND LITERATURE REVIEW

2.1 Petroleum

Petroleum or crude oil is naturally occurring through sediment of organic matters with an intense heat and pressure built up causing the process to change the organic matters into fossil fuel. Petroleum is a mixture of alkanes, cycloalkanes and various aromatic hydrocarbons with other organic compounds contain nitrogen, oxygen and sulfur.

Table 2.1 Composition by weight of crude oil [10]

Element	Percent range
Carbon	83 – 87 %
Hydrogen	10 – 14 %
Nitrogen	0.1 – 2 %
Oxygen	0.05 – 1.5 %
Sulfur	0.05 – 6 %
Metals	< 0.1 %

Petroleum is used mostly for producing fuel oil and gasoline which are primary energy sources. It is also a raw material for petrochemical industry to produce for examples solvents, fertilizers, pharmaceuticals and plastics. Most of the hydrocarbons present in the petroleum are converted into petroleum-based fuels such as gasoline, diesel, jet and heating oil. The lighter grades of crude oil produce a higher yield of these products, however, as the world's reservoir of light and medium oil are reducing; many new technologies have been invented to converted heavy oil and bitumen, which are more complex and have high utility cost, to produce the products required.

Gasoline is primarily used as a fuel for transportation and there are many characteristics that must be met before it is being sold. One of the main concerns is the sulfur content that has been contaminated in the gasoline. The lower sulfur content would allow a reducing emission of SO_X gas that is toxic to both human and environment. SO_X can react with other compounds in atmosphere to form small particles and penetrate into our respiratory system which later cause respiratory diseases. Further oxidation of SO_X forms H_2SO_4 and thus acid rain.[1]

2.2 Crude Oil Treatment Process

Sulfur content in transportation fuels has been continually regulated around the world due to its environmental effects as well as the effects on the engines. As increasingly stringent regulations and fuels specifications for environmental protection in recent years the sulfur content needs the ultra low level. For Euro IV program requires total sulfur content of gasoline to be limited to 50 ppm. There are various techniques to remove sulfur such as hydrodesulfurization, desulfurization by ionic liquid, biodesulfurization and oxidative desulfurization.

2.2.1 Hydrodesulfurization (HDS)

Hydrodesulfurization is one of the oldest methods that has been used in many petroleum plants for sulfur removal. Usually sulfur species are reduced to H_2S in the presence of catalyst and hydrogen gas. H_2S is then catalytically air oxidized to elemental sulfur. This method used severe condition (high temperature and pressure) to get a low concentration of sulfur and due to this sulfur compounds could be reacted into other sulfur products. Under the circumstance the process is costly due to the requirement of stronger reaction vessels and facilities. Furthermore, HDS is not effective for removing heterocyclic sulfur compounds.[11]

2.2.2 Desulfurization by ionic liquid

Ionic liquids are organic salts that are in liquid state at temperature below 100 °C. Ionic liquid have no measurable vapor pressure below their decomposition temperature and can be designed to have different properties depending on their structure, so they can take place of

organic solvents. Desulfurization by ionic liquids is based on extraction theories and it is operated under a mild condition. Organic ions in ionic liquids can be designed in numerous varieties and combine together to make practically unlimited number of ionic liquid. Among these, imidazolium based ionic liquids, such as [BMIM][PF_6], [EMIM][BF_4], [BMIM][$MeSO_4$], [BMIM][$AlCl_4$], [BMIM][$OcSO_4$], have demonstrated a high selective for heterocyclic sulfur-containing molecules.

The purpose of using ionic liquids in future refineries is to economize desulfurization energy requirements, and to decrease CO_2 production. However, the recovery and recycling of ionic liquids during desulfurization process is difficult. Organic solvent extraction techniques can be used to recycle or recover ionic liquids; however, loss of solvents during the extraction process is inevitable and undesirable.[12]

2.2.3 Biological sulfur removal

Various microorganisms have been on researched to reduce sulfur content as some microorganisms can consume the sulfur in thiophenic compounds such as DBT. Microorganisms require sulfur for their growth and biological activities. Desulfurization by microorganisms is potentially advantage because it is carried out in mild temperature and pressure conditions; therefore, it is considered as an energy-saving process and in biological activities, biocatalysts (enzymes) are involved; therefore, the desulfurization would be highly selective.[13]

2.2.4 Oxidative desulfurization (ODS)

This process is an alternative method for selective sulfur removal from liquid hydrocarbons. It can be use in milder condition (room temperature and atmospheric pressure). In this process, sulfur compounds will be converted by chemical oxidation to slightly higher polar compounds, as compared with the hydrocarbons. Consequently, these oxidized products can be removed by extraction with high polar solvents, such as N-methyl pyrrolidone (NMP), N,N-dimethylformamide (DMF), methanol (MeOH) and dimethylsulfoxide (DMSO). The oxidation of

sulfur compounds with H_2O_2 can be achieved over various catalysts, such as acetic acid, formic acid, polyoxometalates and Ti-containing molecular sieve.[14]

2.3 Adsorption

Adsorption is a process through which a certain substance, originally present in one phase, is removed from that phase by accumulation at the interface between that liquid and solid phase. Materials that being adsorbed are called "adsorbate" and materials used to adsorb are called "adsorbent". Most adsorbents are highly porous materials and usually adsorption takes place on the walls of the pores or at specific sites inside the adsorbent. The characteristics of each adsorbents would differ in the surface area, molecular weight, shape or polarity cause some molecules to be held on more strongly than the others or because the size of the pores for the molecules to be admitted is limited to only small molecules. One of the advantages of adsorption process is that after adsorbate is held strongly enough to allow a complete removal of that component from the fluid, regeneration of the adsorbent can then be carried out to obtain the adsorbent in almost a pure form. Adsorption is operative in most natural physical, biological, and chemical systems, and is widely used in industrial applications such as activated charcoal, synthetic resins and water purification. Similar to surface tension, adsorption is a consequence of surface energy. In a bulk material, all the bonding requirements of the constituent atoms of the material are filled. But atoms on the (clean) surface experience a bond deficiency, because they are not wholly surrounded by other atoms. Thus it is energetically favourable for them to bond with whatever happens to be available. The exact nature of the bonding depends on the details of the species involved, but the adsorbed material is generally classified as exhibiting physisorption or chemisorption. [15]

2.3.1 Physisorption

Physisorption is based on the Van der Waals interactions between the adsorbate and the substrate and also between the adsorbed molecules. The weak bonding of physisorption is due to the induced dipole moment of a nonpolar adsorbate interacting with its own polarizable solid. It is completely nonspecific, i.e. almost all gases can physisorb under the correct conditions to almost

all surfaces. A physisorbed molecule can spontaneously leave the surface after a certain time. The energy necessary in order to desorb a physisorbed molecule has the same order of magnitude as the condensation enthalpy (typically ~20 kJ mol^{-1}). Physisorption is therefore observed mostly at low temperatures. At room temperature, retention times are around 10^{-8} s, at 100 K on the order of seconds. Physisorption can occur as a preliminary state to chemisorption.

2.3.2 Chemisorption

Chemisorption occurs when there is the formation of a chemical (often covalent) linkage between adsorbate and substrate. Chemisorption is characterized by an activational energy for the chemical reaction that takes place only in monolayer. The reaction that occurs usually has a high enthalpy change and often higher than 200 kJ mol^{-1} indicating an exothermic reaction. It is a spontaneous process and therefore requires a negative change in the free enthalpy ΔG. Since the adsorbate, when adsorbed, loses freedom of movement, the entropy change ΔS is likewise negative. Since $\Delta G=\Delta H-T\Delta S$, ΔH is also usually negative, meaning that the process is exothermic.[16]

Often with chemisorption a dissociation of the adsorbate is observed at the same time. This effect is very important in catalysis, where chemisorption can represent a low activation energy dissociation route.

Adsorption is usually described through isotherms, that is, functions which connect the amount of adsorbate on the adsorbent, with its pressure (if gas) or concentration (if liquid). One can find in literature several models describing process of adsorption, for examples, Freundlich isotherm, Langmuir isotherm and BET isotherm. The adsorption equilibrium relates mass of adsorbent to equilibrium concentration of adsorbable species in solution. Therefore, the adsorption equilibrium relationship at a given temperature is typically referred to as adsorption isotherm.

2.3.3 Langmuir isotherm

In 1916, Irving Langmuir published an isotherm for gases adsorbed on solids. It is an empirical isotherm derived from a proposed kinetic mechanism. It is based on four hypotheses:

1. The surface of the adsorbent is uniform, that is, all the adsorption sites are equal.

2. Adsorbed molecules do not interact.

3. All adsorption occurs through the same mechanism.

4. At the maximum adsorption, only a monolayer is formed: molecules of adsorbate do not deposit on other, already adsorbed, molecules of adsorbate, only on the free surface of the adsorbent.

The Langmuir isotherm relates the coverage or adsorption of molecules on a solid surface to gas pressure or concentration of a medium above the solid surface at a fixed temperature. The equation was developed by Irving Langmuir in 1916. The equation is stated as:

$$\theta = \frac{\alpha \cdot P}{1 + \alpha \cdot P}$$

θ or theta is the fractional coverage of the surface, P is the gas pressure or concentration, alpha α is a constant.

The constant, α is the Langmuir adsorption constant and increases with an increase in the binding energy of adsorption and with a decrease in temperature.[18]

2.4 Thiophene

Thiophene is a heterocyclic compound with the formula C_4H_4S. Thiophene is a colorless liquid at room temperature. It has a distinct odor similar to benzene. Thiophene is considered to be a highly reactive chemical even though that the sulfur atom is relative unreactive. However, the 2- and 5-positions carbons are easily attack by electrophiles. Thiophene may undergoes many reactions where mostly form hydrogen sulfide (H_2S). [19]

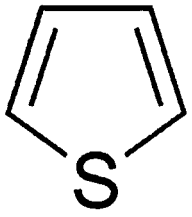


Figure 2.1 Structure of thiophene

Thiophene could be found contaminated with the crude oil in concentrations between 0.5 – 6.0 %. There are many methods that could be used to remove thiophene but the most preferable method is via hydrodesulfurization.

Figure 2.2 Example of hydrodesulfurization reaction at a severe condition

2.5 Zeolites

Zeolites are microporous, aluminosilicate minerals. It has a crystalline solid with well-defined structures. Generally they contain silicon, aluminium and oxygen in their framework. The pores of the zeolites can attack cations, water and other molecules. Zeolites can occur naturally as minerals or synthetically which are made commercially for specific uses. [19]

The frameworks of zeolites are made up of 4-connected network of atoms, usually tetrahedral. This tetrahedral has silicon atom in the center with four oxygen atoms at each corner. The individual tetrahedral is referred to as primary building unit. The tetrahedral is then link together to form secondary building units. [20] The secondary building units are shown in Figure 2.3.

