

CHAPTER IV

RESULTS AND DISCUSSIONS

Results and discussions of the experimental studies are summarized in this chapter. The results are divided into two parts: properties of the adsorbents and removal of mercury compounds.

Silica support and adsorbents were prepared by impregnation technique on silica support. Silica support and adsorbents were dried and calcined before use. After calcination, silica support and adsorbents are analyzed for their physical and chemical properties.

Mercury removal experiments by adsorption was conducted in a batch system. Mercuric chloride and diphenylmercury were used as model compounds for inorganic mercury and organic mercury compounds, respectively. Toluene was used as a liquid hydrocarbon solvent due to its high boiling point. After each experiment, liquid hydrocarbon products and solid samples were collected and analyzed for remaining mercury compounds in liquid phase and quantities of mercury compound deposited on the adsorbents, respectively.

As shown in chapter III, errors in this study is caused by Instrumental analysis, digestion and the experiments. It was found that the errors in early case are lower than 5%.

4.1 Properties of silica support and adsorbents

Adsorbents were prepared so that their metal contents were approximately 2.5% by weight of metal on silica support. The adsorbents are calcined to decompose the impregnated metal compounds with formation of metal oxide. The adsorbents used in the experiments are nickel oxide, chromium oxide, ferric oxide, molybdenum oxide, manganese oxide and mixed-metal oxide adsorbents.

Physical properties of the adsorbents, which include surface area, pore volume, and average pore diameter, are determined by BET technique

Chemical properties, which include metal content and form of metal on surface of adsorbent, are determined by AAs technique and XRD method, respectively.

Table 4.1 summarizes surface area, pore volume and average pore diameter of each adsorbent.

Table 4.1 Comparison of surface area, pore volume and average pore diameter of the adsorbent

Adsorbent	Surface Area (m ² / g)	Pore Volume (cc / g)	Average Pore Diameter (Å)
Silica support	394.15	1.98	168.96
Nickel oxide adsorbent	365.03	1.42	155.57
Manganese oxide adsorbent	352.71	1.12	126.77
Chromium oxide adsorbent	396.32	1.56	156.98
Ferric oxide adsorbent	424.19	1.31	123.09
Molybdenum oxide adsorbent	442.26	1.86	168.53
Mixed-metal oxide adsorbent	415.07	1.64	166.25

It is clearly shown that physical properties of each adsorbent change when they are compared with silica support. The changes in surface area, pore volume and average pore diameter do not have definite pattern. Some types of adsorbent such as ferric oxide, molybdenum oxide and mixed-metal oxide adsorbents, have their surface area higher than surface area of silica support but have equal or less pore volume and pore diameter, while some types of adsorbent such as nickel oxide, chromium oxide and manganese oxide adsorbents, have their surface area lower than surface area of silica support and have equal or less pore volume and pore diameter

Specific surface area is calculated by measuring the volume of nitrogen gas adsorbed on the surface of adsorbent. The adsorption of nitrogen gas is monolayer adsorption. In addition, pore volume and pore size distributions are also calculated from volume of nitrogen gas adsorbed on the surface of adsorbent. Furthermore, it is reported that many metals are suitable for adsorption of gases. Elements such as chromium, ferric,

suspected that nitrogen gas is not adsorbed as monolayer adsorption on the some surface such as Chromium oxide, Ferric oxide, Molybdenum oxide and Mixed-metal oxide adsorbents.

The adsorbents are also determined that metals are loaded onto the surface area including surface area at pores. The basic assumption for pore shape is that the shape of pore is cylindrical and total length of pore length can be calculated for comparison of pore length between silica support and others adsorbents.

The pore-length calculation are determined by:

$$\text{Pore length} = \frac{S}{\pi D_p} \quad (4.1)$$

Where V_p is pore volume (m^3/g), S is surface area (m^2/g) and D_p is average pore diameter (m).

Equation (4.1) is using for calculation of pore length from surface area. Table 4.2 shows the results of pore length calculated using Equation 4.1

Table 4.2 Pore length by calculation from Surface area

Adsorbent	Pore length (10^9 m/g)
Silica support	8.429
Nickel oxide adsorbent	7.473
Chromium oxide adsorbent	8.040
Ferric oxide adsorbent	10.975
Molybdenum oxide adsorbent	8.357
Manganese oxide adsorbent	8.861
Mixed-metal oxide adsorbent	7.950

The value of pore length of chromium oxide adsorbent, molybdenum oxide adsorbent and manganese oxide adsorbent are approximately equal to silica support. Nickel oxide adsorbent and mixed-metal oxide have their pore length higher than pore length of silica support of approximately 15%. Ferric oxide adsorbent has its pore length lower than pore length of silica support of approximately 15%. The results may be caused by the error from volume of nitrogen gas as indicated before.

X-ray Diffraction (XRD) technique is used for certify the form of metal oxide deposit on the adsorbent surface. Figure 4.1 to Figure 4.5 show the XRD diagram for each type of adsorbents.

