

การกำจัดสารประกอบปรอทจากไฮโดรคาร์บอนเหลวโดยการดูดซับบนตัวดูดซับ
คอปเปอร์ออกไซด์และคอปเปอร์ซัลไฟด์



นายวสันต์ ไชคกลาง

สถาบันวิทยบริการ

จุฬาลงกรณ์มหาวิทยาลัย

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต

สาขาวิชาวิศวกรรมเคมี ภาควิชาวิศวกรรมเคมี

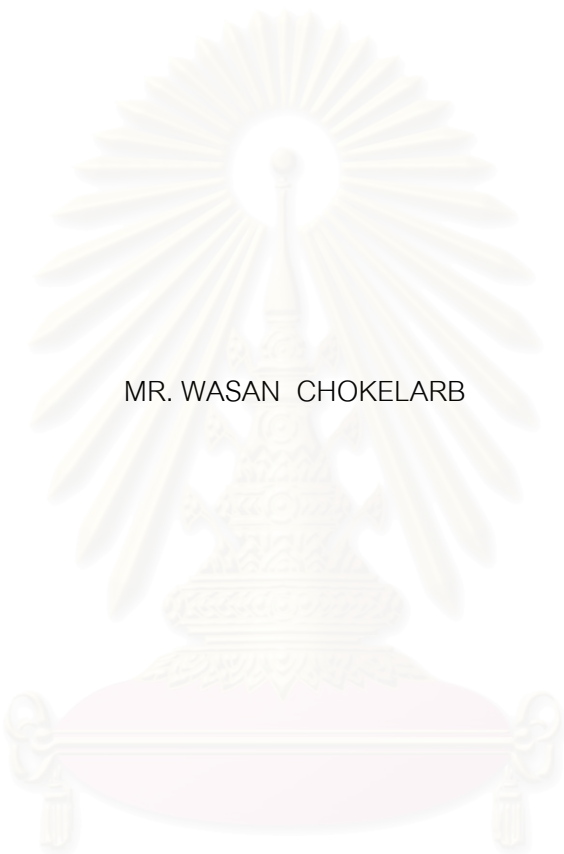
คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

ปีการศึกษา 2543

ISBN 974-13-0663-6

ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

REMOVAL OF MERCURY COMPOUNDS FROM LIQUID HYDROCARBON BY ADSORPTION ON
COPPER OXIDE AND COPPER SULFIDE ADSORBENTS



MR. WASAN CHOKELARB

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering in Chemical Engineering

Department of Chemical Engineering

Faculty of Engineering

Chulalongkorn University

Academic Year 2000

ISBN 974-13-0663-6

ชื่อผู้ทำวิทยานิพนธ์: การกำจัดสารประกอบปรอทจากไฮโดรคาร์บอนเหลวโดยการดูดซับบน
ตัวดูดซับคอปเปอร์ออกไซด์และคอปเปอร์ซัลไฟด์(Removal of Mercury Compounds from
Liquid Hydrocarbon by Adsorption on Copper Oxide and Copper Sulfide
Adsorbents) อ. ที่ปรึกษา : ดร.เจดศักดิ์ ไชยคุนา, 105 หน้า ISBN 974-13-0663-6

การวิจัยครั้งนี้ เป็นการศึกษาการกำจัดสารประกอบปรอทจากไฮโดรคาร์บอนเหลวโดย
การดูดซับบนตัวดูดซับคอปเปอร์ออกไซด์และคอปเปอร์ซัลไฟด์ ทำการทดลองที่ความดันบรรยากาศ
ที่อุณหภูมิ 30 50 และ 70 องศาเซลเซียส ใช้เมอคิวริกคลอไรด์เป็นตัวแทนสารประกอบปรอทในรูป
ของโลหะอินทรีย์และใช้ไดฟีนิลเมอคิวรีเป็นตัวแทนสารประกอบปรอทในรูปของโลหะอินทรีย์
สารตั้งต้นประกอบด้วยสารประกอบของปรอทละลายในโทลูอีนที่มีความเข้มข้นของปรอท 1 ส่วนใน
ล้านส่วน ตัวดูดซับที่ใช้ในการวิจัยครั้งนี้คือ อะลูมินา คอปเปอร์ออกไซด์บนอะลูมินาและ
คอปเปอร์ซัลไฟด์บนอะลูมินา ปริมาณคอปเปอร์บนตัวดูดซับคอปเปอร์ออกไซด์และคอปเปอร์ซัลไฟด์
ร้อยละ 2.5 โดยน้ำหนัก

จากผลการทดลองพบว่าตัวดูดซับคอปเปอร์ออกไซด์และตัวดูดซับคอปเปอร์ซัลไฟด์
มีประสิทธิภาพในการดูดซับปรอทออกจากไฮโดรคาร์บอนเหลวได้ดี ประสิทธิภาพของการดูดซับ
สารประกอบปรอททั้งสองชนิดขึ้นกับอุณหภูมิและชนิดของตัวดูดซับ ประสิทธิภาพการกำจัดปรอทของ
ตัวดูดซับแต่ละชนิดจะเพิ่มขึ้นตามลำดับดังนี้ คอปเปอร์ซัลไฟด์ > คอปเปอร์ออกไซด์ > อะลูมินา โดย
ตัวดูดซับทั้งหมดสามารถกำจัดเมอคิวริกคลอไรด์ได้ดีกว่าไดฟีนิลเมอคิวรี โดยการดูดซับปรอทโดย
ตัวดูดซับคอปเปอร์ออกไซด์และคอปเปอร์ซัลไฟด์คาดว่าเป็นการดูดซับทางเคมี เนื่องจากพบว่าเมื่อ
สารประกอบปรอทถูกดูดซับบนตัวดูดซับแล้วจะเกิดสารประกอบคอปเปอร์เมอร์คิวรี (CuHg) และ
เมอร์คิวรีซัลไฟด์ (HgS) บนตัวดูดซับคอปเปอร์ออกไซด์และคอปเปอร์ซัลไฟด์

ภาควิชา.....วิศวกรรมเคมี.....ลายมือชื่อผู้นิสิต.....
สาขาวิชา.....วิศวกรรมเคมี.....ลายมือชื่ออาจารย์ที่ปรึกษา.....
ปีการศึกษา.....2543.....ลายมืออาจารย์ที่ปรึกษาร่วม.....