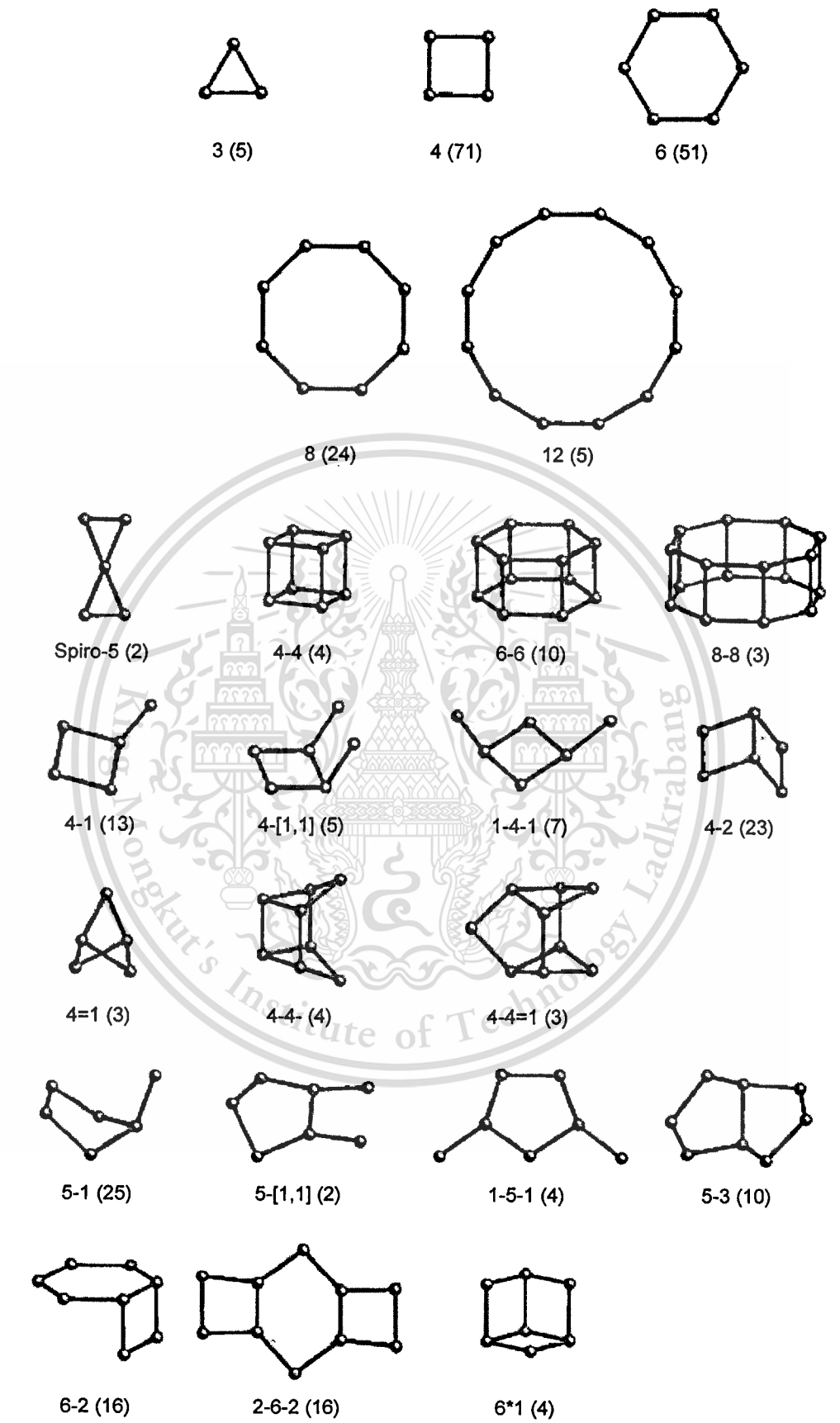


Figure 2.3 Secondary building units of zeolite

2.5.1 Zeolite Y

Zeolite Y with zeolites framework of faujasite is a mineral group with a chemical formula of $(Na_2,Ca,Mg)_{3.5}[Al_7Si_{17}O_{48}]\cdot 32(H_2O)$ by varying the amounts of sodium, calcium and magnesium. A distinctive characteristic of faujasite is that it consists of super cages which are connected through hexagonal prisms. The pore is formed by a 12-membered ring and has a relatively large diameter of 7.4 Å. Zeolite Y has a Si/Al ratio of 2.43 and it is thermally decomposes at 793 °C. [22],[23]

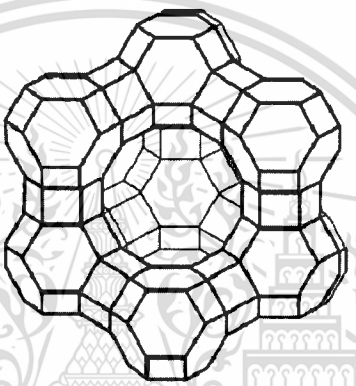


Figure 2.4 Faujasite (FAU) frameworks

2.5.2 ZSM-5

ZSM-5 has a mordenite framework inverted that belongs to the pentasil family of zeolites. Its chemical formula is $Na_nAl_nSi_{96-n}O_{192}\cdot 16H_2O$. The structure composed of many pentasil units linked together by oxygen bridges to form pentasil chains. The estimated pore size is 5.4–5.6 Å. It is a medium pore zeolite with channels defined by ten-membered rings. ZSM-5 zeolite is usually used in the petroleum industry for hydrocarbon interconversion. The main application is in the isomerizations of meta-xylene to para-xylene. The acidic zeolite promotes carbocation isomerization. [24],[25]

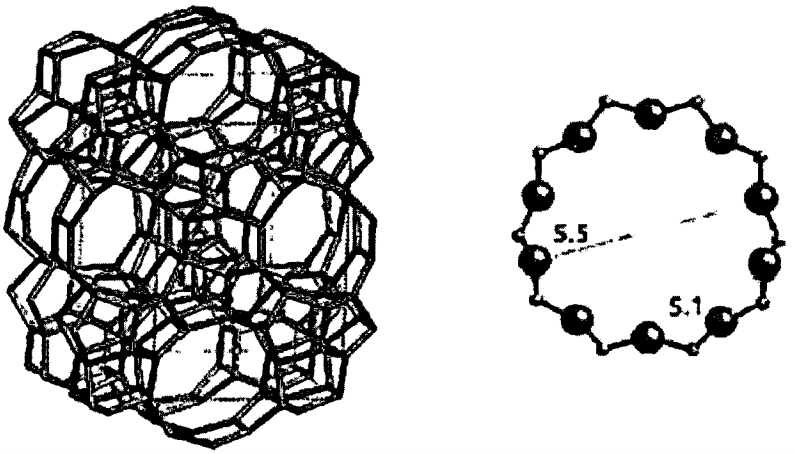


Figure 2.5 Mordenit (MFI) framework and pore size diameter

2.5.3 Application of zeolites [21]

Since zeolites have unique structure, they are widely used in industry including water purification, nuclear processing, production of detergents and medicine. In petroleum and petrochemical industry, zeolites are employed for many cracking and treating to upgrade the quality of the petrol and chemicals.

2.5.3.1 Catalysis

Zeolites have the abitility to act as catalyst for chemical reactions which take place within the internal cavities. An important catalytic reaction is the catalysis by hydrogen-exchanged zeolites, whose protons give rise to high acidity in zeolites framework. This is very useful for crude oil cracking and isomerization. Zeolites are also served as oxidation or reduction catalyst, usually after metals have been exchanged into the framework. These examples are the use of titanium ZSM-5 in the production of caprolactam.

2.5.3.2 Nuclear industry

Due to the selectivity of zeolites that only allow certain cations to get inside the pore and aluminosilicate construction that s extremely durable and resistant to radiation, zeolites have been used to trap many fission products to be removed from the nuclear waste. Once zeolites

are fully loaded with trapped fission products, the zeolite-waste combination can be hot pressed into an extremely durable ceramic form.

2.5.3.3 Heating and refrigeration

The high heat of adsorption and ability to hydrate and dehydrate while maintaining structural stability of the zeolites has been found to be useful as solar thermal collectors and for adsorption refrigeration. The hygroscopic property coupled with rapid and intense exothermic reaction when taken from a dehydrated to a hydrated form, makes zeolites very effective for storage of heat and energy.

2.5.3.4 Medical

In particularly with the naturally occurring zeolites have been developed into a medical-grade oxygen from zeolite-based oxygen concentrator systems. Zeolite is used to purify oxygen from air using its stability to trap impurities.

2.6 Literature Review

Several adsorbents are used to remove thiophene from crude oil such as metal impregnated alumina, acid catalysts, pervaporation and zeolites. There are various kinds of metal oxide catalysts to use in many reaction processes such as MgO and Al_2O_3. Since MgO is a basic oxide, Al_2O_3 is an amphoteric, and thiophene is lewis base, alumina is chosen to be adsorbent for adsorption. P. Jeevanandam studied adsorption of thiophene with impregnated nanocrystalline alumina. Crystalline alumina is a good catalyst with high surface area and high pore volume which is good for adsorption process. However, Al in alumina is hard lewis acid which is not good interaction with soft base like thiophene. One kind of modified alumina is to be impregnated with soft lewis acid metal to improve the efficiency of adsorption thiophene. In this case, Ag was used as a transition metal for impregnation to alumina. The results showed the high efficiency of catalysts to adsorption of thiophenes in hydrocarbons.[26]

Acid catalyst is one choice for eliminate thiophene from hydrocarbon. Jie Zhang studied about removal of thiophene by condensation in the presence of acid catalyst. Formic acid has a proper acidity and was a suitable catalyst for the condensation process. Thiophene in aromatic hydrocarbon can be converted to the compound with higher temperature such as dithienylmethane and di-methyl-di-thienylmethane via condensation with formaldehyde and then readily removed with fractional distillation.[27]

Rongbin Qi studied about removal of thiophenes from n-octane/thiophene mixtures by pervaporation. Polydimethyl siloxane (PDMS)/Polyacrylomitrile (PAN) composite membrane was used to separate thiophene from mixtures. Pervaporation had high separation efficiency and simple operation. PDMS/PAN membrane was studied in a feed temperature 30-70°C and at different initial concentration of thiophenes (thiophene/2-methyl-thiophene) for comparing. The results showed that the increasing feed temperature the higher yield but lower selectivity. PDMS membrane had a more selective to thiophene than 2-methyl-thiophene which cause from the different molecular size and structure. [28]

Feifei Li [29] studied thiophene adsorption in benzene using NaY and CeY. The interaction between thiophene and cation in zeolite can be either as π-type donor by utilizing the delocalized p electrons of the aromatic ring (p bond) to form a p-type complex with metal ions or as an n-type donor by donating the lone-pair electrons that lying in the plane of the ring to the adsorbent (direct S–M bond). [30] In thiophene–NaY system, small quantity of thiophene is firstly adsorbed via p-electronic interaction between thiophene and Na^+ then a large quantity of thiophene is adsorbed via a pore-filling mechanism. The p-electronic interaction not only facilitates the diffusion thiophene molecules into supercage but also lead to adsorption process to be the rate-controlling step. In thiophene–CeY system, thiophenes are firstly adsorbed by forming p-complexation then large quantities of thiophene are adsorbed by directly forming S–M bond. The results showed that CeY obtained the higher efficiency than NaY. [29]

Lisette Jaimes studied adsorption of thiophene under mild condition over ZSM-5 catalyst. HZSM-5 was studied at atmospheric pressure and mild temperature (350-450°C) and

also investigated with gas chromatography (GC). The result showed conversion of thiophene in low sulfur content mixtures over H-ZSM5 shows significant levels of coke. [31]

CHAPTER 3

EXPERIMENTAL DETAILS

3.1 Reagents

1. Zeolite Y (Tosoh Corporation Global Portal, Commercial Grade)
2. Zeolite ZSM-5 (Zeolyst International, Commercial Grade)
3. Thiophene (Aldrich Chemistry, A.R. Grade)
4. n-heptane (Fishe Chemical, A.R. Grade)
5. N-butylacetate (Lab Scan, A.R. Grade)
6. Cyclohexanone (Carlo ERBA, A.R. Grade)
7. Copper(II)acetate (QReC, A.R. Grade)
8. Silver Nitrate (Univar, A.R. Grade)
9. Hydrofluoric acid 48% (Panreac, A.R. Grade)
10. Distilled water

3.2 Apparatus

1. Beakers
2. Volumetric flasks
3. Pipettes
4. Erlenmeyer flask
5. Hot plate and stirrer
6. Magnetic stirrer
7. Stirring Rod
8. Spatula
9. Vials
10. Filter paper
11. Oven

12. Calcine
13. Gas chromatography (3800 Gas Chromatograph Varian)
14. X-Ray Diffractometer (D8 Advance, Bruker AG, Scientific Instruments Service Center, Faculty of Science, KMITL)
15. Atomic Absorption Spectrophotometer (AAS-800, Shimadzu Corporation Japan, Department of Chemistry, Faculty of Science, KMITL)
16. Gas Adsorption Analyzer (Autosorb-1, Quantachrome)

3.3 Experiments

3.3.1 Preparation of the adsorbents

3.3.1.1 Preparation of copper exchanged zeolite Y

5 grams of zeolite Y was ion-exchanged with 500 mL of 0.01 M Na_2CO_3 into sodium form. Then, NaY was calcined before ion-exchanged with initial temperature at 30°C and increase to 450°C holding for 3 hours. Weighed 1.8163 grams of copper acetate and diluted with 1000 mL of distilled water in volumetric flasks to obtain 0.01 M of copper acetate solution. Then, 5 grams of NaY-zeolite was stirred in about 500 mL of copper solution for 12 hours at 40°C. The ion-exchanged zeolite was filtered and washed extensively with distilled water. Dry the zeolite at 105°C overnight. This sample was referred to as CuY.