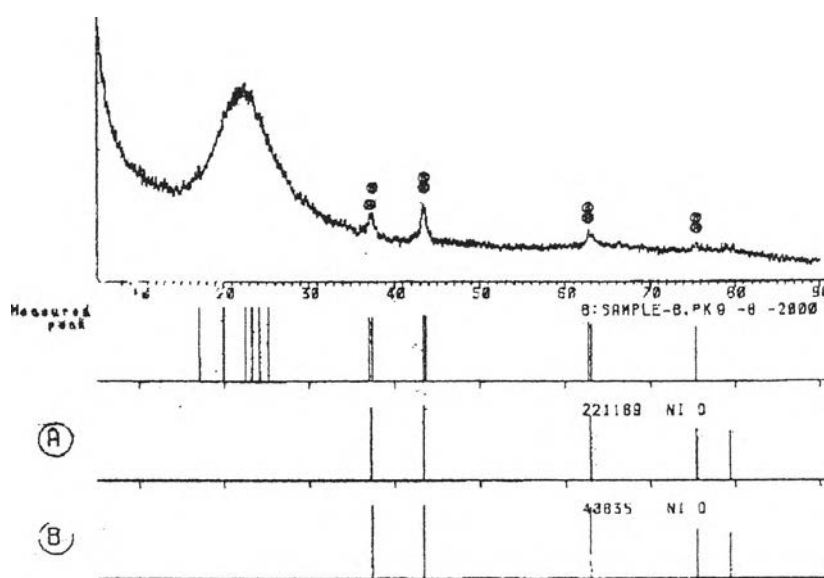


Figure 4.1 XRD-Pattern of Nickel oxide Adsorbent

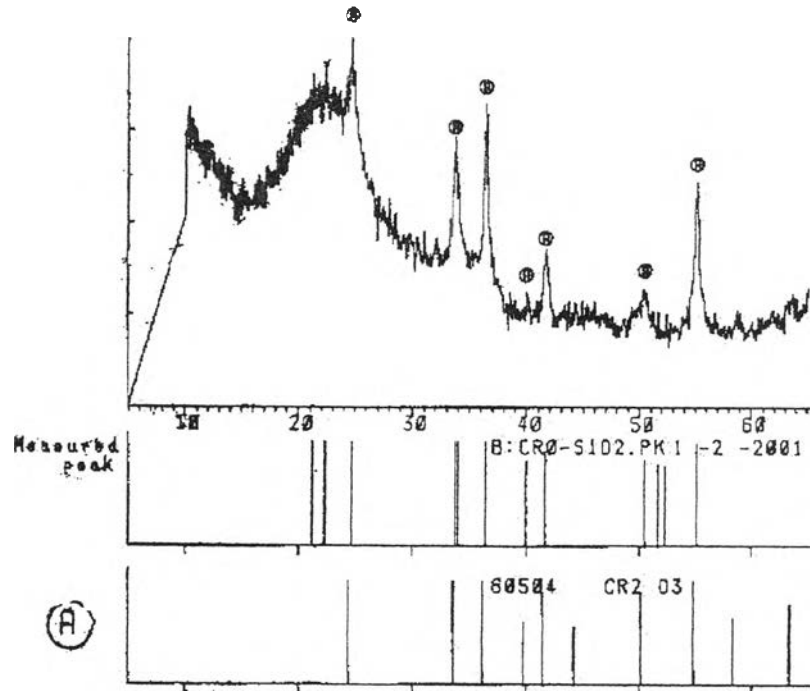


Figure 4.2 XRD-Pattern of Chromium oxide Adsorbent

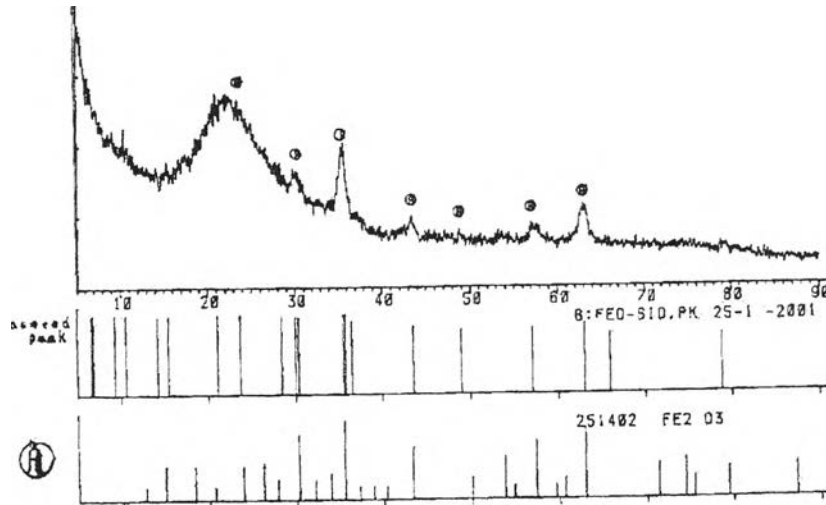


Figure 4.3 XRD-Pattern of Ferric oxide Adsorbent

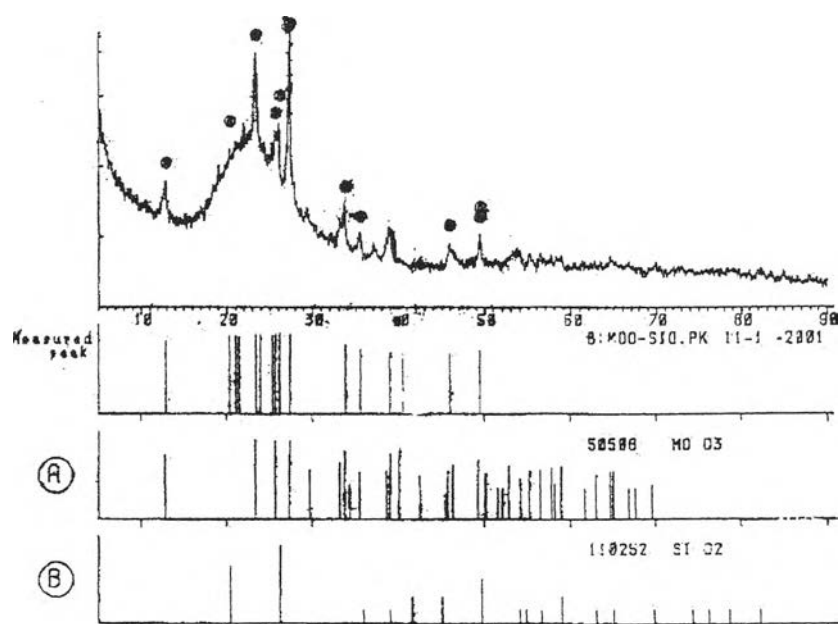


Figure 4.4 XRD-Pattern of Molybdenum oxide Adsorbent

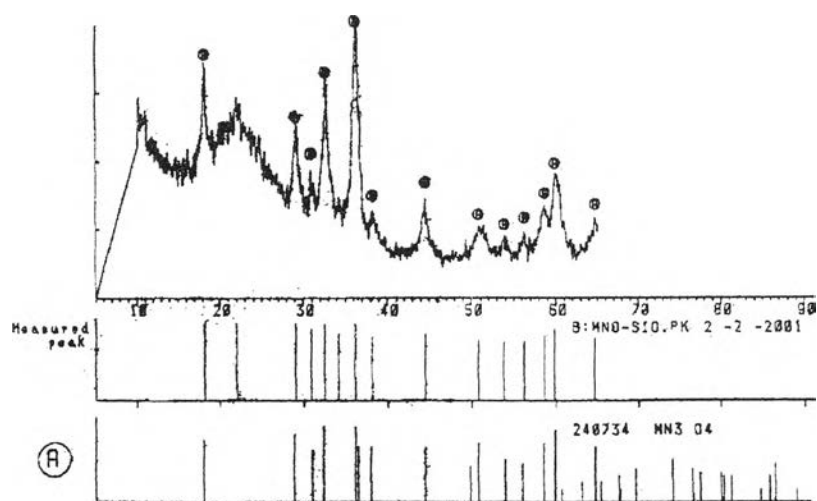


Figure 4.5 XRD-Pattern of Manganese oxide Adsorbent

Figures 4.1 to 4.5 clearly show that nickel, chromium, ferric, molybdenum and manganese are in oxide form. Unfortunately, XRD pattern for mixed metal oxide adsorbent does not show formation of metal oxide.

Each metal oxide adsorbent is prepared in order that it contained approximately 2.5% by weight of metal. Results of metal content deposit on surface of adsorbent are presented in Table 4.3.

Table 4.3 Results of metal content deposit on surface of adsorbent

Adsorbent	Weight of metal loading (%)					Weight total of metal loading (%)
	Ni	Cr	Fe	Mo	Mn	
silica support	-	-	-	-	-	-
Nickel oxide adsorbent	2.14	-	-	-	-	2.14
Chromium oxide adsorbent	-	2.15	-	-	-	2.15
Ferric oxide adsorbent	-	-	2.32	-	-	2.32
Molybdenum oxide adsorbent	-	-	-	2.24	-	2.24
Manganese oxide adsorbent	-	-	-	-	2.18	2.18
Mixed-metal oxide adsorbent	0.35	0.39	1.46	0.06	0.05	2.31

The results show that metal content on each adsorbent is less than 2.5% by weight. It is suspected that the metal salts, used for preparation of impregnation solution, adsorb moisture from the atmosphere resulting in an increase in their weight.

ASTM D 2216-98 is used to determine moisture content in each metal salt and the results are presented in Table 4.4.

Table 4.4 Percent of moisture in metal salts

Metal salts	Percent of moisture
Nickel nitrate	36.5
Chromium nitrate	38.2
Ferric nitrate	41.6
Ammonium molybdate tetrahydrate	24.8
Manganese nitrate	38.5

It is clearly observed that there was moisture in metal salts. Because of moisture, concentration of metal in impregnation solution was less than desired value.

4.2 Mercury compounds removal by adsorption

In this study, the experiments were conducted in a batch system. Adsorbents were prepared by methods as described in Chapter III. Mercuric chloride and diphenylmercury were used as model compounds for inorganic and organic mercury, respectively. Toluene was used as a liquid hydrocarbon solvent due to its high boiling point and good solubility for both of mercury compounds at 1 ppm. Temperatures were set to 30°C, 50°C and 70°C for adsorption experiments, and was set at 70°C for desorption experiments.

The ability of adsorbents on mercury compounds removal is considered by the quantity of mercury compounds concentration remaining in toluene in each experiment. The less mercury compounds concentration remaining in product would indicate high ability of adsorbent to remove mercury compound from feedstock. The mercury compounds concentration remaining on silica support experiment is used as reference amount of mercury compound, which can be removed by the support itself and is compared with other adsorbents. The results of each experiment are summarized in Appendix A.

Because mercury compounds concentration in the feedstock of each experiment varied in the range between 950 ppb to 1050 ppb, percent removed of mercury compound is used for comparison in stead of actual mercury compounds concentration. Percent removal is defined as Equation (4.2)

$$\text{Percent removal} = \frac{C_i - C_f}{C_i} \times 100 \dots\dots\dots(4.2)$$

Where C_i is initial mercury compounds concentration of feed (ppb) and C_f is mercury compounds concentration of product (ppb)

Desorption studies were conducted on selected silica support and spent adsorbents to determine the desorption capability of adsorbed mercury compounds on the adsorbents. The spent support and adsorbents were stirred in fresh toluene and atmospheric pressure. The liquid samples were separated after each experiment to analyze for mercury compounds concentration.

After adsorption experiments, Spent adsorbents were separated from liquid hydrocarbon and digested to measure mercury compounds that is adsorbed on the adsorbents as guideline in ASTM 1977-91.

The operation of both of experiments, adsorption and desorption, are summarized in the condition set in Table 4.5.