4070409721 : MAJOR CHEMICAL ENGINEERING DEPARTMENT

KEY WORD: MERCURY COMPOUNDS / ADSORBENT / COPPER OXIDE / COPPER SULFIDE

WASAN CHOKELARB : REMOVAL OF MERCURY COMPOUNDS FROM LIQUID
HYDROCARBON BY ADSORPTION ON COPPER OXIDE AND COPPER SULFIDE
ADSORBENTS. THESIS ADVISOR : JIRDSAK TSCHEIKUNA, Ph.D., 105 pp.
ISBN 974-13-0663-6

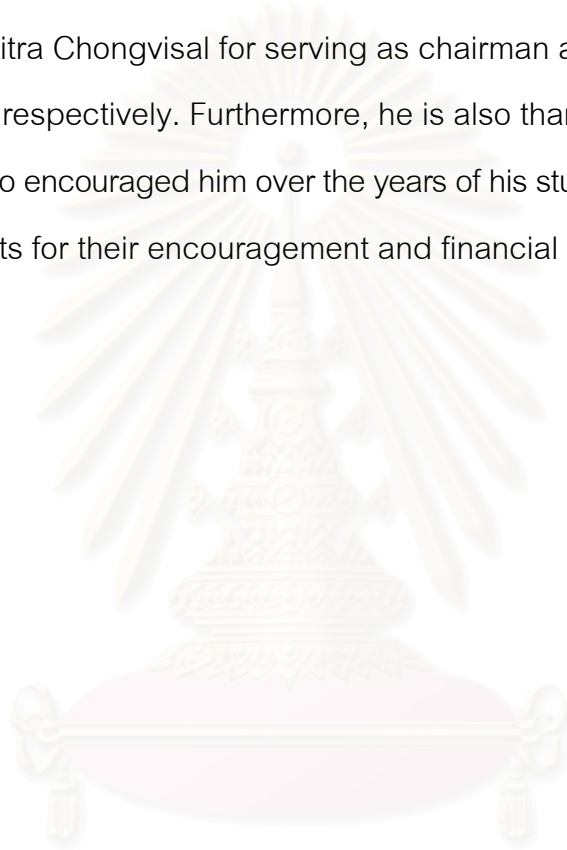
Removal of mercury compounds from liquid hydrocarbon was investigated in this study. The experiments were conducted at atmospheric pressure and at temperature of 30 °C, 50 °C and 70 °C. Mercuric chloride and diphenylmercury are used to represent ionic and organic form of mercury compounds. These compounds were dissolved in toluene to obtain solutions containing 1 ppm of mercury. The adsorbents were alumina, copper oxide on alumina support and copper sulfide on alumina support. Copper loading on copper oxide and copper sulfide adsorbents were 2.5% by weight.

The results showed that copper oxide and copper sulfide adsorbents can be used effectively in the removal of mercury compounds from hydrocarbon. Removal of mercury depended on temperature. In addition, it also depended on the types of mercury compound types. The results show that mercuric chloride can be removed more effectively than diphenylmercury by all adsorbent. Efficiency of adsorbent on mercury removal is in the following order: copper sulfide > copper oxide > alumina. Based on the experimental results, it is expected that the adsorption of mercuric chloride and diphenylmercury on copper oxide and copper sulfide adsorbent are a chemical adsorption. Formation of copper mercury (CuHg) and mercury sulfide (HgS) were detected on spent copper oxide and copper sulfide adsorbent respectively.

Department.....Chemical..Engineering.....Student's signature.....
Field of study...Chemical..Engineering.....Advisor's signature.....
Academic year.... 2000.....Co-advisor' signature.....

ACKNOWLEDGEMENT

The author would like to express his gratitude and appreciation to his advisor, Dr.Jirdsak Tscheikuna, for his guidance, valuable help and supervision during this study. In addition, he is also grateful to Associate Professor Dr. Chirakarn Muangnapoh, Assistant Professor Dr. Sasithorn Boon-Long, Assistant Professor Dr. Vichitra Chongvisal for serving as chairman and member of the thesis committee, respectively. Furthermore, he is also thankful to his friends and all encouraged who encouraged him over the years of his study. Finally, he would like to thank his parents for their encouragement and financial support throughout this study.



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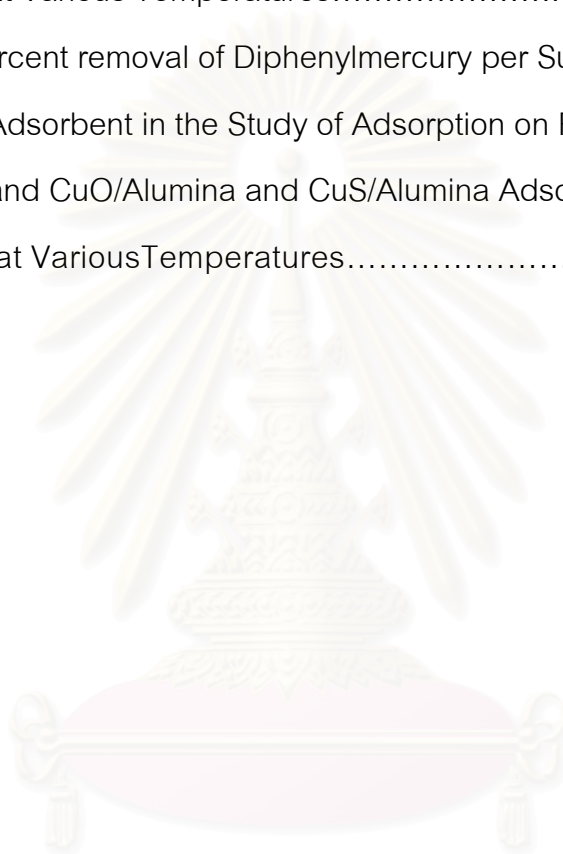
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CHAPTER I

Introduction

Petroleum for refinery and petrochemical process may contain some impurities. These impurities are usually found in the form of sulfur, nitrogen, oxygen and metal compounds such as nickel, vanadium and iron, especially mercury. Mercury is metal compound found in wide range of petroleum such as natural gas, condensate, and crude oils. Quantities of mercury depend on the sources of petroleum feedstocks. Natural gas is found to have mercury contents of 200-300, 180, 50-80, 1-9 and 0.005-0.04 ppb (part per billion) from Sumata, Groningen, Algeria, the Middle East, and America, respectively (Jamal A., 1991). The associated condensate is found to have mercury 10-3000 ppb (Sarrasin, 1993). North Sea and San Joaquin crudes have mercury contents of 55 and 110 ppb, respectively (Stockwell 1993).

Although mercury is found in trace quantity, it can cause processing and environmental concern. Mercury can attack process equipment made of copper and especially aluminum. Catalyst that used in catalytic process such as catalytic hydrocarbon is susceptible to mercury poisoning. Furthermore, mercury in oil and condensate can be emitted in air upon combustion, causing concern in air pollution, wastewater and soil. To protect the equipment and environment, it is desirable to remove the mercury from hydrocarbon condensate and crude oil or reduce it to level that are as low as possible.

Several methods have been proposed for mercury removal from both gas and liquid hydrocarbons. It can be classified into two groups: chemical treatment and adsorption on inorganic material. First method, mercury reacts

with some chemical and convert to mercury compounds such as mercuric sulfide. There are some contaminate substances in product. Adsorption is the most commonly used method for removal of mercury. It provides a process for removal of mercury by contacting the feedstock with an adsorbent and mercury will be adsorbed on the adsorbent. The adsorption provides a high efficiency of mercury removal.

From the literature reviews, many types of adsorbents are proposed for removal of mercury from liquid hydrocarbon but the most common one is copper oxide and copper sulfide adsorbents. The role of CuO and CuS in mercury removal process was studied and compared with other metal. (Yan, 1995) However, there is no indication that what types of mercury can be adsorbed by copper oxide and copper sulfide adsorbent.