3.3.1.2 Preparation of copper exchanged ZSM-5

5 grams of ZSM-5 was ion-exchanged with 500 mL of 0.01 M $NaNO_3$ into NaZSM-5 then followed the same procedures as that of preparation of copper ion-exchanged with zeolite Y. This sample was referred to as CuZSM-5.

3.3.1.3 Preparation of silver exchanged zeolite Y

5 grams of zeolite Y was ion-exchanged with 500 mL of 0.01 M Na_2CO_3 into sodium form. Then, NaY was calcined before ion-exchanged with initial temperature at 30°C and increase to 450°C holding for 3 hours. Weighed 1.6987 grams of silver nitrate and diluted with 1000 mL of distilled water in volumetric flasks to obtain 0.01 M of silver nitrate solution. Then, 5 grams of NaY was stirred in about 500 mL of copper solution for 12 hours at 40°C. The ion-exchanged zeolite was filtered and washed extensively with distilled water. Finally zeolite was dried at 105°C overnight. This sample was referred to as AgY.

3.3.1.4 Preparation of silver exchanged ZSM-5

5 grams of ZSM-5 was ion-exchanged with 500 mL of 0.01 M $NaNO_3$ into NaZSM-5 then followed the same procedures as that of preparation of silver ion-exchanged with zeolite Y. This sample was referred to as AgZSM-5.

3.3.2 Characterization of adsorbents

3.3.2.1 Atomic Absorption Spectroscopy (AAS)

The silicon/aluminium ratio and copper content of the adsorbent were determined by Atomic Absorption spectrometry. 0.1 grams of solid sample was dissolved with 5 mL of HF. After that, 0.1 mL of diluted sample was marked up to 50 mL with distilled water. Then, the sample was transferred to AAS cell.

3.3.2.2 X-Ray Diffraction (XRD)

The structure of the adsorbents was determined by powder X-Ray Diffraction. CuK_α x-ray beam was used for analysis. The sample was finely grinded to allow the sample to pack into the XRD sample holder homogeneously and randomly distributed. The XRD pattern

was obtained by scanning the sample over the angle range from 2θ = 5 to 60, step angle of 0.04 degree and detection time of 1.5 seconds/step.

3.3.2.3 Gas adsorption analysis (BET)

Surface area of the adsorbents was determined using gas adsorption analysis. Approximately 0.01 grams of sample was loaded into a dried sample cell. Then, the sample was heated for degassing at out-gas station at 300°C for 7 hours. After that filled the cell with nitrogen gas and the sample was moved to analysis station. The adsorption isotherm was measured in a pressure range of 0.00-1.00 P/P_0.

3.3.3 Adsorption testing.

Before the adsorption testing was carried out, 0.5 gram of adsorbent in an Erlenmeyer flask was preheated in the oven at 200°C for 12 hours. After taken out of the oven, rubber cap must be placed immediately to prevent the adsorbent from moisture and volatile organic.

The adsorption of thiophene from hydrocarbon representative (n-heptane) was carried out at 30°C. 20 grams of sample solution was injected into the Erlenmeyer flask with preheated adsorbent. The schematic of thiophene adsorption testing is shown in Figure 3.1.

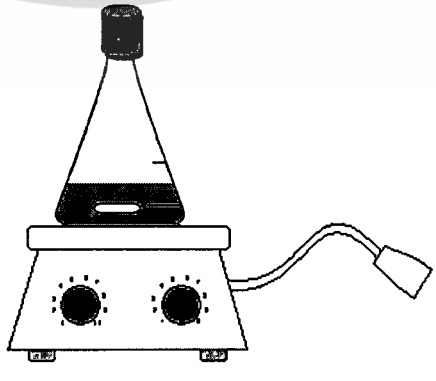


Figure 3.1 Schematic of thiophene adsorption testing

The sample was collected every 30 minutes for 1 hour then every 60 minutes for the next 4 hours. The solution was analyzed with gas chromatography (GC) using HP5 column for thiophene uptake. N-butyl acetate and cyclohexanone were used as solvent and internal standard, respectively. Each vial contained 0.3 mL of 5%wt of cyclohexanone in n-butyl acetate.

Table 3.1 Summary of adsorption testing of each adsorbent with different concentration.

Type of zeolites	Cation loading	Thiophene concentration (wt%)
Zeolite Y	NaY	6.0, 4.5, 3.0, 2.0, 1.5
	AgY	6.0, 4.5, 3.0, 2.0, 1.5
	CuY	6.0, 4.5, 3.0, 2.0, 1.5
ZSM-5	NaZSM-5	6.0, 4.5, 3.0, 2.0, 1.5
	AgZSM-5	6.0, 4.5, 3.0, 2.0, 1.5
	CuZSM-5	6.0, 4.5, 3.0, 2.0, 1.5

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Characterization of adsorbents

The crystallinity of parents and metal loading zeolites were investigated using X-Ray Diffraction (XRD) method. After ion exchange with copper acetate and silver nitrate for CuY and AgY, the adsorbents showed the characteristic intensity at 2-Theta of 6.34, 15.76, 23.76 and 31.56. When compared to the original parent zeolite (zeolite Y), the intensity had decreased which could be because the size of the transition metals loaded are much larger than that of sodium cations originally presented in the zeolite Y. This could clearly be observed particularly in the d-spacing at 2-Theta between 0-30 where it indicates the pore size of the zeolite. As the intensity decreased, it suggests metals are present in the pore. Transition metal has a high electron density that could adsorb diffracted x-ray. This would lead to lower intensity of diffracted signal that could be detected.

One may expect that the decreasing in intensity could have cause by acidity or basicity of the metal solutions which could damage the structure of the zeolite and hence slightly reduce the crystallinity. However, both Figure 4.1 and 4.2 showed that 2-Theta between 30-60 did not have any decreasing in intensity which indicated that the structures of zeolites were not affected by this phenomenon.

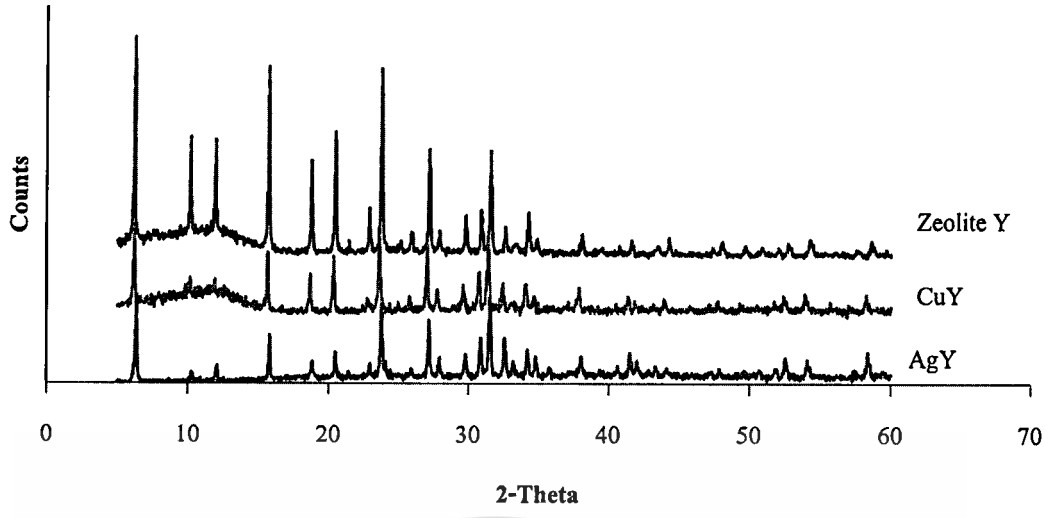


Figure 4.1 XRD patterns of zeolite Y before and after ion-exchanged with copper solution and silver solution.

The characteristic peaks of CuZSM-5 and AgZSM-5 in Figure 4.2 showed a well define crystalline phase. However, the intensity had also showed some decrease in peak intensity at 2-theta showing at 7.88, 8.84, 23.0 and 23.24. This is due to the incorporation of large metal cations as discussed earlier.

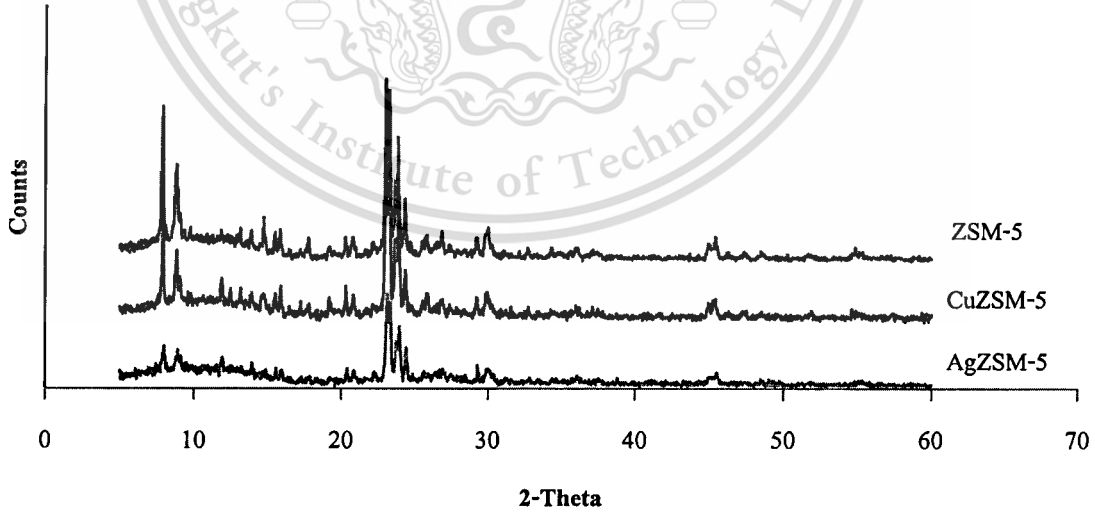


Figure 4.2 XRD patterns of ZSM-5 before and after ion-exchanged with copper solution and silver solution.

Surface area of zeolites was determined using BET method as shown in Table 4.1. Zeolite-Y and ZSM-5 had surface area of 725 m^2/g and 370 m^2/g, respectively. After ion-exchange with Ag^+ and Cu^{2+}, the surface area of CuY was not decreased whereas AgY was decreased to 656 m^2/g. Since silver cation is larger than copper cation, it would relatively occupy more space in the pore of zeolites leading to a lower surface area as observed.

On the other hand, both the surface areas of AgZSM-5 (670 m^2/g) and CuZSM-5 (749 m^2/g), were two-folded higher than that of parent ZSM-5. This is because ammonium ions originally were present in ZSM-5 and once it was ion-exchanged into sodium form, an incomplete ion-exchange occurred. It meant that ammonium ions were still remained in some of the pores. After calcinations at 450 °C, these ammonium ions were decomposed to an acid site (H^+) which occupy relatively less space as compared to NH_4^+, Ag^+ and Cu^{2+}. Hence, the surface area of metal loaded adsorbents of ZSM-5 was higher than that of ZSM-5.

Table 4.1 Characteristics properties of adsorbents

Adsorbents	AAS Metal Content (%)	Surface area (m^2/g)
Zeolite Y	-	725
CuY	5.61	725
AgY	10.62	656
ZSM-5	-	370
CuZSM-5	6.72	749
AgZSM-5	10.99	670

Metal content that had been loaded into zeolites are shown in Table 4.1 as determined by atomic absorption spectroscopy. Approximately 5-6% of copper metal and 10-11% of silver metal had been loaded. Since the charge number of copper cation is a divalent cation whereas silver cation is monovalent, therefore the content of copper would be lower than that of silver. Theoretically, one copper cation would interact with two negative framework charges in zeolite.