Table 4.5 Experimental details

Operating conditions	
Type of experiment	Batch system with speed-controllable propeller
Temperature	30°C, 50°C and 70°C
Pressure	ambient pressure
Support used	silica support
Adsorbent used	nickel oxide adsorbent (NiO), chromium oxide adsorbent (CrO), ferric oxide adsorbent (FeO), molybdenum oxide adsorbent (MoO), manganese oxide adsorbent (MnO) And mixed-metal oxide adsorbent (Mixed)
Adsorbent weight	1 gram for each experiment
Experimental period	1 hour for each experiment
Feed identification	
Initial concentration	1 ppm for mercuric chloride and 1 ppm for diphenylmercury
Solvent used	Toluene as liquid hydrocarbon
Feed weight	100 grams for each experiment

4.2.1 Mercury compounds removal by silica support

This section is to find the removal ability of mercury compounds on the support and to confirm that mercury compounds are not significantly removed by the support due to its inert properties for adsorption of mercury compounds.

Percent removal is shown in Figure 4.6. Removal of mercuric chloride is approximately 11 to 14%. The same trend is also observed for diphenylmercury. Percent removal is approximately 5 to 11%. It indicates that mercuric chloride and diphenylmercury are not significantly removed by silica support.

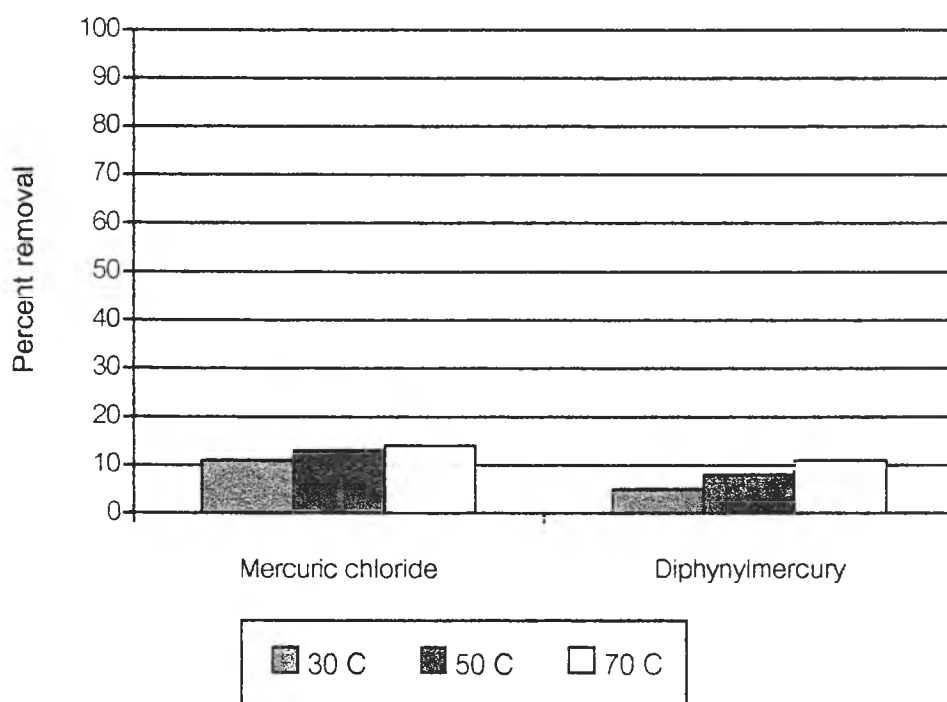


Figure 4.6 Percent removal of mercury compounds which used silica support at various temperature

It can be observed that the removal ability of both mercury compounds on various temperature at given condition is approximately the same. The spent supports in experiments of mercuric chloride removal at 30°C and diphenylmercury at 30°C are collected for desorption study of mercury compound adsorbed on their surface. The results of the desorption experiments show in Appendix A.

4.2.2 Mercury compound removal by Adsorbents

A set of experiment was designed to study ability of each adsorbent on removal of mercury compounds.

Mercury compound removal ability of adsorbents are categorized as follows;

1. Mercury compounds removal ability of nickel oxide (NiO), chromium oxide (CrO), ferric oxide (FeO), molybdenum oxide (MoO) and manganese oxide (MnO) adsorbents as monometallic adsorbents.
2. Mercury compounds removal ability of nickel oxide, chromium oxide, ferric oxide, molybdenum oxide and manganese oxide adsorbent as multimetallic adsorbents (Mixed).

Mercury compounds removal ability of nickel oxide (NiO), chromium oxide (CrO), ferric oxide (FeO), molybdenum oxide (MoO) and manganese oxide (MnO) adsorbents as monometallic adsorbents

The abilities of adsorbents on mercury compound removal are considered by comparison of the percent removal of mercury compound with silica support in each experiment

Mercury compounds removal by Nickel oxide adsorbent

Figures 4.7 and 4.8 show percent removal versus the temperature from 30°C to 70°C for nickel oxide adsorbent. It is shown that percent removals of mercury compounds are higher when nickel oxide was impregnated on silica support. Similar results are corresponding to mercuric chloride and diphenylmercury. These results indicate that impregnation of nickel oxide on silica support improve ability of adsorbent on mercury compound removal from liquid hydrocarbon.

It can be observed that ability of mercury compounds removal increases when the temperature increases over the range of the experiments.

In addition, it is suspected that most of mercury compounds is preferentially adsorbed on nickel oxide surface. The spent nickel oxide adsorbent is measured the stoichiometry of the compositions on surface by X-ray Diffraction (XRD). XRD pattern of the surface does not show any of interacted composition.

The results of desorption experiments, in Appendix A, show that mercury compounds can be found in studies of mercuric chloride and diphenylmercury. It may be suspected that both of mercury compounds can be partly desorbed from nickel oxide adsorbent.

Some spent nickel oxide adsorbents were digested to determine the amount of mercury compounds that deposited on their surface. The results are shown in Appendix B. The results do not agree with the results from adsorption studies. It can be observed that the deposited mercury compounds is less than the amount of mercury compounds removal from liquid hydrocarbon. It is expected that some parts of mercury compounds vaporized while adsorbents were digested with acids.

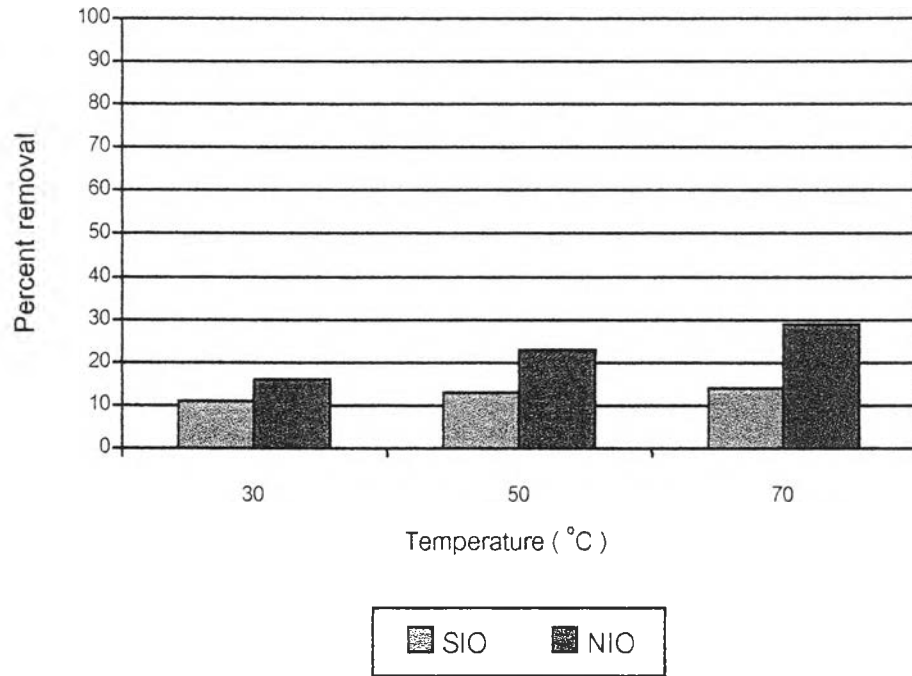


Figure 4.7 Comparison of percent removal on mercuric chloride between SiO and NiO adsorbent at temperature ranging from 30°C to 70°C