In this study, the role of copper oxide and copper sulfide adsorbents on removal of ionic and organic forms of mercury is investigated. This study is to study the effect of types of mercury compounds and temperature which can effect for the removal of mercury from liquid hydrocarbon and to study the efficiency of each adsorbent. Copper sulfide form is chosen because metal sulfides are less sensitive to liquid hydrocarbon but their inherent reactivity to mercury. Toluene containing mercury compounds is used as the feed model. Toluene is used because of its solubility. Mercuric chloride is used as mercuric compound in inorganic form. Mercuric chloride is chosen because it commonly occurs in crude oils. Diphenylmercury is used as mercuric compound in organometallic form. Diphenylmercury is chosen for the following reasons. Diphenylmercury has the strongest metal-carbon bond of the common organic mercury compound. It would therefore be reasonable to say that if it is able to

adsorb diphenylmercury, it is able to adsorb all mercury bonds to common organic ligands. Liquid product and spent catalysts are digested with permanganate persulfate solution, nitric acid, and sulfuric acid which conform to ASTM D-3223 to obtain the ionic form in aqueous phase and reduce analytical interference before analysis by atomic absorption spectrometry. Total surface area, pore volume and pore size distribution of each fresh and spent catalysts are analyzed by BET method.



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CHAPTER II

Literature Reviews

2.1 Mercury Compounds

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 radical, alkoxyalkyl compounds, aryl compounds particularly the diphenylmercury. The various chemical forms of mercury exhibit significantly different chemical and physical behavior. (Lenihan and Fletcher, 1977)

Mercury is the only metallic element in that it is liquid at ordinary temperatures. Its atomic number is 80 and its atomic weight is usually given as 200.59. Its valences are of 1 and 2. Mercury is capable of forming hundreds of compounds, each with its own chemical properties. Mercury readily 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 usually decomposed to mercury. Mercury has a relatively high vapor pressure at ordinary temperatures. The rate of vaporization increases with increasing in temperature.

2.2 Mercury in Petroleum

Elemental mercury and several mercury compound occur naturally in hydrocarbons. At ambient temperature, element mercury (Hg^0) is soluble in liquid aliphatic hydrocarbons to few (1-3) ppm which is several times greater than its 0.05-ppm solubility in water. Elemental mercury is highly adsorptive and

adsorbs on metallic surface and on solid materials (sand) suspended in liquids. Elemental mercury in hydrocarbon depends strongly on temperature, hence, when saturated liquids are cooled. Elemental mercury can precipitate in equipment.

Organic mercury compounds (RHgR and RHgCl where $\text{R}=\text{CH}_3$, C_2H_5 , etc.) are highly soluble in crude oil and gas condensate. Dialkylmercury compounds partition to hydrocarbon liquids in separation and to distillation fractions according to their boiling points. Dialkylmercury compounds have been detected in gas condensate and crude oil using chromatographic techniques. Mercuric Halides (HgCl_2) are more soluble than Hg^0 in gas condensate and oil. Mercury (sulfur) complexes (HgK where K is an organic sulfide, thiol, thiophene or mercaptan) are postulated to exist in some crude oils and condensates.

Boiling points of organic compounds (Table 2.1) assist prediction of distribution of compound in distillation of crude oil (S.W.Wilhelm and N.Bloom, 2000)

Table 2.1 Boiling points of volatile mercury compound

Hg compound	Boiling point (°C)
Hg^0	357
$(\text{CH}_3)_2\text{Hg}$	96
$(\text{C}_2\text{H}_5)_2\text{Hg}$	170
$(\text{C}_3\text{H}_7)_2\text{Hg}$	190
$(\text{C}_4\text{H}_9)_2\text{Hg}$	206

The solubility of some mercury compound in hexane are compiled in Table 2.2 and are useful to predict the distribution of compounds in phase separation.

Table 2.2 Solubility of some mercury compounds in hexane

Species	Solubility (ppm)	Temperature (°C)
Hg ⁰	1,200	27.5
HgCl ₂	11,500	27.5
CH ₃ HgCl	>1,000,000	20.0
(CH ₃) ₂ Hg	∞	

Because of its volatility, element mercury vapor is the dominant species in natural gas. Dialkylmercury may also be present in gas, especially close to the wellhead where the gas is hot. oil (S.W.Wilhelm and N.Bloom, 2000) The organic mercury compounds in gas partition to separated hydrocarbon liquids as the gas is cooled.(Mercury is a metal compound found in wide range of petroleum such as natural gas, condensate and crude oils. Forms and quantities of mercury depend on the source and type of petroleum feedstock .

Mercury found in natural gas is generally in metallic form and its concentration varies from 1 to 75 $\mu\text{g}/\text{m}^3$ (Sarrazin, 1993). On the other hands, natural gas associated condensate is different from natural gas. The mercury which is found in the condensate is presented in various chemical states; elemental, ionic and organometallic (Yamada et al., 1995). The concentration ranges of mercury in natural gas condensate are generally 10-3000 ppb (Sarrazin, 1993), 15-450 ppb (Yan, 1987). When natural gas condensate from the Gulf of Thailand was determined for the mercury content in the laboratory, it was found that it contained 300 ppb of mercury.

2.3 Disadvantages of Mercury Compounds in Petroleum

2.3.1 Effects of mercury on processing

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 production of ethylene (Audeh, 1991). A natural gas condensate is commonly passed through a heat exchanger constructed of aluminum. It has been found that mercury tends to amalgamate with the aluminum and creates the risk of corrosion cracking. The failures occur, at the LNG plant at Skikda, Algeria, from tube corrosion in the spiral wound exchangers. Corroded tubes contained white deposits: aluminum oxide, aluminum hydroxide and aluminum carbonates, with trace of elemental mercury (Leeper, 1980).

2) Mercury in gas plant products affects downstream processes. Gas plant products used for chemical manufacture, especially olefins, ethylene, aromatics and MTBE, are at risk to mercury in process feed due to the cited equipment problems and due to catalyst poisoning.

3) Mercury contaminates treatment process such as molecular sieve and glycol dehydration units, and amine acid gas removal system. Contaminated treatment liquids and spent molecular sieve adsorbent are difficult to dispose and to regenerated.

4) Mercury deposition in equipment poses a health and safety risk for workers involved in maintenance or inspection activities. Sludge containing

mercury from water treatment system, separators, desalters and heat exchangers represents a toxic waste stream that is difficult to store or process for disposal.