4.2 Adsorption of thiophene in n-heptane

4.2.1 Adsorption Kinetics

The kinetic profiles from the adsorption of thiophene in n-heptane, a light hydrocarbon representative, on three different cations of zeolite Y are shown in Figure 4.3. Thiophene uptakes, given by a fraction of millimole of thiophene adsorbed over a gram of adsorbent, are plotted as function of time. This is called *kinetic profile of adsorption*.

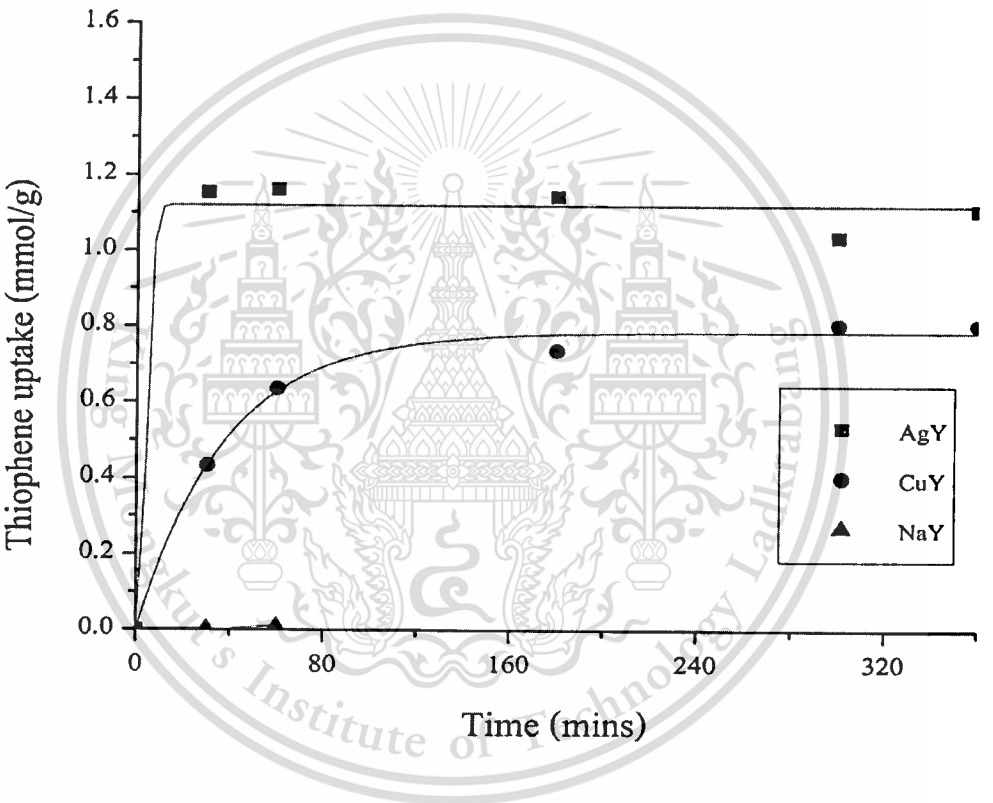


Figure 4.3 Adsorption profiles of (a) AgY and (b) CuY and (c) NaY with 0.5 wt% of thiophene solution.

From Figure 4.3, the results showed that AgY possessed a highest slope followed by CuY and NaY. The adsorption was completed within the first 30 minutes with approximately 1.1 mmol/g of the thiophene uptake. The adsorption rate of CuY was slower as compared to AgZSM-5 with only 0.75 mmol/g of thiophene uptake. For NaY only 0.89% of thiophene could be adsorbed and it took up to 24 hours for a complete adsorption with 0.309 mmol/g of thiophene

uptake. This showed that the rate of NaY with thiophene was extremely slow as there was only a weak interaction between the sodium cations and thiophene. This suggested that metal cations on the zeolite play a significant role in the adsorption kinetics of thiophene. Accordingly, only adsorption on AgY and CuY were focused for the kinetic study

The rates of adsorption with metal loading zeolites were evaluated using a first order equation to find the kinetic models. The rate equation can be expressed as

$$-d[A]/dt = k[A]$$

where [A] are the amount of thiophene adsorbed, 'k' is slope of the graph and the rate of the reaction and t is the time.

After integration, the kinetic is expressed as

$$\ln([A]_0/[A]) = kt$$

where $[A]_0$ are the amount of thiophene adsorbed at equilibrium.

From the plot between $\ln([A]_0/[A])$ VS t, it yielded a straight line graph as shown in Figure 4.4 confirming that the rate of adsorptions for AgY and CuY were first order and the adsorption was depended on the transition metal loaded. It could be clearly observed that AgY possesses adsorption rate faster than CuY. Again as NaY showed extremely slow rate of adsorption, it is not possible to demonstrate kinetic of adsorption at such low concentration (0.5 wt%).

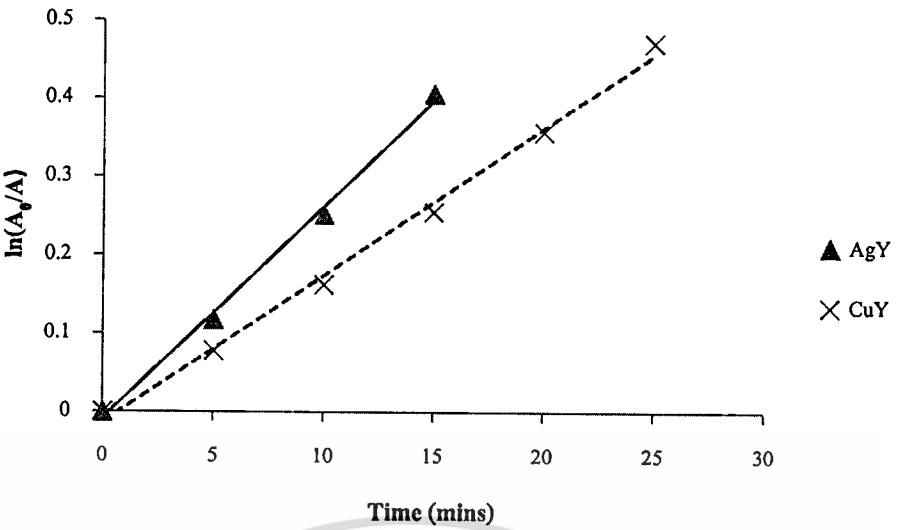


Figure 4.4 Kinetic of adsorption of AgY and CuY

A faster adsorption rate of AgY than CuY could be explained by Hard Soft Acid Base (HSAB) principles which states that hard acids prefer to associate with hard bases and vice versa. The d-orbital in transition metal ion can readily accept the lone pair electrons of sulfur in thiophenic molecule. The transition metal present in the adsorbents can adsorb thiophene by electron donor-acceptor mechanism as shown in Figure 4.5.

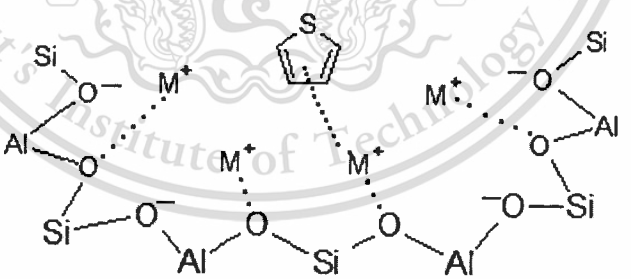


Figure 4.5 Electron donor-acceptor mechanism of thiophene and adsorbents

Since, Ag^{+} is softer acid, as compared to Cu^{2+} and in this case thiophenic compound acts as soft base. Accordingly, it would prefer to interact more strongly with Ag^{+} as compared to Cu^{2+} via π bonds. (Figure 4.5)

For ZSM-5, three kinetic profiles of different adsorbents are shown in Figure 4.6

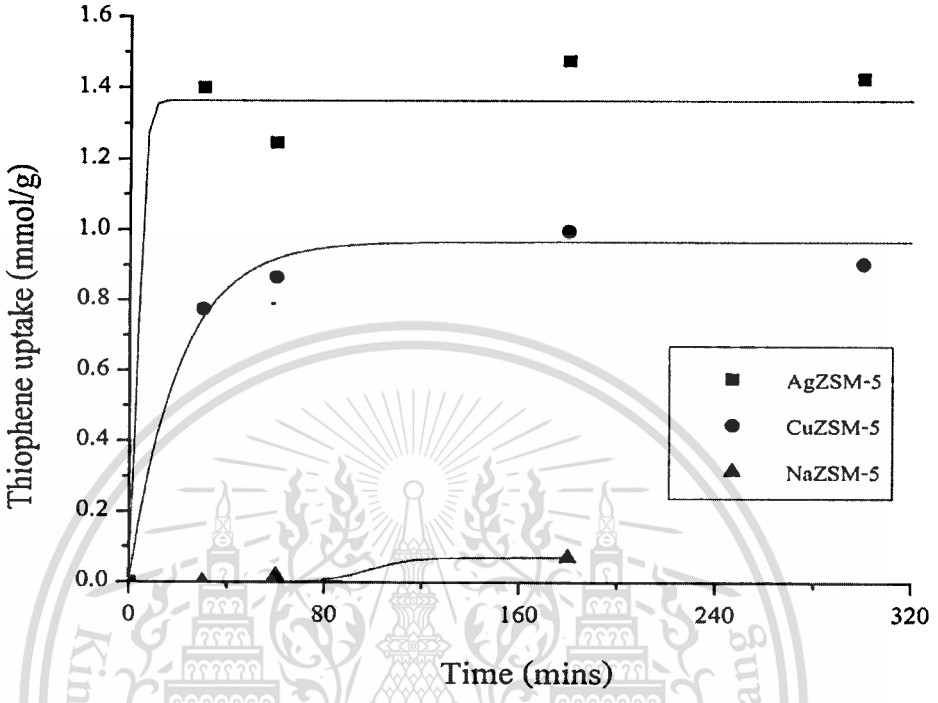


Figure 4.6 Adsorption profiles of (a) AgZSM-5 and (b) CuZSM-5 and (c) NaZSM-5 with 0.5 wt% of thiophene solution.

The results of ZSM-5 adsorbent exhibit similar trend to that of zeolite Y adsorbents. The patterns of the profiles were also similar where AgZSM-5 had a sharp increase in thiophene uptake in the first 30 minutes whereas CuZSM-5 showed a longer period to reach the equilibrium. Kinetic profile of NaZSM-5 showed that it took at least 30 minutes until the adsorbent could readily adsorb and it took almost 24 hours for a complete adsorption. The slow adsorption rate was due to a weak interaction between sodium cations and thiophene as discussed earlier. Again, kinetic of adsorption of NaZSM-5 could not be demonstrated at this concentration.

Figure 4.7 has shown that metal loading into ZSM-5 adsorbents could also be fit into first order reaction and it could clearly be observed that AgZSM-5 performs a faster rate of adsorption than CuZSM-5.

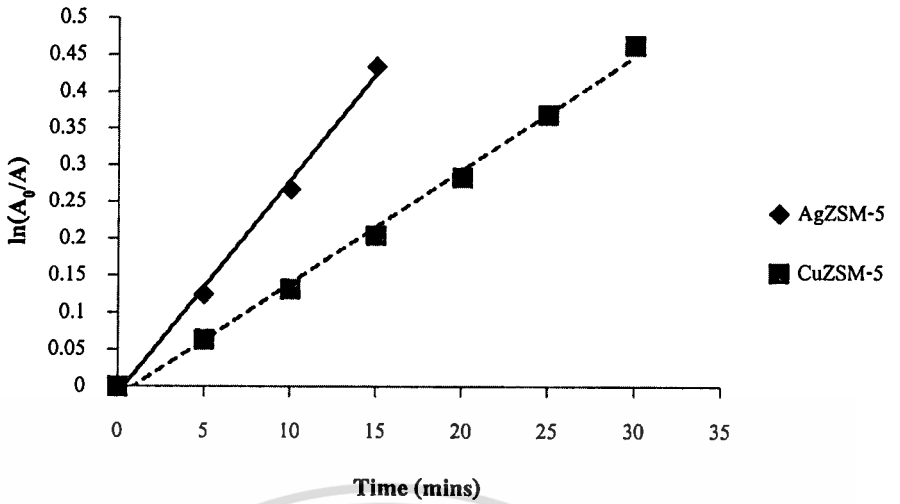


Figure 4.7 Kinetics of adsorption of AgZSM-5 and CuZSM-5.