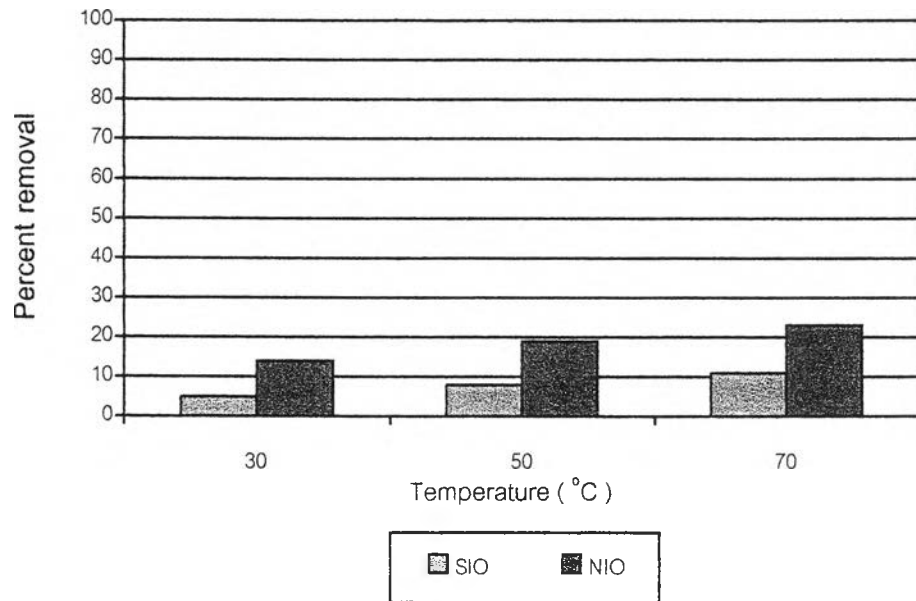


Figure 4.8 Comparison of percent removal on diphenylmercury between SiO and NiO adsorbent at temperature ranging from 30°C to 70°C

Mercury compounds removal by Chromium oxide adsorbent

Figures 4.9 and 4.10 show percent removal versus the temperature from 30°C to 70°C for chromium oxide adsorbent. It is shown that percent removals of mercury compounds are higher when nickel oxide was impregnated on silica support. Similar results are corresponding to mercuric chloride and diphenylmercury. These results indicate that impregnation of chromium oxide on silica support improve ability of adsorbent on mercury compound removal from liquid hydrocarbon.

It can be observed that ability of mercury compounds removal increases when the temperature increases over the range of the experiments.

The spent chromium oxide adsorbent is measured the stoichiometry of the compositions on surface by X-ray Diffraction (XRD). Figure 4.11 shows that mercuric chloride is interacted with chromium oxide and is formed to HgCrO_4 . Unfortunately, XRD pattern does not show any of interacted composition between chromium oxide and diphenylmercury.

The results of desorption experiments, in Appendix A, show that mercury compounds can be found in studies of mercuric chloride and diphenylmercury. It may be suspected that both of mercury compounds can be partly desorbed from chromium oxide adsorbent.

Some spent chromium oxide adsorbents were digested to determine the amount of mercury compounds that deposited on their surface. The results are shown in Appendix B. The results do not agree with the results from adsorption studies. It can be observed that the deposited mercury compounds is less than the amount of mercury compounds removal from liquid hydrocarbon. It is expected that some parts of mercury compounds vaporized while adsorbents were digested with acids.

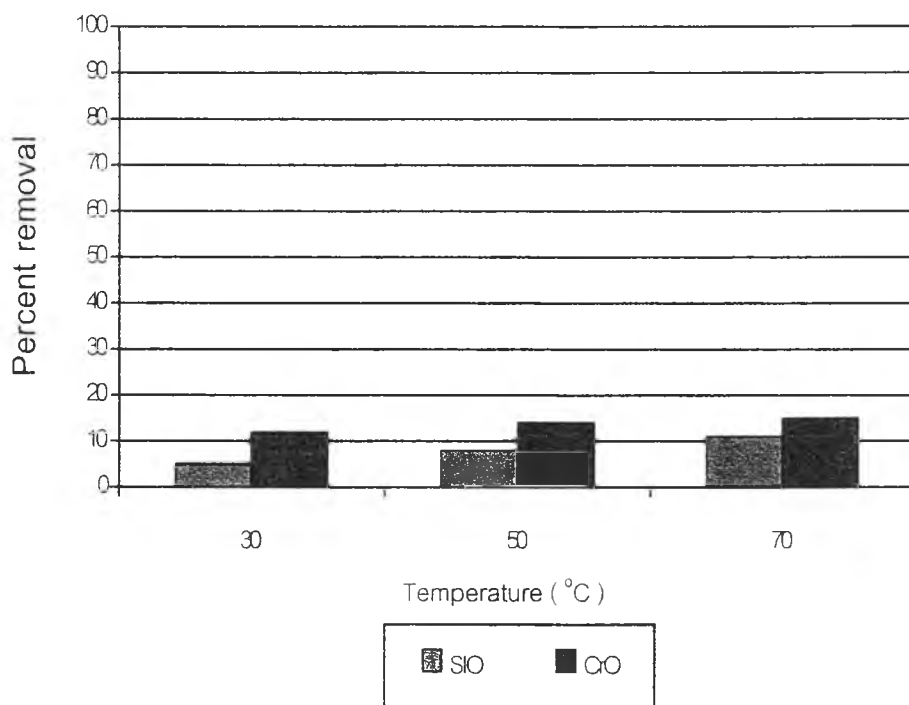


Figure 4.9 Comparison of percent removal on mercuric chloride between SiO and CrO adsorbent at temperature ranging from 30°C to 70°C

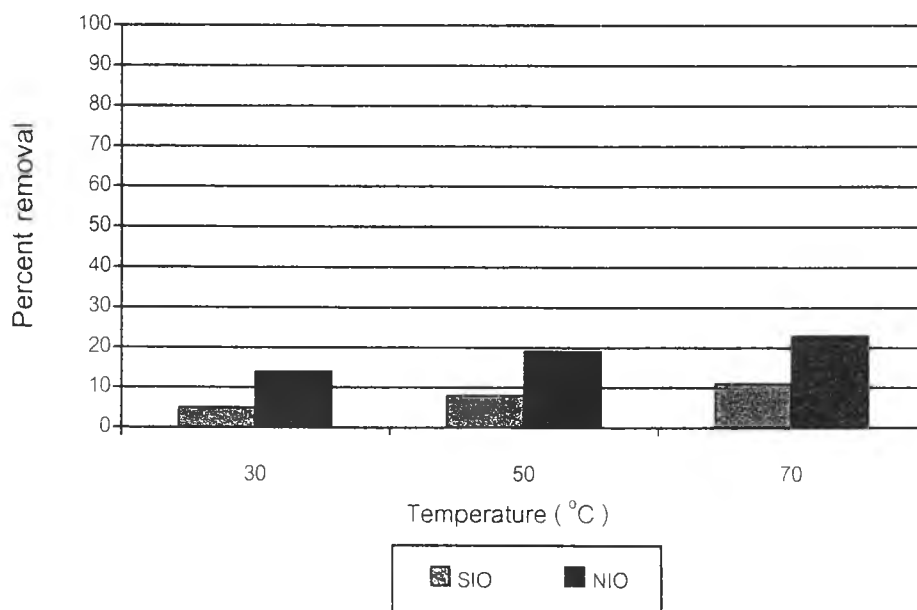


Figure 4.10 Comparison of percent removal on diphenylmercury between SiO and CrO adsorbent at temperature ranging from 30°C to 70°C