5) Waste water streams that contain high levels of mercury must be treated to remove mercury prior to discharge thus adding significant costs to plant operational expense. (S.W.Wilhelm and N.Bloom, 2000)

2.3.2 Catalyst deactivation

Catalytic process such as selective hydrogenation can be deactivated by mercury poisoning (Sarazin, 1993). Poisoning is catalyst deactivation due to the adsorption of some of the impurities in the feed stream, such as nitrogen, sulfur, oxygen, and metal. The poisoning deactivation by metal impurities can permanently deposit on the active sites of the catalyst and causes a loss of catalytic activity. Several researchers studied an effect of mercury on catalyst deactivation. Perepelitsa et al. (1979) studied the effect of mercury on hydrogen adsorption on palladium. They found that Hg inhibited the adsorption of hydrogen without changing significantly the bond energy and the ionization kinetics of the adsorbed hydrogen. The loss of adsorption capacity depended on structure of Pd. Grichina et al. (1991) studied the effect of Hg poisoning on Rh, Ru catalysts. They found that Hg poisoning decreased the amount of adsorbed hydrogen on catalyst and the heat of adsorption was also decreased. They suggested that the Hg poisoning occurred by chemisorption and blockage of the surface of catalyst. In addition, the poisoning of mercury on Pd catalyst in the liquid phase was studied by Sokol'skii et al. (1982). They found that mercury had no appreciable effect on the selectivity but it decreased the activation energy. Morales et al. (1979) studied the poisoning effect on the hydrogenolysis of cyclopentane in which Pt alumina was used as the catalyst. The result showed that Hg^{2+} changed the reaction rate constant and adsorption properties of Pt.

In addition, mercury compounds are extremely toxic with man and animals, especially organic compounds. They damage nervous system on inhalation or ingestion. The major mercury specific considerations for health and safety of workers in petroleum processing involve exposure of worker to mercury vapor. Mercury and its compounds are neurotoxins. Hg^0 is readily absorbed into the blood stream via the lungs.

2.4 Study of Removal of Mercury Compounds from Petroleum

Several methods have been proposed for mercury removal from both gas and liquid hydrocarbons. The methods can be classified into two groups: chemical treatment and adsorption.

2.4.1 Chemical treatment

This method, mercury reacts with some chemical substance and converts to a mercuric compound such as mercuric sulfide that is insoluble in hydrocarbon and easy to remove from hydrocarbon feedstock. The chemical substance used is usually a sulfur compound, such as alkali polysulfide. Polysulfide ions react with mercury to give HgS , according to



Several researchers proposed this method. Yan (1990) proposed a method to remove mercury from liquid hydrocarbons, such as natural gas condensate and crude oil, by contacting the hydrocarbon with dilute aqueous alkali solution of alkali metal sulfide salt, Na_2S_x and aqueous NaOH solution. Volume ratios of aqueous solution to hydrocarbon liquid preferably range from 0.1 to 10. Mixing and settling temperatures can be ranged from 50°F to 300°F . The residence time for the mixture react is 0.001 to 100 seconds depending upon

the temperature and type of sulfur compound used. The result showed that 80% to 90% of mercury presented in heavy condensate could be removed.

In addition, Yan (1991) studied the removal of trace mercury in natural gas by scrubbing with dilute polysulfide solution. The residual mercury in the gas can be removed from about 0.1 to below 0.01 ppb, a reduction of 90%. In the system, the gas was contacted with stainless steel packing wetted with a solution containing about 3 ppm of polysulfide salt. The mercury in the gas reacts with the polysulfide to form insoluble mercuric sulfide and then it is removed from the gas. In addition, unexpectedly, the stainless steel packing alone, wetted with water, was found to be effective for removing mercury from gases.

Audeh (1989) proposed a process by firstly contacting the liquid condensate with a solution of an alkalipolysulfide and subsequently recovering a liquid hydrocarbon by separating into a hydrocarbon phase and aqueous phase. Then the two phases were separated. After treating, the mercury content decreased from 13 ppb to 0.01 ppb.

Torihata and Kawashima (1989) used a cupric compound or stannous compound or both to remove mercury from hydrocarbon oils by contacting the cupric compound and/or stannous compound with the oil. The cupric compound and/or stannous compound used in this method may be in any suitable form such as a powder, an aqueous solution or an alcoholic solution and may be supported on porous adsorbent such as activated clay, silica gel, zeolite, alumina etc.

2.4.2 Adsorption

The adsorption method comprises contacting the hydrocarbon with an adsorbent at various conditions, depending on type of adsorbent used. Many researchers proposed adsorbents for removal mercury from hydrocarbon.

Audeh (1991) proposed a process for removal of mercury from natural gas condensate by contacting natural gas condensate with elemental selenium in a reactor vessel. The operating condition, the pressure could be set from about 1 to 40 atm. The temperature could be ranged from about 15-217°C. The space velocity kept below about 20. It could reduce the amount of mercury in condensate from above 1,100 ppb to below 20 ppb. Yan (1990) used a molecular sieve comprises 0.001-15% elemental silver or gold in or on zeolite A for removing mercury from hydrocarbon fluid.

Tan et al. (1996) proposed a method for removal of organic mercury compound from hydrocarbon fraction by heat treatment. High-temperature heat treatment was used to convert an organic mercury compound into an inorganic mercury compound or elemental mercury at a temperature about 200°C to 900°C. Then hydrocarbon fraction was contacted with an adsorbent in the form of active carbon having at least one of calcium and a calcium compound supported there on. The adsorbent was efficient to remove mercury and cost low capital on an industrial large scale, achieving an extremely low mercury concentration.

Torihata and Nishimura (1989) proposed the method for removing mercury from hydrocarbon. The process was heating hydrocarbon oil containing mercury compounds and then bringing hydrocarbon oil into contact with treating agent. The treating agent was activated carbon itself or activated carbon upon whose

surface layer was supported one kind of metal selected from iron, nickel, copper, zinc, tin, aluminum and cadmium.

Ou (1990) used an adsorbent to remove mercury from liquid hydrocarbon. The adsorbent was packed in a column and the mercury-contaminated hydrocarbon was passed through the column at temperatures ranging from about ambient to about 100°C and at pressures from ambient to about 300 psig. The adsorbents used were 1) reduced copper on zinc oxide and alumina, 2) reduced nickel on clay. The hydrocarbon feed was Algerian condensate containing 32 ppb of mercury. The result indicated that Ni adsorbent removed approximately 90% of mercury while Cu adsorbent virtually removed all mercury in the condensate.

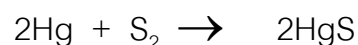
In addition, some methods combined between chemical reaction and adsorption. These methods may be known as chemisorption. This method may use the sulfur supported on the adsorbents, such as activated carbon and alumina. Mercury reacts with sulfur supported on the adsorbents and converts to a mercuric sulfide. Mercuric sulfide will deposit on adsorbent. Several methods have been proposed.

Denny et al. (1992) proposed a method for removing mercury from liquid or gaseous feed stream. This method comprises contacting mercury containing feed stream with an adsorbent comprising a metal sulfide. The suitable metals were iron and copper. Forming a precursor comprising a copper or iron compound and then contacting the precursor with gaseous stream containing sulfur compound prepared the presulfided adsorbent. The sulfur compounds were used to sulfide the precursor such as hydrogen sulfide, carbonyl sulfide,

mercaptans and polysulfide. The mercury removal process is conducted at a temperature below 100°C and is preferably at temperature at 20°C.

Furuta (1990) proposed a method for removing mercury from a liquid hydrocarbon. The method comprised contacting the liquid hydrocarbon with adsorbent composing of multi-component metal sulfide supported on a carrier. The first metal component was molybdenum and second metal was selected from the group consisting of cobalt and nickel. It was found that the mercury in the form of elemental, inorganic and organic compounds could be adsorbed.