From these kinetic profiles, kinetic parameters for each adsorbent could be calculated and obtained (Table 4.2).

Table 4.2 Kinetic of adsorptions of various adsorbents

zeolites	Rate (mol/L.min)	R^2
AgY	0.0270	0.9964
CuY	0.0187	0.9953
AgZSM-5	0.0289	0.9958
CuZSM-5	0.0153	0.9956

From Table 4.2, it could be concluded that the rates of adsorption only depend on incorporated of transition metal. Therefore, the diffusion of thiophene in zeolite Y and ZSM-5 played no role in adsorption kinetics. The transition metals that are soft acid, i.e. Ag^{+}, would interact better with thiophene as compared to the hard acid transition metals, i.e. Cu^{2+} and hence perform a faster adsorption rate.

Adsorption profiles and first order reaction kinetics of NaY and NaZSM-5 can be demonstrated only with 6 wt% of thiophene solution as shown in Figure 4.8 and Figure 4.9. It also took 24 hours upon completion in both of the adsorbents.

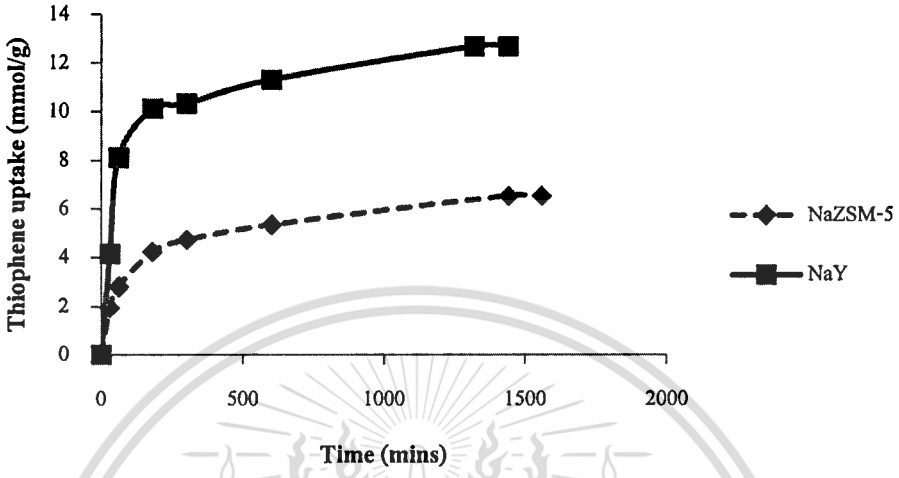


Figure 4.8 Adsorption profiles of NaZSM-5 and NaY with 6 wt% of thiophene solution

It has shown earlier that when 0.5 wt% thiophene was adsorbed on NaY and NaZSM-5, thiophene uptake was extremely slow and it could not be fit into kinetic model. However when 6 wt% of thiophene solution was experimented, the adsorption profiles could be fit in first order reaction kinetic as shown in Figure 4.9.

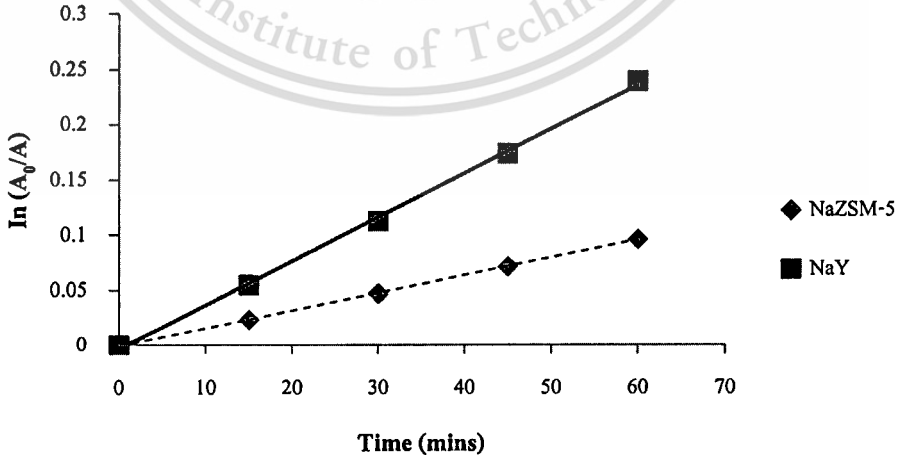


Figure 4.9 Kinetic of adsorption of NaZSM-5 and NaY with 6 wt% of thiophene solution

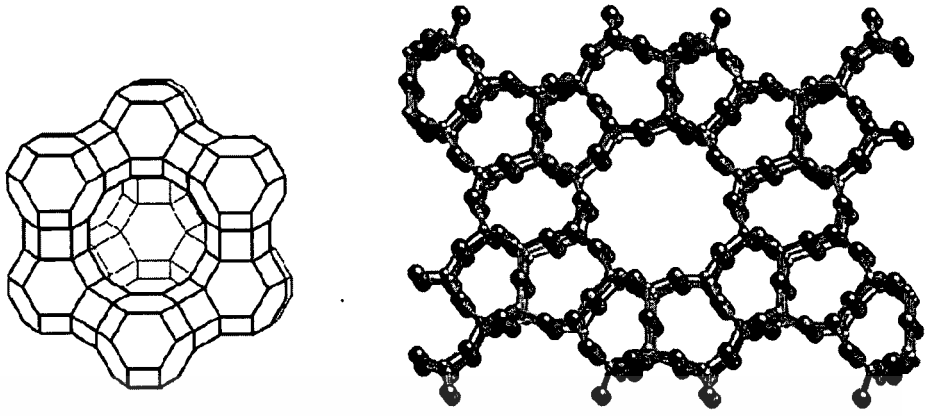
From the kinetic profiles, kinetic parameters for sodium loaded adsorbents could be calculated as shown in Table 4.3.

Table 4.3 Kinetic adsorption of NaY and NaZSM-5 with 6wt% thiophene solution

zeolites	Rate (mol/L.min)	R^2
NaY	0.0040	0.9988
NaZSM-5	0.0016	0.9998

Table 4.3 showed that the adsorption rate of NaY was slightly higher than that of NaZSM-5. Such difference cannot be observed when transition metal is incorporated in the zeolites (i.e. Ag and Cu) since there was a strong interaction between the metal cations and the thiophene. However, when sodium ions were present, the interaction was very weak and the diffusion of thiophene in the pore of zeolites became more significant when 6 wt% of thiophene solution was experimented. The pore size of zeolite Y (7.4 Å) is relatively larger than that of ZSM-5 (5.6 Å) in addition the pore size of ZSM-5 is similar to the kinetic diameter of thiophene (around 4.6 Å). Therefore, when thiophene diffused into zeolites, it could easily enter into the pore of zeolite Y as compared to that of ZSM-5.

Moreover, NaY that exhibits the faujasite (FAU) structure is a super cage with a three-dimensional pore opening and the pore size determined by 12-ring oxygen atoms. On the other hand, NaZSM-5 is a channel structure with a unique two-dimensional pore system defined by ten-membered rings. Hence, this structural characteristic allows thiophene diffusion to be more readily facilitated into the pore of zeolite Y (Figure 4.10). In turn pore structure of ZSM-5 would retain in the cavity. Hence rate of zeolite Y was faster than ZSM-5 as observed



(a) (b)

Figure 4.10 Pore structures of (a) zeolite Y and (b) ZSM-5

4.2.2 Adsorption isotherm of thiophene in n-heptane

The adsorption isotherms of thiophene on various adsorbents at 30°C are shown in Figure 4.11. Thiophene uptake of AgY was found to be higher than the other adsorbents.

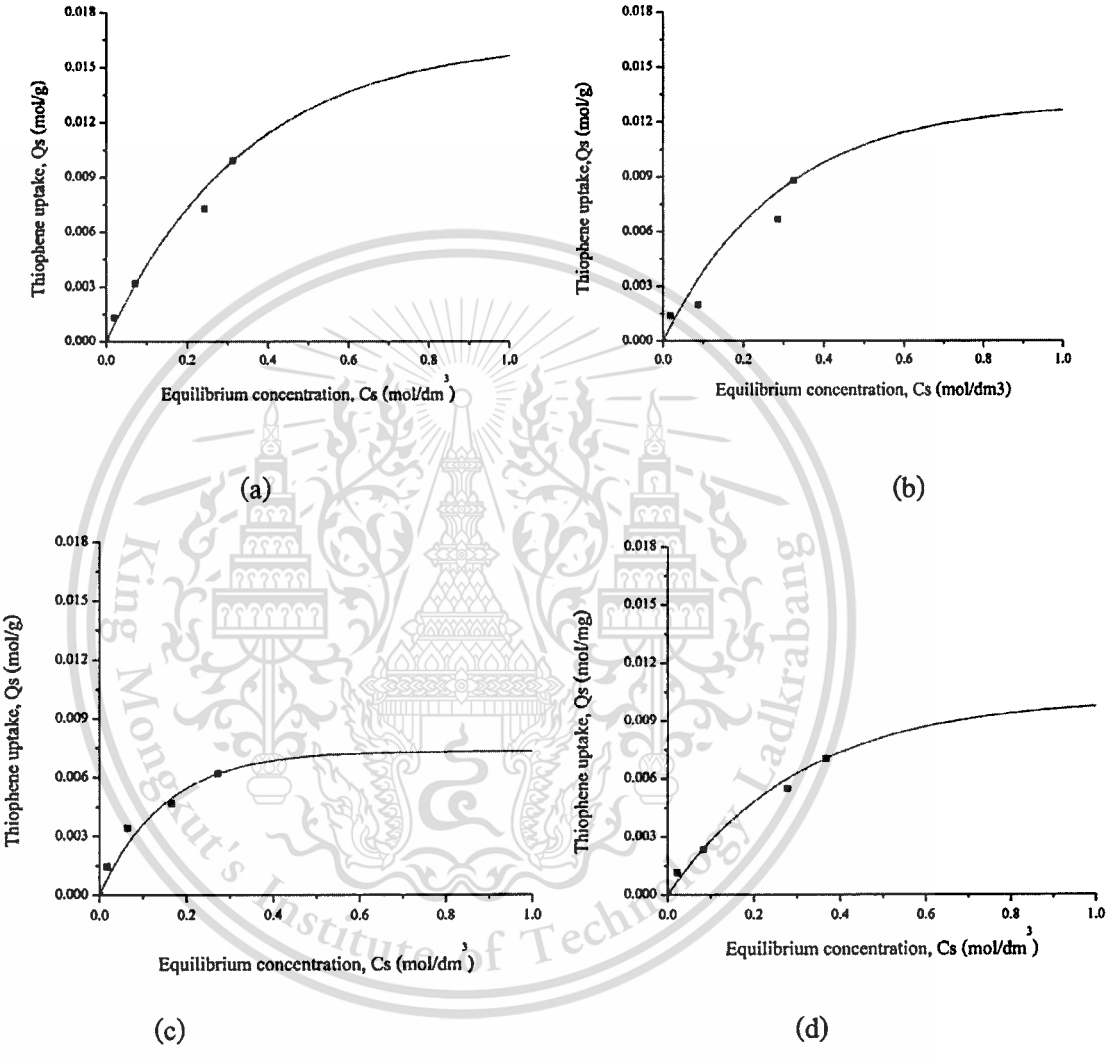


Figure 4.11 Adsorption isotherms on (a)AgY (b)CuY (c)AgZSM-5 and (d)CuZSM-5

The experimental data could be fit into Langmuir isotherm where the Langmuir equation is represented in

$$C_s/Q_s = 1/(Q_m b)+C_s/Q_m$$

where Q_s is the sulfur uptake (mol/g), Cs is the equilibrium sulfur concentration in solution (mol/dm^3), Q_m is the maximum adsorption capacity (mol/g), and b is the adsorption constant (dm^3/mol).