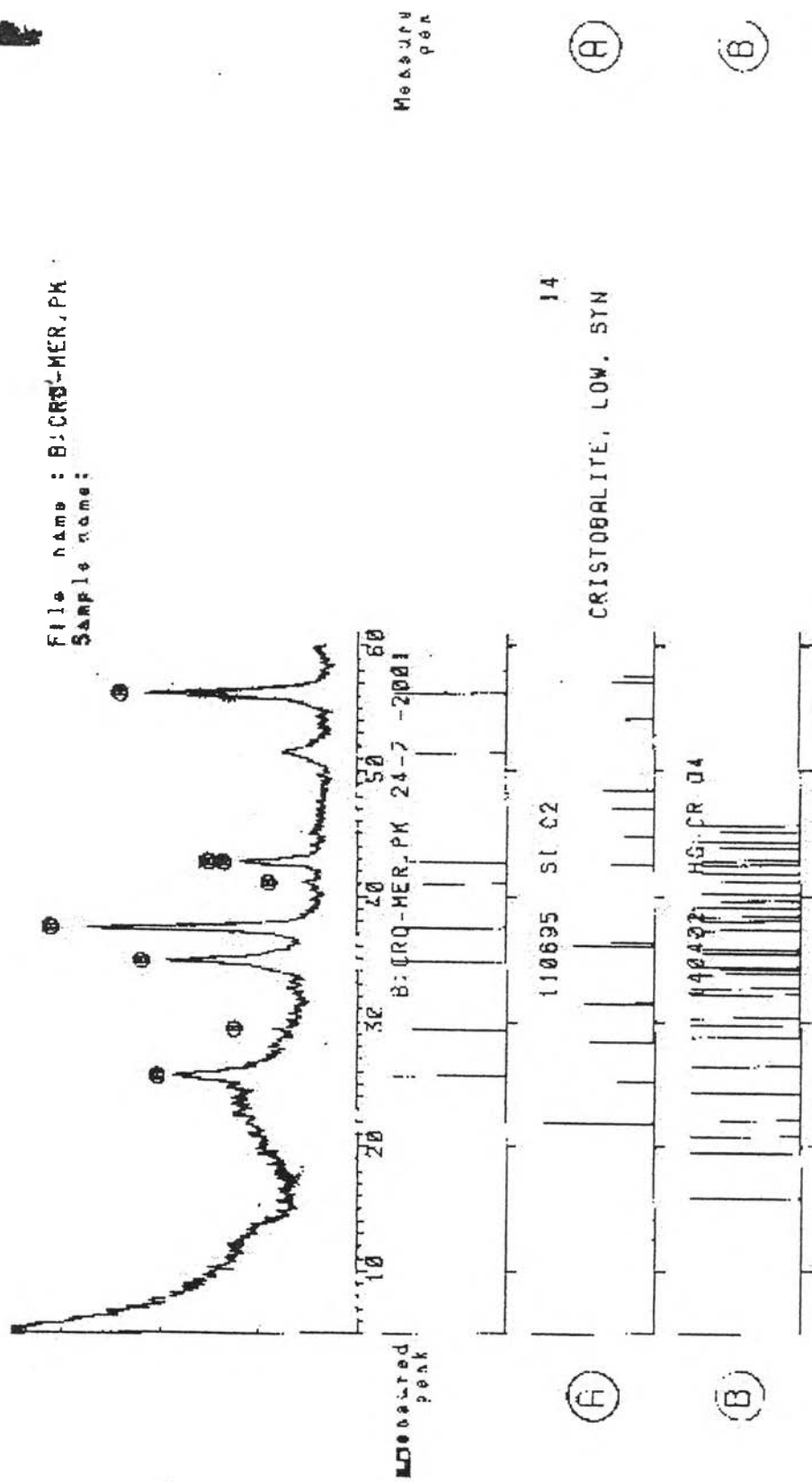


Figure 4.11 XRD pattern of spent chromium adsorbent

Mercury compounds removal by Ferric oxide adsorbent

Figures 4.12 and 4.13 show percent removal versus the temperature from 30°C to 70°C for nickel oxide adsorbent. It is shown that percent removals of mercury compounds are higher when ferric oxide was impregnated on silica support. Similar results are corresponding to mercuric chloride and diphenylmercury. These results indicate that impregnation of ferric oxide on silica support improve ability of adsorbent on mercury compound removal from liquid hydrocarbon.

It can be observed that ability of mercury compounds removal increases when the temperature increases over the range of the experiments.

In addition, it is suspected that most of mercury compounds is preferentially adsorbed on ferric oxide surface. The spent ferric oxide adsorbent is measured the stoichiometry of the compositions on surface by X-ray Diffraction (XRD). XRD pattern of the surface does not show any of interacted composition.

The results of desorption experiments, in Appendix A, show that mercury compounds can be found in studies of mercuric chloride and diphenylmercury. It may be suspected that both of mercury compounds can be partly desorbed from ferric oxide adsorbent.

Some spent ferric oxide adsorbents were digested to determine the amount of mercury compounds that deposited on their surface. The results are shown in Appendix B. The results do not agree with the results from adsorption studies. It can be observed that the deposited mercury compounds is less than the amount of mercury compounds removal from liquid hydrocarbon. It is expected that some parts of mercury compounds vaporized while adsorbents were digested with acids.

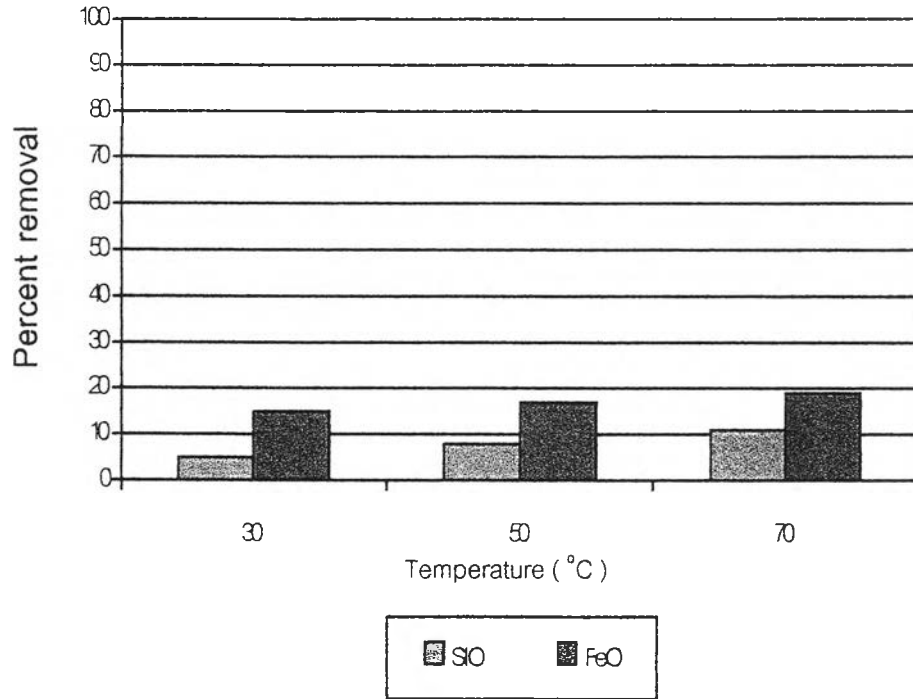


Figure 4.12 Comparison of percent removal on mercuric chloride between SiO and FeO adsorbent at temperature ranging from 30°C to 70°C

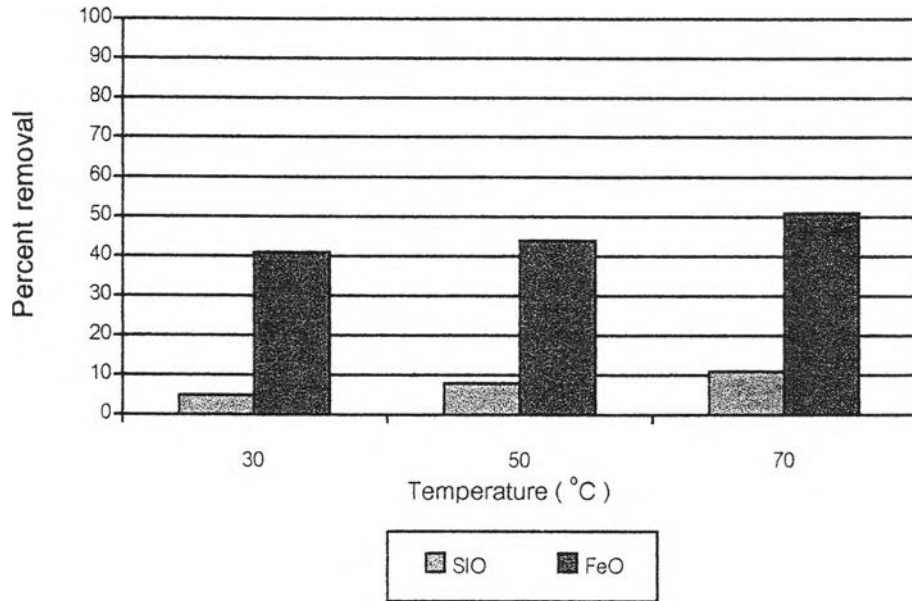


Figure 4.13 Comparison of percent removal on diphenylmercury between SiO and FeO adsorbent at temperature ranging from 30°C to 70°C

Mercury compounds removal by Molybdenum oxide adsorbent

Figures 4.14 and 4.15 show percent removal versus the temperature from 30°C to 70°C for molybdenum oxide adsorbent. It is shown that percent removals of mercury compounds are higher when molybdenum oxide was impregnated on silica support. Similar results are corresponding to mercuric chloride and diphenylmercury. These results indicate that impregnation of molybdenum oxide on silica support improve ability of adsorbent on mercury compound removal from liquid hydrocarbon.

It can be observed that ability of mercury compounds removal increases when the temperature increases over the range of the experiments.

The spent molybdenum oxide adsorbent is measured the stoichiometry of the compositions on surface by X-ray Diffraction (XRD). Figure 4.16 shows that mercuric chloride is interacted with molybdenum oxide and is formed to HgMoO_4 . In addition, XRD pattern of the surface does not show any of interacted composition between molybdenum and diphenylmercury.