Yan (1996) developed a process for removing mercury compounds from oil by used high-temperature reactive adsorption. The process based on high-temperature chemisorption for selective adsorption of mercury and used a special CuS/C adsorbent, which is effective for removing most type of mercury compounds. In the process, the condensate from the stabilizer at 400-500°F and 220 psi was directly passed over the adsorbent at about 10 LHSV for mercury removal. Laboratory tests showed that the process was capable of removing up to 99% of mercury. In addition, Yan (1989) proposed a process and compositions for removing elemental mercury vapor from a gas such as natural gas. The mercury-containing gas was contacted with a solid support such as carbon containing elemental sulfur and at least one metals which catalyzes the reaction



The elemental sulfur was deposited on the solid supported by using of a solvent, which distributes the sulfur in elemental form thereupon. The catalysts of the present invention were selected from the group of Ag, Au, Pd, Pt, Rh, Ir, Mn,

Cr and Mo. Pd and Pt were the most preferred catalysts. The demercuration process was carried out at a temperature below 170°F.

Audeh (1989) proposed a process for remove mercury from gas or liquid hydrocarbon stream. Hydrocarbon stream contaminated with mercury was contacted with a molecular sieve pretreated with an alkali polysulfide. The pretreatment consisted of saturating the sieve with an aqueous solution of the polysulfide and drying the treated molecular sieve to remove the moisture.

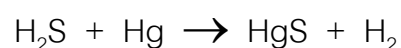
Furthermore, Chao (1984) proposed a method for preparation of polysulfide containing adsorbent composition and a process for adsorption of mercury from gaseous or liquid stream by using polysulfide-containing adsorbent.

Yamada et al. (1995) studied the effect of mercury types and their reactivity to develop a mercury removal process applicable for natural gas condensates. Mercury compounds contained in natural gas condensate were classified in to three types; elementary, ionic, and organic by using the JGC's analysis method. Mercury compounds, especially organic mercury compound, could not be adsorbed on any types of agents. However, the organic mercury compounds could be easily decomposed and converted into elementary mercury by catalytic decomposition method with the catalyst. Therefore, the process for mercury removal composed of catalytic decomposition stage and adsorption stage. The elementary mercury could be removed to less than 1 ppb with the adsorbent which a main component was metal sulfide

Courty (1995) proposed a process for removing mercury and arsenic in hydrocarbons. This process used two reactors. In the first reactor, hydrocarbon

containing 0.005-3% by weight of sulfur and mercury compound was reacted with hydrogen in the presence of a catalyst to active and convert mercury compound to material which will react with a mercury collection mass in a second reactor. The catalyst contained 0.05-5% by weight of at least one metal selected from the group consisting cobalt and 5-10% by weight of at least one metal selected from the group consisting molybdenum and tungsten. Besides, at least one of metal containing in catalyst was in sulfurized form. The effluent from first reactor was passed to a second reactor containing mercury collection mass that contained a sulfide of at least one metal selected from the group consisting of copper, iron, and silver and an active phase support. The process was conducted with an operating of 1-50 absolute bars, a hydrogen flow of 1-1000 liters of gaseous hydrogen at STP per liter of liquid charged, LHSV 0.1-30, an operating temperature of the catalyst of 180-450°C, and an operating temperature of the mercury collection mass of 0-400°C.

Audeh (1991) proposed the method, which comprise a process for removal of mercury from a natural gas condensate wherein hydrogen sulfide (H₂S) was mixed into the natural gas condensate. Then this mixture was passed into a reactor containing a catalyst along with a stripping gas such as methane (CH₄). The catalyst may be any hydrodesulfurization (HDS) catalyst, for example, CoMo, NiMo, etc. During the experiment, mercury in the condensate reacts with the hydrogen sulfide according to the following formula



Then HgS deposit on the catalyst. This process preferably operates at the pressure of 3-10 atm, the temperature of 210-250°C, and the space velocity

below 20. Suitable feed ratios of the condensate-hydrogen sulfide mixture comparing to the stripping gas was 1:600 to 1:750. This process could reduce the amount of mercury in natural gas condensate from above about 200 ppb to below about 20 ppb. In addition, hydrogen sulfide could pass into the reactor by containing in gas stream that gives the similar results. The mercury content in the natural gas condensate could be determined by conventional methods, such as ASTM method D-3223.

2.5 Method for Preparing Adsorbent (Cameron et al., 1994)

The supports are normally chosen from the group consisting of carbon, activated carbon, coke, silica, alumina, silica-alumina, aluminated and silico-aluminated and quite advantageously alumina is used.

The condition of obtaining support having a mean pore diameter of at least 50 Angstroms (10^{-8}) are sufficiently well known. Usually, the preferred supports have a specific surface area of approx. 20 to 300 m^2/g , these values not being limitative. The incorporation of a copper compound into support may be carried out by any method, for example by mixture with a copper compound or by impregnation using a solution of a copper compound. The copper compound which are normally used are compounds which are readily transformable into copper oxide at relatively low temperature.

As an example of a copper compound: the copper oxides, copper hydroxide $\text{Cu}(\text{OH})_2$, the basic copper salts for example the carbonates to formulae CuCO_3 , $\text{Cu}(\text{OH})_2$ and $2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$; the salt of these organic complexes of copper such as the salt of carboxylic acids, for example formiates, acetates, tartrateds, citrates, benzoates, oxalates, malonates, succinates, glycolates, lactates and acetacetonated and copper nitrate.

Normally, it is preferable to introduce the copper compound by impregnating the support with an aqueous or organic solution of a copper compound. Advantageously, an aqueous solution of copper nitrate is used. The quantity of copper introduced into support normally represents from 0 to 5% by weight. Other metals may likewise be present, for example iron, silver. The support comprising a copper compound is then possibly calcined in order at least partially to convert the copper compound to copper oxide. During the course of this calcination stage, the working conditions are preferable so chosen that for the most part, that is to say at least 50%, and preferably at least 80% and very advantageously 100% of the copper compound present is converted to copper oxide. In fact, the Applicant has found that copper is particularly well fixed in form of copper oxide. Calcination may be conducted in a neutral or in an oxidizing atmosphere. It is likewise possible to work in the presence of a mixture of oxygen and inert gas containing for example 1 to 60 % by weight of oxygen or even in the presence of substantially pure oxygen.

Calcination is preferably conducted in an oxidizing atmosphere and advantageously air is used, but it is likewise possible to use air enriched with oxygen. The calcination temperature is normally about 200 to 1000 °C. and even more advantageously 350 to about 600 °C. The spatial velocity per hour (VVH) expressed as a volume of gas per volume of recovery mass and per hour is normally approx. 100 to approx. 20,000 h⁻¹ and often approx. 300 to 5000 h⁻¹. This calcination stage normally lasts about half an hour to approx. 12 hours and even more advantageously from 1 hour to approx. 10 hours.

For copper sulfide adsorbent, the copper oxide is then brought into the presence of elementary sulfur at least partly in the form of an organic solution or even in the form of solid sulfur or even in the form of vapor, the sulfur condensing on the support during the course of the heat treatment.