Langmuir plot of AgY and CuY are shown in Figure 4.12.

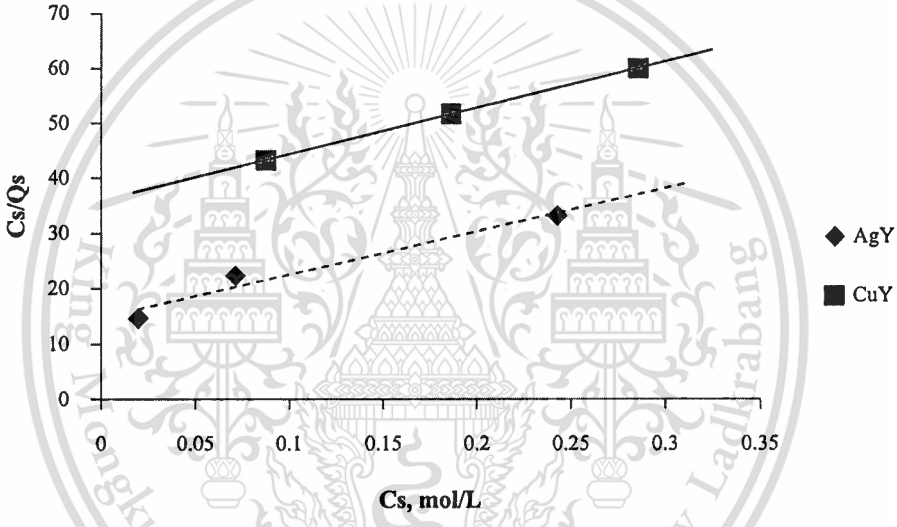


Figure 4.12 Langmuir plots on AgY and CuY

Calculated maximum adsorption capacity (Q_m) and the adsorption constant (b) of AgY and CuY from Langmuir isotherm are shown in Table 4.3.

Table 4.4 Adsorption parameters on various adsorbents

Zeolites	Maximum adsorption capacity, Q_m (mmol/g)	Adsorption constant, b (dm^3/mol)
AgY	12.76	5.319
CuY	11.84	2.346
AgZSM-5	7.75	11.946
CuZSM-5	9.47	6.527

From this evaluation, AgY had a slightly higher adsorption capacity than that of CuY. The softness of Ag^+ with high polarization of valence electrons allows it to interact more strongly with thiophene as compared to Cu^{2+}. This assumption was also supported by the higher adsorption constant of AgY (5.319 mol/dm^3) as compared to that of CuY (2.346 mol/dm^3). This constant reflects the adsorption strength between the adsorbent and thiophene molecule. Such strong interaction is formed via π bond where one lone pair on aromatic ring forms a π type complex with the metal.

Figure 4.13 and Table 4.4 also show Langmuir isotherm and adsorption parameters of metals loading zeolites of ZSM-5 adsorbents, respectively.

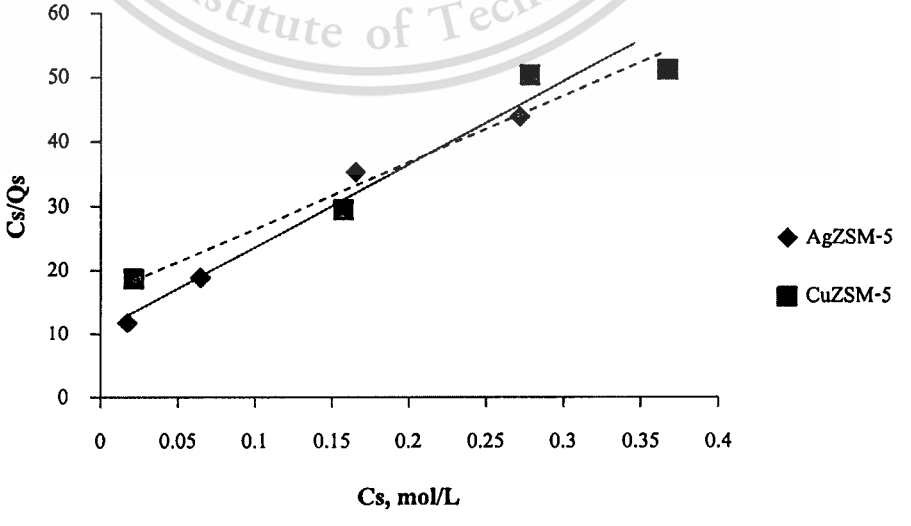


Figure 4.13 Langmuir plots on AgZSM-5 and CuZSM-5

CuZSM-5 had shown a higher capacity for a maximum adsorption when compared with AgZSM-5. This is consistent with the content of metal from AAS method that has been discussed earlier. Since copper is a divalent ions whereas silver is only a monovalent, the number of copper cations present in the zeolites would be less than the number of silver cations in order to satisfy the same charge balancing on the zeolite framework. Therefore, the pore space of copper loaded adsorbents was higher as compared to the pore space of silver loaded adsorbents. Hence, the capacity of CuZSM-5 adsorbent would be higher as compared to that of AgZSM-5.

On the other hand, the adsorption constant (b) of AgZSM-5 showed a higher value as compared to CuZSM-5. This value indicates that AgZSM-5 possessed stronger adsorption strength due to its softness as discussed earlier.

Although the capacity of thiophene adsorption of AgY is higher than AgZSM-5 but adsorption constant of AgY is approximately two-folded lower than that of AgZSM-5 as shown in Table 4.4. Since the kinetic diameter of thiophene (4.6 Å) is similar to the pore of ZSM-5 (5.6 Å), it would create a short range interaction that strongly retain thiophene in the cavity of ZSM-5 as thiophene adsorbed on the pore.

On the other hand, the larger pore size of zeolite Y (7.4 Å) explains a low adsorption constant. A long range interaction would expect for a molecule with relatively smaller kinetic diameter as compared to the pore. When thiophene adsorbed in the pore of zeolite Y, there are more empty space and thiophene would fit more loosely in zeolite Y cavity, as compared with ZSM-5 (Figure 4.14). This results in weak interaction between zeolite Y and thiophene as seen in the lower adsorption constant (b).

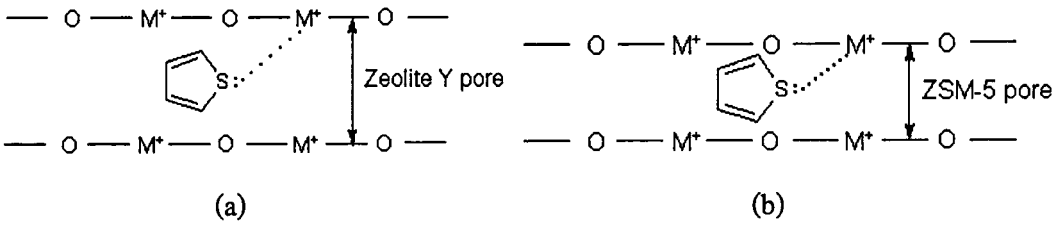


Figure 4.14 Interaction between thiophene and metals inside the zeolite pore.

(a) in zeolite Y pore with long range interaction (b) in ZSM-5 pore with short range interaction

CHAPTER 5

CONCLUSIONS AND SUGGESTIONS

5.1 Conclusion

Zeolites with transition metals loaded (CuZSM-5, AgZSM-5, CuY and AgY) were chosen as suitable adsorbents for removal of thiophene. XRD technique identified that the crystallinity of the adsorbents were well-defined. From ion-exchange with copper acetate and silver nitrate, there was no effect on the crystallinity of the adsorbents. AAS confirmed that approximately 5% of copper were loaded and that 11% of silver were loaded. Surface areas of zeolite Y adsorbents (~650 – 720 m^2/g) were regarded as a high surface area with a complete ion-exchange regarding that no significant changed was observed when compared to the parent zeolite Y. However, the surface area of metals loading adsorbents of ZSM-5 was increased (from 370 m^2/g to ~700 m^2/g) due to an incomplete ion-exchange where ammonium ions were decomposed to hydrogen ions during calcination.

The adsorption profiles for metal loaded adsorbents could be fit into first order of kinetic. A descending order of the rate of adsorption was AgZSM-5 (0.0289 mol/L.min) > AgY (0.0270 mol/L.min) > CuY (0.0187 mol/L.min) > CuZSM-5 (0.0153 mol/L.min). This order suggested that the softness of silver cations allow the adsorbent to strongly interact with hard base thiophene via π bonding complexation. For the case of NaY and NaZSM-5 where the adsorption was extremely slow due to a very weak interaction between the sodium cations and thiophene, the adsorption profiles could not be demonstrated at low concentration (0.5 wt%). When 6.0 wt% of thiophene solution was experimented, NaY showed a slightly higher rate as compared to that of NaZSM-5 because the pore size of zeolite Y (7.4 Å) is larger than that of ZSM-5 (5.4 Å) causing the diffusion of thiophene into the pore of zeolites to be easier.

Adsorption isotherms of thiophene could be fit into Langmuir model. From the results, AgY (12.76 mmol/g) possessed a higher adsorption capacity as compared with

CuY (11.84 mmol/g) due to the strong interaction of silver to thiophene, as discussed earlier. This was consistent with the adsorption constant of AgY (5.319 dm^3/mol) being higher than that of CuY (2.346 dm^3/mol). On the other hand, CuZSM-5 (9.47 mmol/g) exhibited higher adsorption capacity as compared with that of AgZSM-5 (7.7.5 mmol/g). This is due to the charge balancing on the zeolite framework. As the number of silver cations present in the zeolites would be higher than copper, the pore volume of silver loaded adsorbents would be lower as compared to that of copper loaded adsorbents. The higher value of adsorption constant of AgZSM-5 (11.946 dm^3/mol) also showed that silver ions strongly interact with thiophene when compared with CuZSM-5 (6.527 dm^3/mol). Theoretically the pore size of ZSM-5 (5.6 Å) is similar to thiophene (4.6 Å) which created a short range interaction in the cavity of ZSM-5 whereas a long range interaction occur in the pore of zeolite Y. This is confirmed by a higher adsorption constant of AgY as compared to that of AgZSM-5.

5.2 Suggestions

In thiophene adsorptions, there are many variables that could affect the thiophene uptake. Adsorbent and transition metal loaded are the two variables that had been studied in this project. However, other factors such as temperature or metal content could be investigated. By varying these variables, optimum physical characteristics of adsorbents and adsorption condition could enhance the removal of thiophene.

The frequency of collecting the samples especially during the first hour is important. From the experiments, collecting the samples should be more often to understand the diffusion of thiophene.

There are many isotherm models that are related to adsorption for example Freundlich. The data from thiophene removal should be fit into different models to prove that whether it is a Langmuir model.