The results of desorption experiments, in Appendix A, show that mercury compounds can be found in studies of mercuric chloride and diphenylmercury. It may be suspected that both of mercury compounds can be partly desorbed from molybdenum oxide adsorbent.

Some spent molybdenum oxide adsorbents were digested to determine the amount of mercury compounds that deposited on their surface. The results are shown in Appendix B. The results do not agree with the results from adsorption studies. It can be observed that the deposited mercury compounds is less than the amount of mercury compounds removal from liquid hydrocarbon. It is expected that some parts of mercury compounds vaporized while adsorbents were digested with acids.

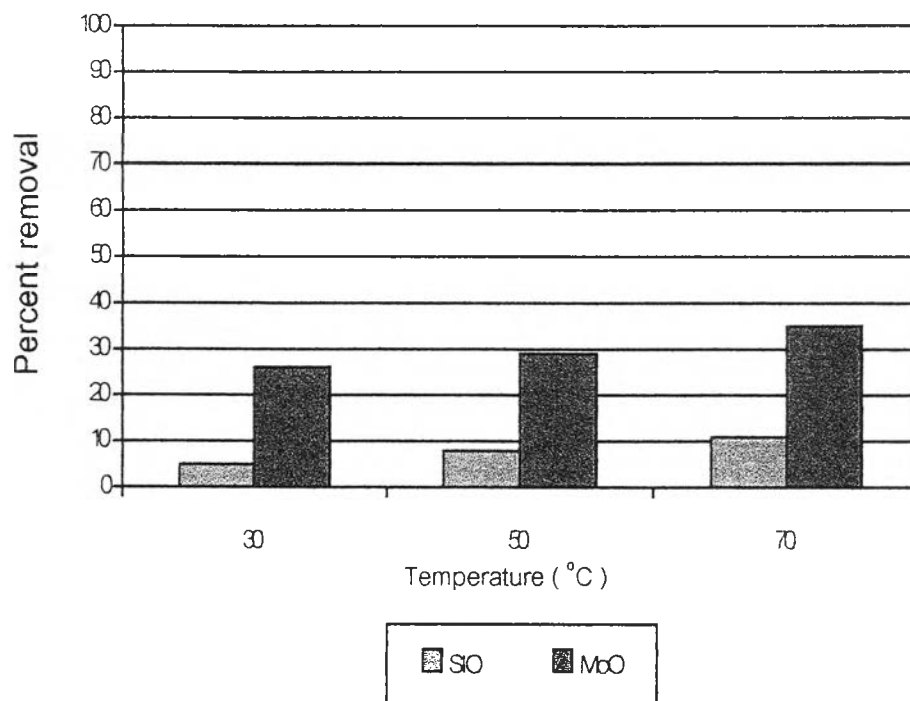


Figure 4.14 Comparison of percent removal on mercuric chloride between SiO and MoO adsorbent at temperature ranging from 30°C to 70°C

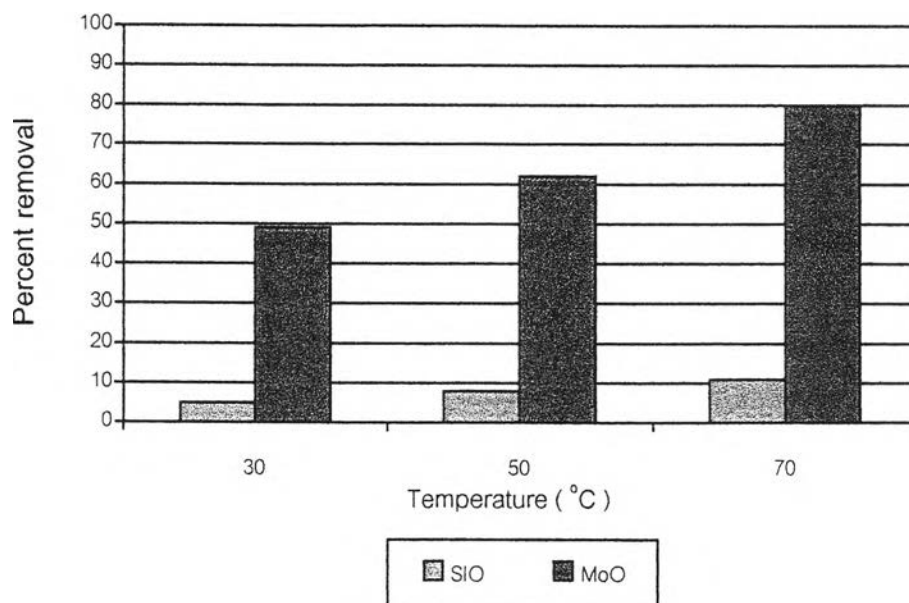


Figure 4.15 Comparison of percent removal on diphenylmercury between SiO and MoO adsorbent at temperature ranging from 30°C to 70°C

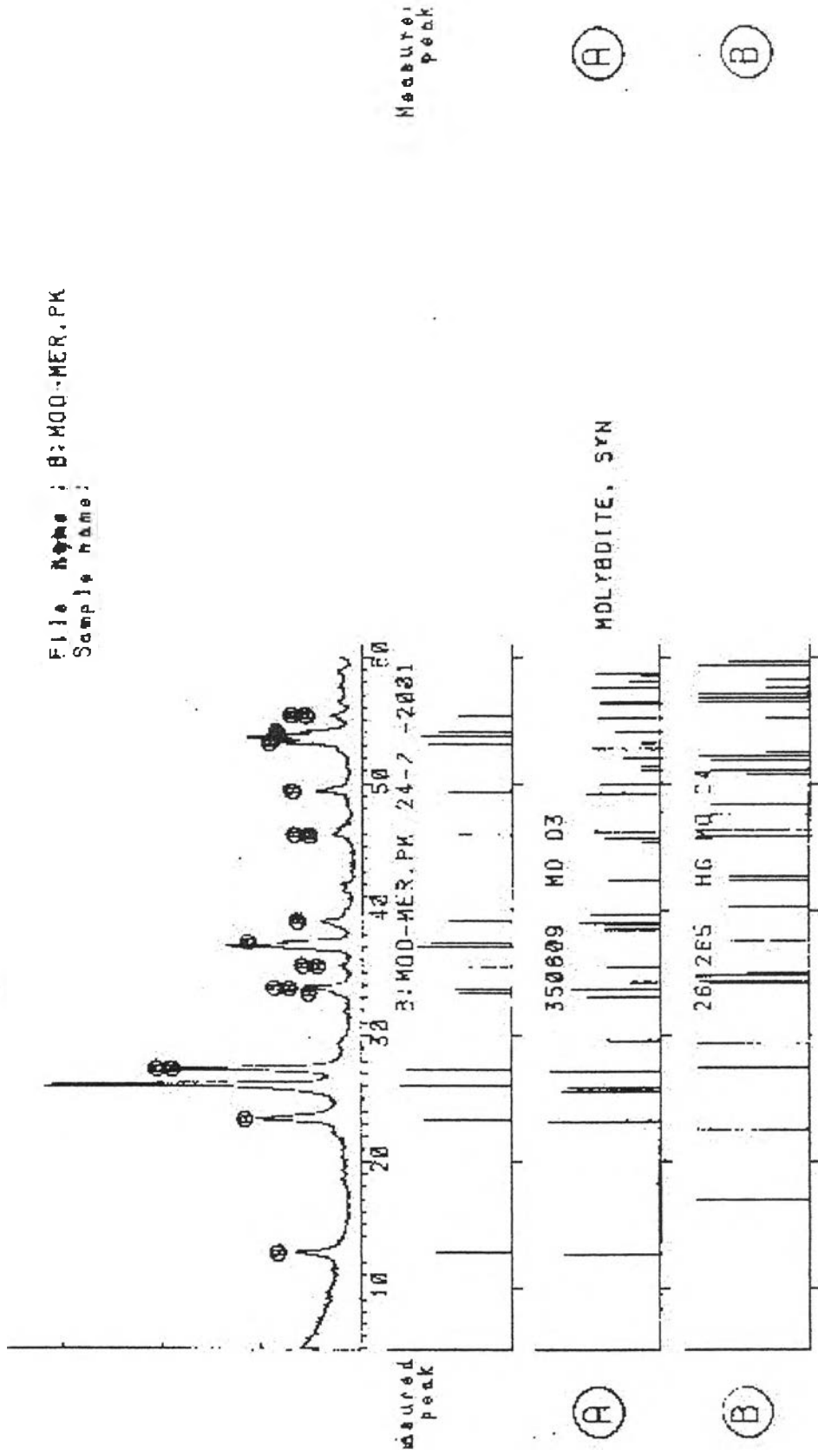


Figure 4.16 XRD pattern of spent molybdenum adsorbent

Mercury compounds removal by Manganese oxide adsorbent

Figures 4.17 and 4.18 show percent removal versus the temperature from 30°C to 70°C for manganese oxide adsorbent. It is shown that percent removals of mercury compounds are higher when manganese oxide was impregnated on silica support. Similar results are corresponding to mercuric chloride and diphenylmercury. These results indicate that impregnation of manganese oxide on silica support improve ability of adsorbent on mercury compound removal from liquid hydrocarbon.