It is in particular possible to use as an organic sulfur solution particle of sulfur in the form of flowers of sulfur, the mean diameter being for example less than 20 micron and preferably comprised between 0.01 and 10 micron in solution at least partly and possibly also in suspension in an organic compound of which the boiling temperature is below 250 C such as for example toluene, benzene, methyl alcohol, acetone or carbon disulfide.

The support is impregnated with the said organic solution, the total quantity of sulfur being introduced in one or possibly several operation of impregnation with intermediate drying at a temperature below 150 C. It is necessary to carryout this while avoiding premature crystallisation of the sulfur on the support, particularly by virtue of there being too great a difference in temperature between the support and the organic impregnation solution. To achieve this objective, it may be advantageous firstly to heat the support to the same temperature as the impregnation solution.

The objective being to convert copper oxide at least partly into copper sulfide, so reducing the elementary to sulfur it has likewise been discovered that this objective can be improved by adding to the one reducing compound chosen for example from the group consisting of hydrogen, formaldehyde, acetaldehyde, formic acid, hydrazine etc.

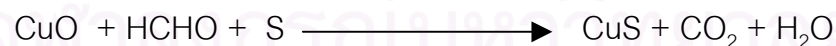
The quantity of sulfur incorporated into the adsorbent is ideally chosen to allow subsequently the conversion of the copper compound contained in the adsorbent at least partially into copper sulfide. The quantity of sulfur may easily be adjusted according to the quantity and stoichiometry of copper sulfide which it is desired to obtain.

The adsorbent containing the sulfur and the copper oxide is treated in the current inert gas at a temperature approx. 100 to approx. 250 C with a spatial hourly velocity (VVH) expressed in term of volume of gas per volume of recovery mass and per hour, approx. 500 to 2000 h⁻¹. The period of this treatment accompanied by gas scavenging is normally half an hour to about 10 hours.

During the course of the heat treatment, there is a chemical interaction between the copper oxide, possibly promoted by sulfur. A release of SO₂ is observed according to a possible reaction:



When at least one reducing agent has been added to the sulfur the proportion of sulfur eliminated in the form of SO₂ may preferably be reduced as follow :



After the heat treatment, the adsorbent cooled down to ambient temperature. The adsorbent obtained contains 8 to 25 % by weight of copper sulfide and preferable approx. at least 80% copper (by weight) in the sulfide state.

Structure analysis show that the sulfide is at least partly in the form of CuS and generally the greater part of sulfide is in this form. Other sulfide may be present which have as their formula C_xS_y in which x, y represent a whole number between 1 and 10.



สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

Literature summary

1. Mercury in petroleum is in elementary, inorganic and organometallic form.
2. Mercury is found in petroleum can be a potential cause of process problem, catalysts poison, corrosion, and pollution of environment.
3. Methods for mercury removal are classified in to two methods: chemical treatment and adsorption. Adsorption is the most widely used method because it provides high efficiency on mercury removal and more convenient.
4. There are many adsorbents used for removed mercury such as Mo, Ni, Cu, Zn, Pb or Fe. The copper adsorbent has been frequency used for removed of mercury in petroleum. Metal sulfides on adsorbent are widely used to remove mercury compound especially copper oxide and copper sulfide on alumina.
5. The study of effect of forms of mercury compounds on the adsorption of mercury is not clearly known. There is no indication that what forms of mercury can be adsorbed by copper-oxide and copper-sulfide adsorbent.
6. The operating conditions for removing mercury by adsorption in liquid phase depends on the adsorbent used. In general, the pressure range from 10-1000 psig, and the temperature interval 30°C - 200°C .

CHAPTER III

EXPERIMENTS, ANALYSIS TECHNIQUES AND EXPERIMENTAL ERROR

This chapter is divided into two sections. Section one describes methods for preparation of adsorbents, experimental procedure and analysis techniques of both liquid product and adsorbents used in this study. Section two summarizes blank test, results of possible experiment and analysis error encountered in the study.

3.1 Experiments and Analysis Techniques

Preparation of Adsorbents

Figure 3.1 shows a schematic diagram of the impregnation apparatus. The apparatus consists of a 10-ml burette, a 50-ml round-bottomed flask, a heating mantel and a vacuum pump. The flask was connected to the burette and heated by the heating mantel. Figure 3.2 shows a schematic diagram of the calcination apparatus. The apparatus consists of a pyrex tube, a combustion boat, a temperature controller and air or nitrogen gas. The pyrex tube was connected to zero air or nitrogen gas and vented to the atmosphere. The pyrex tube was heated in the muffle furnace. The vacuum pump was used to keep the flask under pressure.

Neutral alumina manufacture by addrich was used as the support material for copper oxide and copper sulfide adsorbents. The adsorbents were prepared by dry impregnation method followed by calcination method as described below.

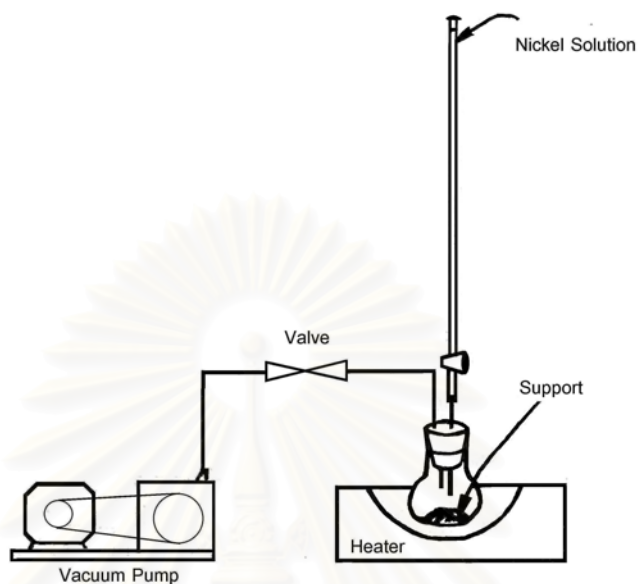


Figure 3.1 A Schematic Diagram of the Impregnation Apparatus

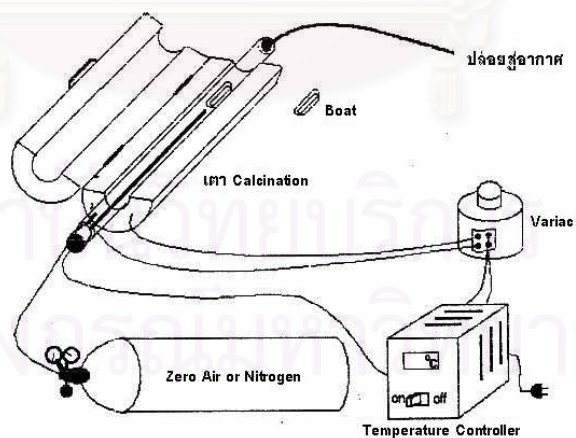


Figure 3.2 A Schematic Diagram of the Calcination Apparatus

Preparation of Alumina Adsorbent

1. Approximately 10 grams of neutral alumina was put in the ceramic crucible and placed in the Pyrex tube following placed in the muffle furnace.
2. Air was allowed to flow through the Pyrex tube at a flow rate of 12 l/hr.
3. The temperature of the furnace was increased at a rate of 1 °C/min from room temperature to 400 °C and maintained at 400 °C for 4 hour.
4. Alumina was allowed to cool to room temperature in air flow before the adsorbent was taken out and kept it in the desiccator before use in an experiments.