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APPENDICES

APPENDIX A

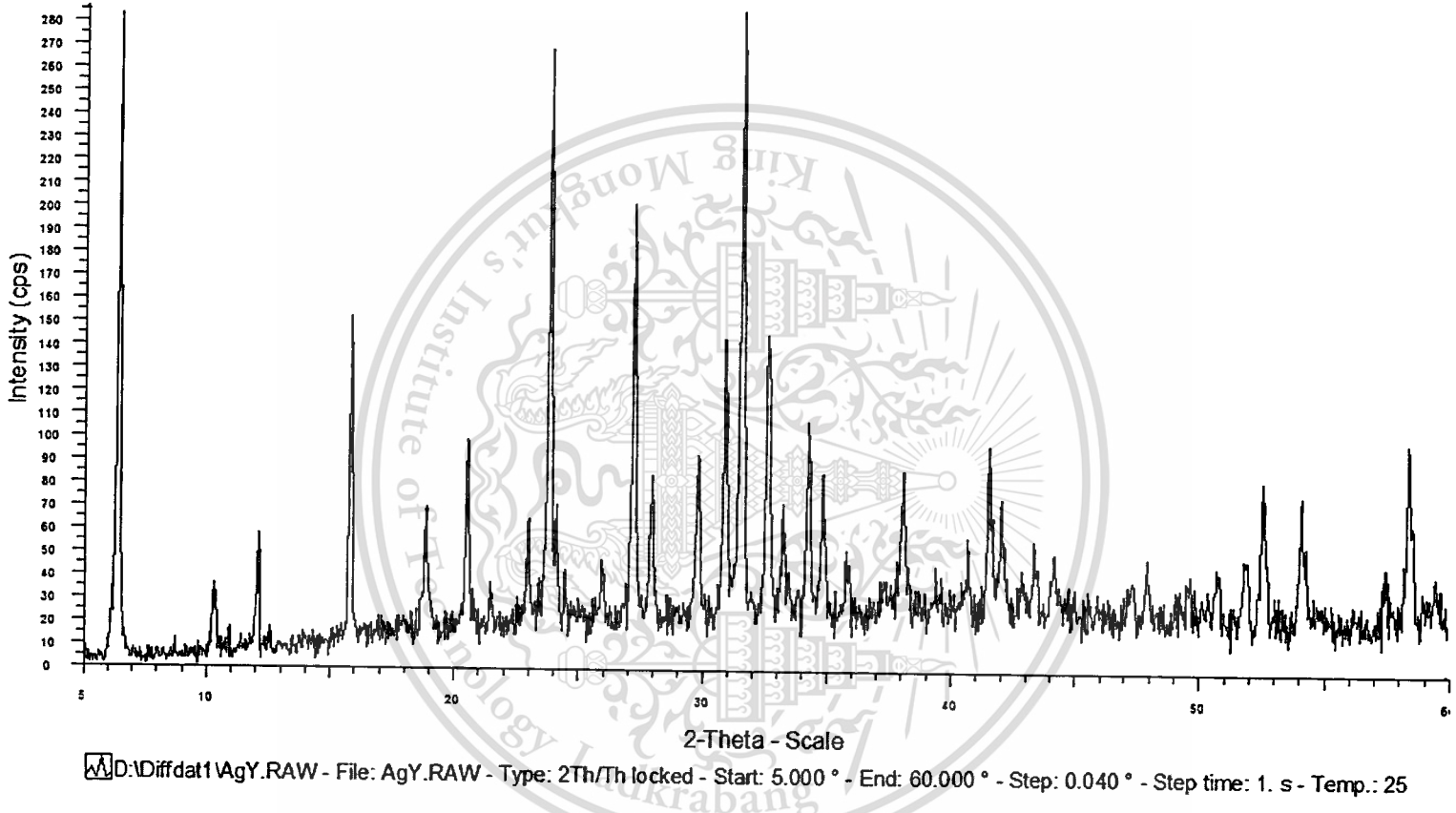

Figure A.1 X-ray diffraction pattern of AgY

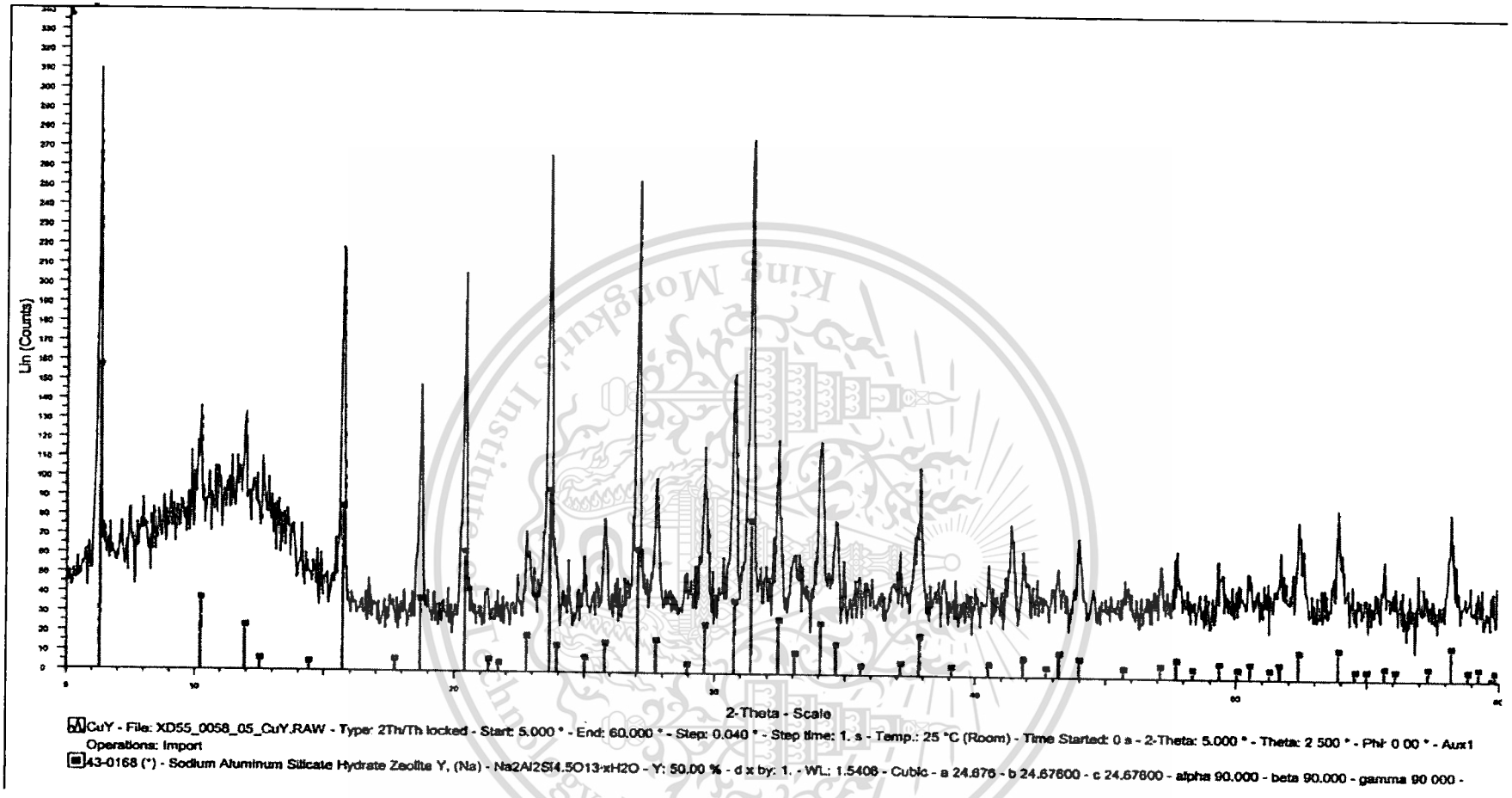

Figure A.2 X-ray diffraction pattern of CuY

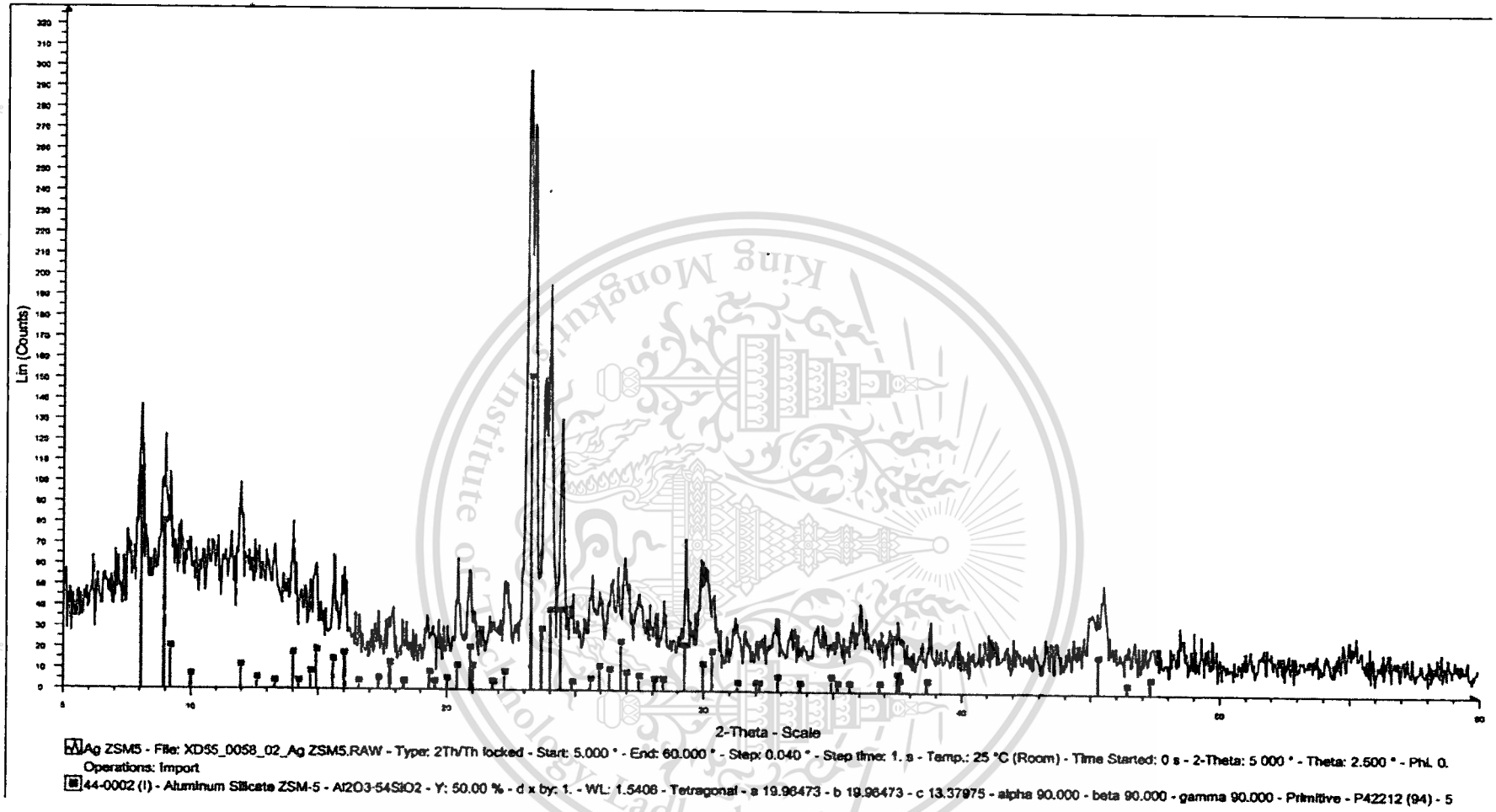

Figure A.3 X-ray diffraction pattern of AgZSM-5

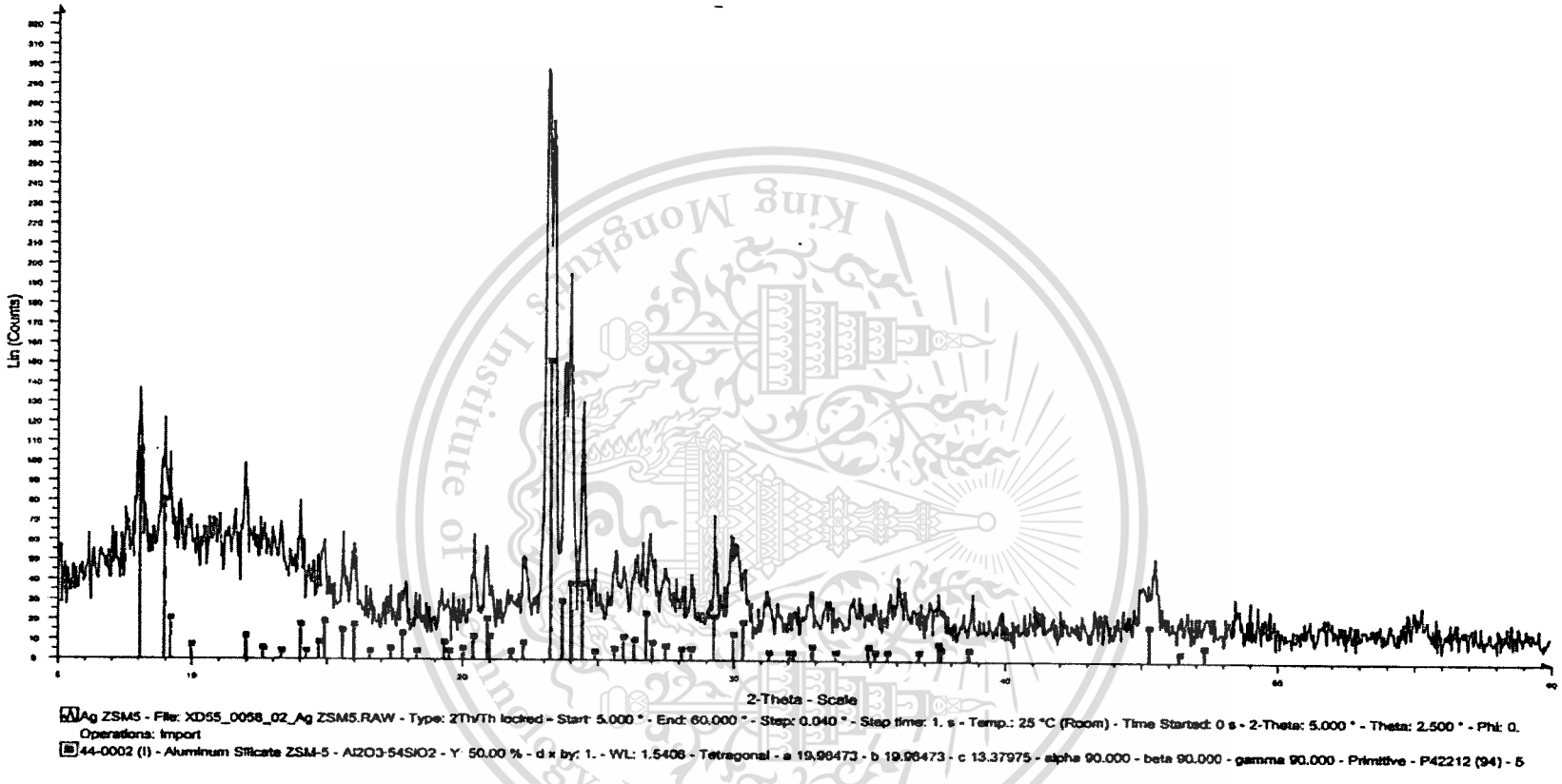

Figure A.4 X-ray diffraction pattern of CuZSM-5

APPENDIX B

Atomic Absorption Spectroscopy (AAS)

Atomic Absorption Spectroscopy (AAS) was used to determine the metal content in each of the adsorbents. Standard metal solution was diluted and used to calibrate the curve as shown in Figure B.1 for copper metal.

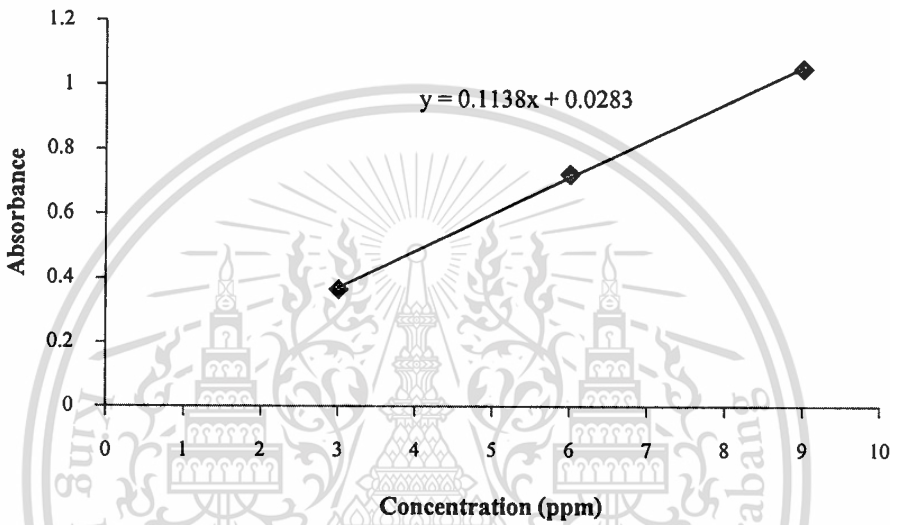

Figure B.1 Calibration curve for copper metal

0.1 gram of adsorbent was dissolved in 5 mL of HF then 0.1 mL of the dissolved solution was diluted with 50 mL of distilled water which the concentration of the diluted solution was read 2.088 ppm (mg/L). The analyzed concentrations from AAS of CuY and CuZSM-5 are shown in Table B1.

Table B.1 Concentration readings and calculated metal content of CuY and CuZSM-5.

Trial	CuY		CuZSM-5	
	Concentration (ppm or mg/L)	Metal Content (%)	Concentration (ppm or mg/L)	Metal Content (%)
1	2.088	5.22	2.742	6.85
2	2.257	5.64	2.677	6.69
3	2.389	5.97	2.646	6.62
Average	2.245	**5.61**	2.688	**6.72**

Therefore, concentration of solution = 2.088 x 500 = 1,044 mg/L

If 1000 mL of solution contains 1,044 mg of Cu

Then, 5 mL of solution contains 5.22 mg of Cu

Therefore, $$\% \text{ Cu} = \frac{5.22 \text{ mg}}{0.1 \text{ g} \times \frac{1000 \text{ mg}}{\text{g}}} \times 100 = 5.22 \%$$

Calibration curve of silver metal content in adsorbent from standard solution is shown in Figure B.2.

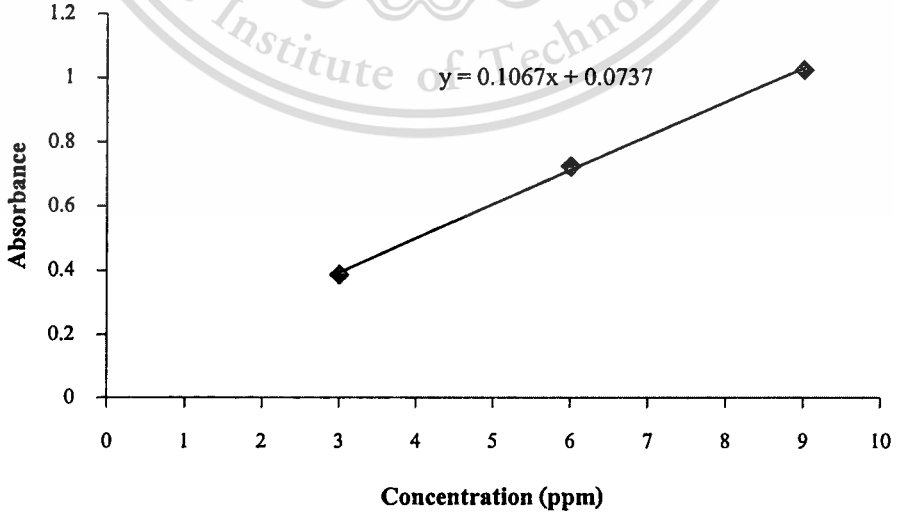

Figure B.2 Calibration curve for silver metal absorbance

Metal content calculation of AgY and AgZSM5 is similar to that of CuY and CuZSM-5 shown above. Percentage of metal present in AgY and AgZSM-5 are shown in Table B.2.

Table B.2 Concentration readings and calculated metal content of AgY and AgZSM-5.

Trial	AgY		AgZSM-5	