It can be observed that ability of mercury compounds removal increases when the temperature increases over the range of the experiments.

In addition, it is suspected that most of mercury compounds is preferentially adsorbed on manganese oxide surface. The spent manganese oxide adsorbent is measured the stoichiometry of the compositions on surface by X-ray Diffraction (XRD). XRD pattern of the surface does not show any of interacted composition.

The results of desorption experiments, in Appendix A, show that mercury compounds can be found in studies of mercuric chloride and diphenylmercury. It may be suspected that both of mercury compounds can be partly desorbed from manganese oxide adsorbent.

Some spent manganese oxide adsorbents were digested to determine the amount of mercury compounds that deposited on their surface. The results are shown in Appendix B. The results do not agree with the results from adsorption studies. It can be observed that the deposited mercury compounds is less than the amount of mercury compounds removal from liquid hydrocarbon. It is expected that some parts of mercury compounds vaporized while adsorbents were digested with acids.

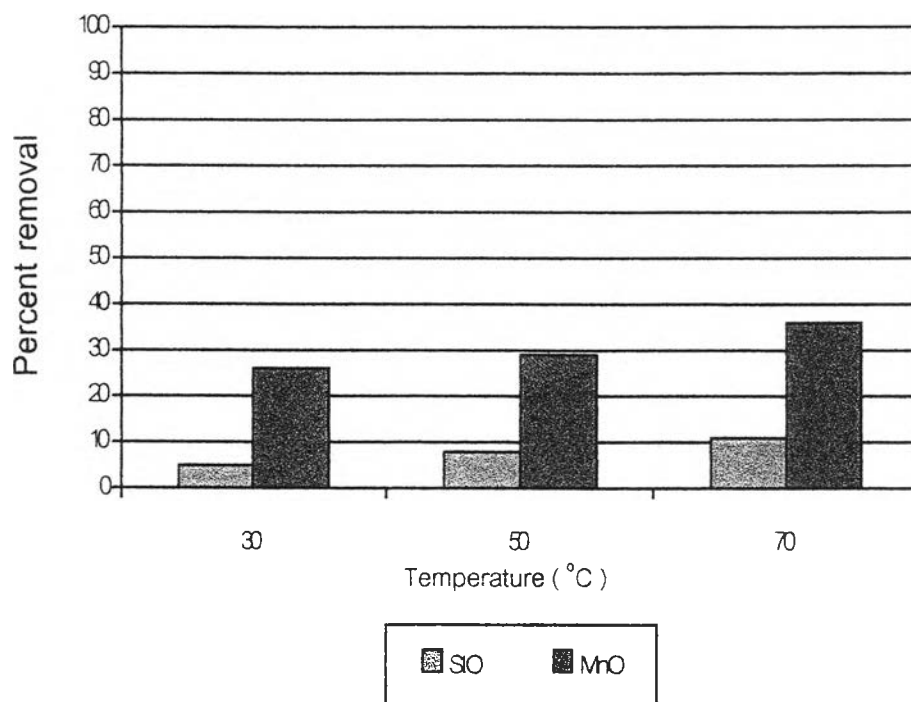


Figure 4.17 Comparison of percent removal on mercuric chloride between SiO and MnO adsorbent at temperature ranging from 30°C to 70°C

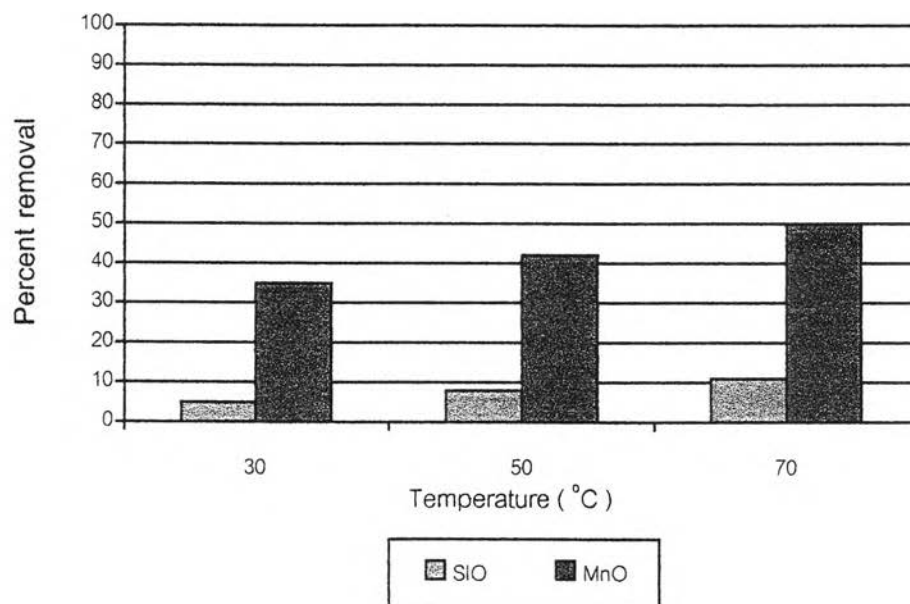


Figure 4.18 Comparison of percent removal on diphenylmercury between SiO and MnO adsorbent at temperature ranging from 30°C to 70°C

Mercury compounds removal ability of nickel oxide, chromium oxide, ferric oxide, molybdenum oxide and manganese oxide as monometallic (Mixed) adsorbents

The abilities of adsorbents on mercury compounds removal are considered by comparison of the percent removal of mercury compound with silica support in each experiment.

Mercury compounds removal by mixed-metal oxide adsorbent

Figures 4.19 and 4.20 show percent removal versus the temperature from 30°C to 70°C for mixed-metal oxide adsorbent. It is shown that percent removals of mercury compounds are higher when mixed-metal oxide was impregnated on silica support. Similar results are corresponding to mercuric chloride and diphenylmercury. These results indicate that impregnation of mixed-metal oxide on silica support improve ability of adsorbent on mercury compound removal from liquid hydrocarbon.

It can be observed that ability of mercury compounds removal increases when the temperature increases over the range of the experiments.

In addition, it is suspected that most of mercury compounds is preferentially adsorbed on nickel oxide surface. The spent mixed-metal oxide adsorbent is measured the stoichiometry of the compositions on surface by X-ray Diffraction (XRD). XRD pattern of the surface does not show any of interacted composition.

The results of desorption experiments, in Appendix A, show that mercury compounds can be found in studies of mercuric chloride and diphenylmercury. It may be suspected that both of mercury compounds can be partly desorbed from mixed-metal oxide adsorbent.

Some spent mixed-metal oxide adsorbents were digested to determine the amount of mercury compounds that deposited on their surface. The results are shown in Appendix B. The results do not agree with the results from adsorption studies. It can be observed that the deposited mercury compounds is less than the amount of mercury compounds removal from liquid hydrocarbon. It is expected that some parts of mercury compounds vaporized while adsorbents were digested with acids.