Preparation of Copper-Oxide Adsorbent:

- 1) Approximately 10 grams of neutral alumina were put in the round-bottom flask and kept under pressure by connecting the vacuum pump. The alumina was heated at 120 °C in heating mantel about 3 hours.
- 2) The alumina was allowed to cool to room temperature.
- 3) The flask was connected to the 10-ml burettes and vacuum pump. It was impregnated by solution of copper nitrate under vacuum pressure. The amount of aqueous solution that used was equal to the pore volume of the adsorbent. The amount of aqueous solution used was approximately 3.8 ml and the concentrations of the solution was 1.06 mole/liter of copper nitrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) in distilled water that calculated from the metal loading on the adsorbents.
- 4) The impregnated adsorbent was adjusted to the atmospheric pressure.
- 5) The impregnated adsorbent was allowed to rest at atmospheric pressure for 24 hours at room temperature before dried at 110 °C for 12 hours in oven.

- 6) The methods of calcination follow the same procedure as preparation of alumina but hydrogen gas was allowed to use before air at the same flow rate.

Preparation of Copper-Sulfide Adsorbent

Copper-sulfide adsorbent was prepared by using of copper oxide adsorbents as described the procedure of preparation before.

- 1) The method of impregnation follows the same procedure as preparation of copper oxide adsorbent but it was impregnated by solution of ammonium sulfide 20%vol in water. The amount of aqueous solution used was approximately 1.39 ml that calculated from the metal loading on adsorbents.
- 2) The excess sulfur is eliminated by calcination at 200°C for 10 hour with nitrogen gas. During the course of heat treatment, there is a chemical interaction between copper oxide, possibly promoted by sulfur.
- 3) The adsorbent was allowed to cool under nitrogen gas to room temperature and kept it in the desiccator before use.

Experiments

Figure 3.3 shows a schematic diagram of the apparatus for the experiment. The apparatus consists of a 250-ml erlenmeyer flask, a stirrer, an oil bath, a heater and a temperature controller. The flask was connected to the propeller. The temperature of the system was controlled in the oil bath.

The experiments are carried out at atmospheric pressure and at temperature of 30 °C, 50 °C and 70 °C in the 250-ml erlenmeyer flask. Mercuric chloride and diphenylmercury are used to represent ionic and organic forms of

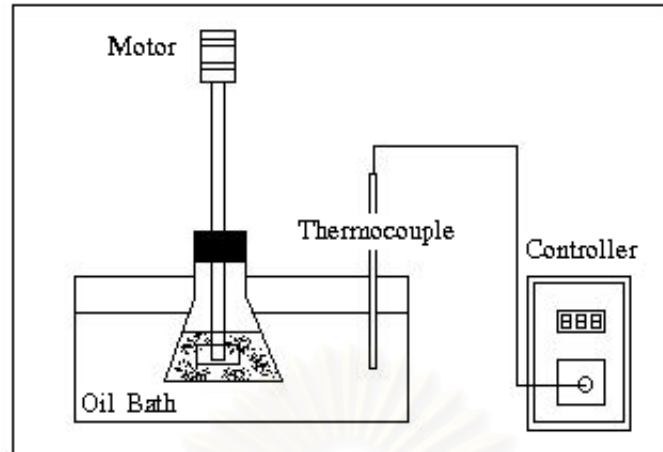


Figure 3.3 A Schematic Diagram of the Experiment Apparatus.

mercury compounds. These compounds were dissolved in toluene to obtain solutions containing 1 ppm of mercury. The adsorbents were copper oxide and copper sulfide on alumina support. The adsorption time was 60 minutes in each experiment. The temperature of system was controlled at 30 °C, 50 °C and 70 °C in oil bath. The propeller was used for stirring the system.

After each experiment, the adsorbents and liquid solution are separated and both samples are analyzed for metal content using Atomic Absorption Spectroscopy techniques. The spent adsorbents are also analyzed for their surface area and pore volume.

Experimental Procedure

- 1) Approximately 1 gram of adsorbent was put into the 250-ml flask.
- 2) The flask was connected to the 10-ml burette and vacuum pump. The toluene was filled into the 10-ml burette. The adsorbent was filled with toluene into the pore.
- 3) Approximately 100 grams of liquid feed were put into the flask.

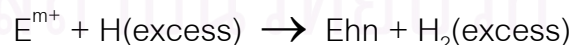
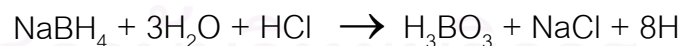
- 4) The flask was placed into the oil bath that controlled the temperature. The experiment was taken place about 60 minutes with stirring at constant temperature.
- 5) After each experiment, the products were filtrated with filter papers Whatman No.1 to separate the spent adsorbents from liquid product. The adsorbents and liquid solution were separated and both samples were analyzed.

Analysis Techniques

After each experiment, liquid feed, product and adsorbents used were analyzed for mercury content. Fresh and spent adsorbents were analyzed for their characteristics.

Mercury Content

Flow Injection Mercury Hydride System Analysis is a high sensitivity and suitable technique for measurement of mercury. The hydride technique involves the reaction of acidified aqueous samples with a reducing agent such as sodium borohydride. The sodium borohydride/acid reduction generates hydrides as shown in the following equations



where E = the analyze of interest and m may or may not equal n

This reaction generates a volatile hydrides which was transported to a quartz cell by argon carrier gas. In the quartz cell, the hydrides were converted to gaseous metal atoms. Although this technique is suitable for measuring of mercury in water-phase, it is applicable to the analysis of materials other than water-phase if and only if, an initial procedure for digesting and oxidizing the sample is carried out. Digestion and oxidization was performed to ensure that

the mercury in the sample was converted to the mercuric ion, and dissolved in aqueous media. The digestion method used in this study is applied from ASTM D-3223 which is a standard method for determining of total mercury in water.

Mercury Digestion

Figure 3.4 shows a schematic diagram of the apparatus for digestion. The apparatus consists of a 250 ml boiling flask, a condenser, an oil bath, a heater and controller. Assemble the components of the apparatus as illustrated in Figure 3.4.

Digestion Procedure

- 1) The sample (about 30g) was weighed directly into the 250-ml round-bottomed flask.
- 2) After that 5-ml of concentrated sulfuric acid and nitric acid were added and mixed after each addition.
- 3) Then, 15-ml of potassium permanganate solution was added to each flask. The mixture was stirred vigorously for at least 15 min.
- 4) Then, 8-ml of potassium persulfate was added to the flask.
- 5) The flask at the top was equipped with a reflux condenser and subsequently heated in oil bath at 95 °C for approximately 2 hours.
- 6) After that the flask was cooled to ambient temperature, and added 6-ml of sodium chloride-hydroxylamine hydrochloride solution.
- 7) Then, shaken for a few seconds. The solution was transferred into 250-ml separating funnel and shaken vigorously.
- 8) After that, acid-phase was separated from toluene-phase. The remaining toluene-phase was extracted by water for transferring mercury to water phase. The acid-phase and the extracted water were mixed and made the total volume to 100 ml.