	Concentration (ppm or mg/L)	Metal Content (%)	Concentration (ppm or mg/L)	Metal Content (%)
1	4.345	10.86	4.275	10.68
2	4.285	10.71	4.379	10.94
3	4.118	10.30	4.548	11.37
Average	4.249	**10.62**	4.413	**11.00**

APPENDIX C

Analysis and calculation

C1. Calibration curve

The content of thiophene left in n-heptane solution was determined by gas chromatography using flam ionization detector (FID) with HP-5 column. The curve was plotted in ratio of thiophene to cyclohexanone (internal standard solution) versus concentration of thiophene (wt%).

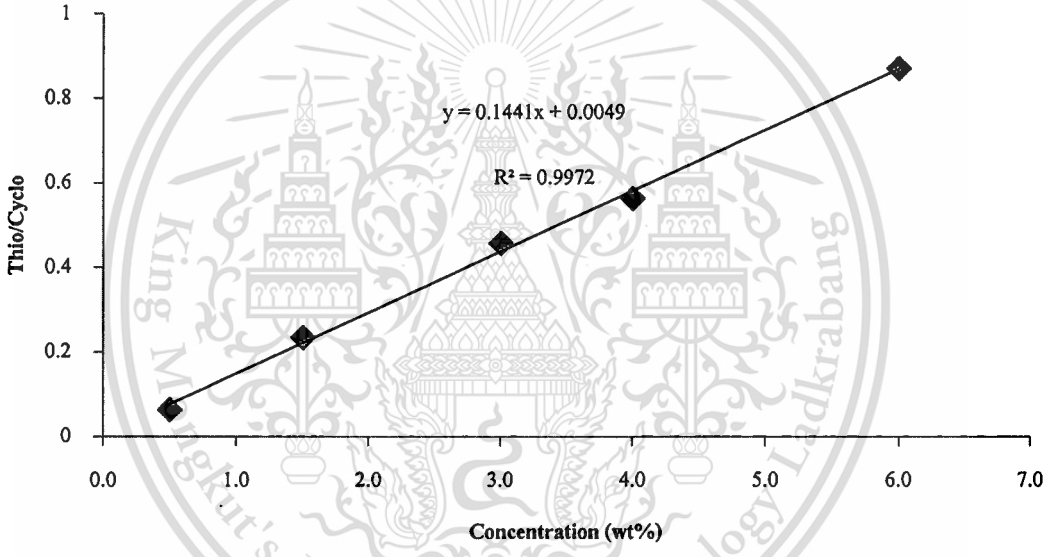

Figure C.1 Calibration Curve of concentration and peak area ratio in thiophene determination

C2. Analysis

The performance of each adsorbent could fundamentally be determined by the percentage removal of thiophene (% removal) from n-heptane solution. The following equation was used for calculation.

$$\% \text{ thiophene remove} = \frac{x_i - x_t}{x_i} \times 100$$

where x_i = initial concentration of thiophene at 0 min (wt%)

x_t = concentration of thiophene at the time (wt%)

In reporting the thiophene adsorption, it would be reported in term of millimole of thiophene per 1 gram of adsorbent.

$$\text{thiophene uptake (mmol/g)} = \frac{\left[\frac{\frac{\% \text{ thiophene removal}}{100} \times \text{mass of thiophene in solution} \times 1000}{\text{molecular weight of thiophene}}\right]}{\text{mass of adsorbent}}$$

Table C.1 Percentage of thiophene removal and thiophene uptake in each batch.

Adsorbents	Thiophene concentration (wt%)	% Thiophene removal	Thiophene uptake (mmol/g)
AgY	6.0	35.76	9.90
	4.5	33.58	7.28
	3.0	25.80	3.72
	2.0	42.12	3.17
	1.5	56.43	1.32
CuY	6.0	33.31	9.80
	4.5	21.73	4.68
	3.0	23.60	3.58
	2.0	28.68	2.00
	1.5	62.76	1.42
AgZSM-5	6.0	29.00	8.58
	4.5	25.56	6.18
	3.0	32.38	4.67
	2.0	47.89	3.41
	1.5	62.77	1.45
CuZSM-5	6.0	24.57	7.05
	4.5	23.78	5.50
	3.0	35.58	5.27
	2.0	32.03	2.31
	1.5	45.96	1.14
NaY	6.0	33.11	10.12
	4.5	N/A	N/A
	3.0	26.43	3.56
	2.0	23.15	1.68
	1.5	11.85	0.26

Adsorbents	Thiophene concentration (wt%)	% Thiophene removal	Thiophene uptake (mmol/g)
NaZSM-5	6.0	19.85	4.42
	4.5	N/A	N/A
	3.0	24.20	3.12
	2.0	N/A	N/A
	1.5	11.80	0.066