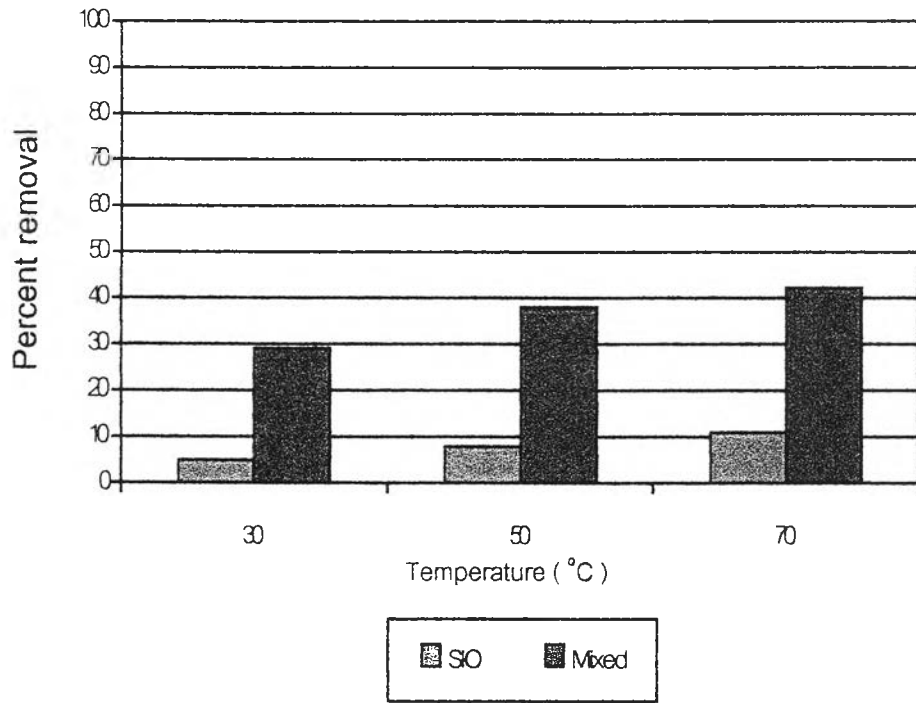


Figure 4.19 Comparison of percent removal on mercuric chloride between SiO and Mixed adsorbent at temperature ranging from 30°C to 70°C

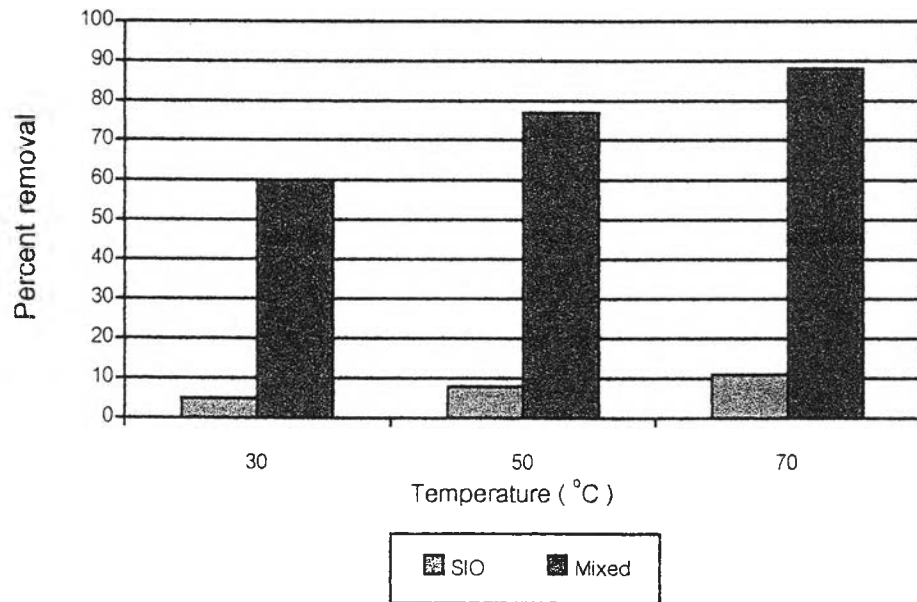


Figure 4.20 Comparison of percent removal on diphenylmercury between SiO and Mixed adsorbent at temperature ranging from 30°C to 70°C

4.3 Comparison of adsorbent on mercury compounds removal

The study on mercury compounds removal for each type of adsorbent with respect to silica support is reported. The considerations of mercury compounds removal by adsorbents and effect of temperature are also discussed.

Figure 4.21 and 4.22 shows the percent removal versus type of adsorbent at various temperatures. The removal of mercuric chloride in each of temperature used can be indicated that molybdenum oxide and manganese oxide adsorbent can be removed more effective than the others at every temperature. However, mixed metal oxide adsorbent also shows a high effectiveness in removal of mercuric chloride. It is because mixed metal oxide adsorbent consists of both molybdenum and manganese oxide on its surface. Adsorption efficiency of adsorbents for removal of mercuric chloride increases in the following order: Mixed > MnO > MoO > NiO > FeO > CrO.

Removal of diphenylmercury indicates that chromium oxide is the most effective removed. However, molybdenum oxide and mixed metal oxide adsorbent also show a high effectiveness in removal of diphenylmercury at 70°C. Adsorption efficiency of adsorbents for removal of diphenylmercury increases in the following order: CrO > Mixed > MoO > FeO > MnO > NiO.

The results show that all of adsorbents can be used effectively in removal of mercury compounds from liquid hydrocarbon. Although, mercury compounds removal also depend on operating temperature. Removal of both mercuric chloride and diphenylmercury increase with increasing of operating temperature for all types of adsorbent. The ability of metal oxide adsorbent is depending on the ability of the nature of metal loading on surface of adsorbent.

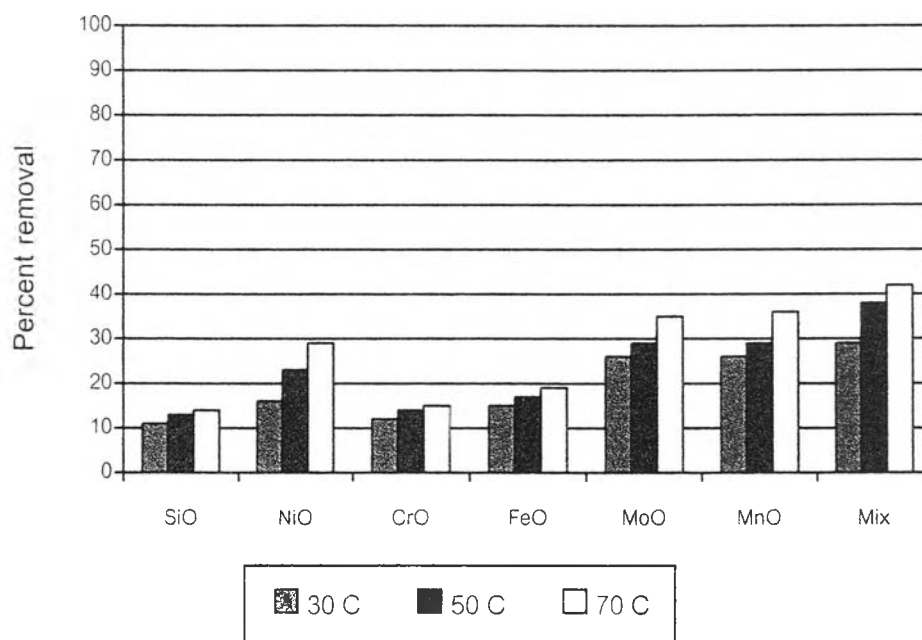


Figure 4.21 Comparison of adsorbents in study of mercuric chloride removal at various temperature

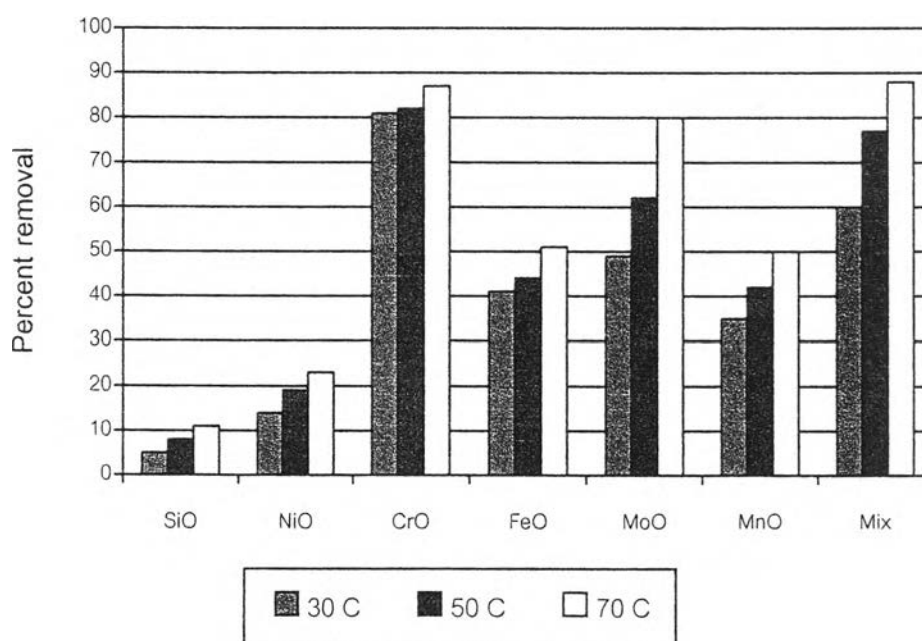


Figure 4.22 Comparison of adsorbents in study of diphenylmercury removal at various temperature