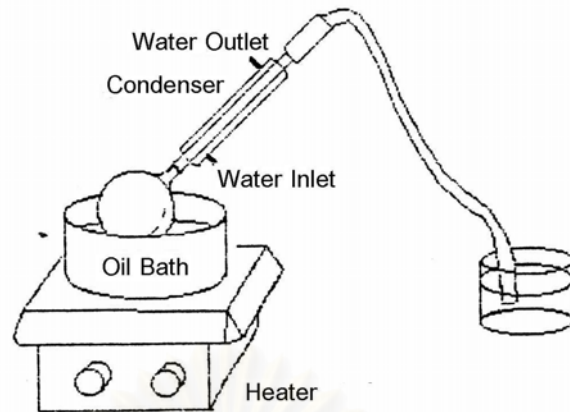


Figure 3.4 A Schematic Diagram of the Digestion Apparatus

Adsorbent Characterization

In order to understand the behavior of an adsorbent it is essential to be adequately characterized. In this study the properties studied included metal content, surface area, pore volume and pore size distribution of adsorbents are aimed to analyze. A brief description of these measurements is given below.

Copper content:

Copper contents of the adsorbents were determined by standard method of ASTM (base on designation: D1977-91). This method was used for decomposing and dissolving samples for atomic absorption spectroscopy.

- 1) Approximately 500-mg of the adsorbent sample was weighed into a crucible.
- 2) The sample was added with 10 ml of distilled water, 10 ml of concentrated sulfuric acid, 10 ml of concentrated nitric acid, and 5 ml of concentrated hydrofluoric acid.
- 3) The mixture in crucible was placed on a hot plate and stirred slowly.

The adsorbent was first dissolved in acid solution and then precipitated

again after the acid was evaporating. A sample was continually evaporated to near dryness.

- 4) Then, the crucible was removed from the hot plate and allowed to cool at room temperature.
- 5) The sample was introduced again with 20 ml of 19% hydrochloric acid and 30 ml of 3% hydrogen peroxide, covering with watch glass and returning crucible to the hot plate.
- 6) The sample was continually heated to boil until the precipitate was dissolved totally.
- 7) After complete dissolution, the crucible was removed from the hot plate and cooled to room temperature.
- 8) The sample was then diluted with distilled to 100 ml and stored in polyethylene bottle

Surface Area, Pore Volume and Pore Size Distribution:

Surface area and pore characteristics of the samples were measured by the BET method, with nitrogen as the adsorbent using a micromeritics model ASAP 2000. The ASAP 2000 system consisted of two sample preparation ports and one sample analysis ports.

Approximate 100 mg of the adsorbent was weighted and transferred into the sample preparation tube. Most solid adsorbents adsorbed moisture and other contaminants when used. The adsorbent must have been cleaned in sample preparation tube by thermal treating before analysis was performed. The sample preparation tube was attached to the vacuum system and placed around by the heater. Sample preparation would then require more time to achieve the desiring condition before proceeding with and analysis. Once sample preparation was completed, the sample tube might be allowed to cool to ambient

temperature. The sample tube would then remove from the sample preparation port and placed onto the analysis port.

3.2 Blank Test and Experimental Error

Blank Test

The experiments in this section are conducted to study the stability of each metal compound at adsorption temperature and to verify adsorption of metal compounds on glassware wall. No adsorbent is used in this test. The concentration of mercury product is plotted with the operating temperature and shown in Figure 3.5. Percent loss from feed at various temperatures is summarized in Table 3.1. This indicates that all model compounds does not adsorb on the glassware and does not disappear by other parameters. The difference of concentration between feed and product is considered as the error in analysis.

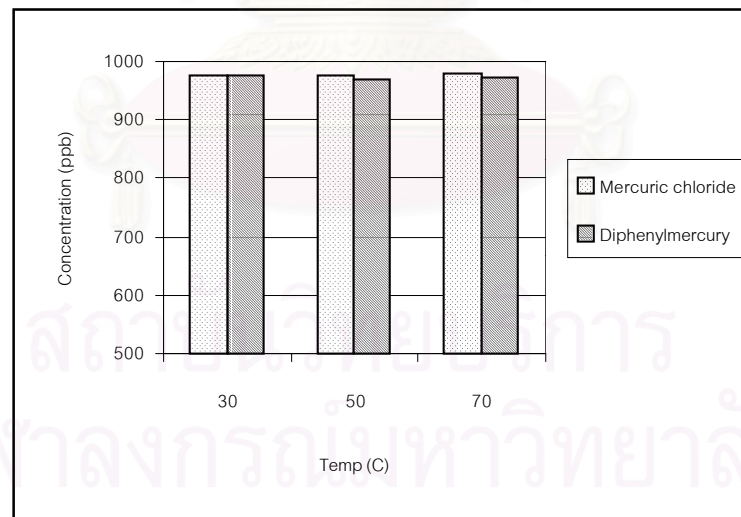


Figure 3.5 Remaining of Mercury in the Study on Blank Test at Various Temperatures

Table 3.1 Percent Loss from Feed at Various Temperatures.

Component	Percent loss from feed (%)		
	30°C	50°C	70°C
Mercuric chloride	1.57	2.08	1.04
Diphenylmercury	1.00	1.50	1.45

Experimental and Analysis Error

Possible experiment and analysis error is divided into three sections. Experimental error, instrumental error and digestion error are considered in this section.

Experimental Error

In this section, the experiments are conducted to verify repeatability, average and deviation of the experiments and to find error limits cover whole ranges of the experiments. The adsorbents are used copper oxide and copper sulfide on alumina adsorbent. The experiment is repeated for 5 times at the same condition. Average concentration of mercury and percent deviation are calculated and shown in Table 3.2 to 3.5. Percent of the deviation from average value of experiments are calculated according to the following equation:

$$\text{Percent of the deviation from average value} = \frac{\text{Value conc.} - \text{Average conc.}}{\text{Average conc.}} * 100$$

From analysis it is certain that the values of remaining mercury deviate in the range of 44% for mercuric chloride removal, 18% for diphenylmercury removal.

Table 3.2 Amount of Mercury Remaining in Adsorption on CuO/Alumina Repeatability Study.

Temperature (°C)	Compounds	1 (ppb)	2 (ppb)	3 (ppb)	4 (ppb)	5 (ppb)
30	Mercuric chloride	98.7	83.8	96.3	98.3	122.3
	Diphenylmercury	825.8	776.0	741.4	756.7	752.9
50	Mercuric chloride	149.3	171.4	144.8	156.0	171.3
	Diphenylmercury	757.2	716.9	703.5	678.7	688.8
70	Mercuric chloride	183.3	202.0	181.0	184.3	210.4
	Diphenylmercury	678.5	619.8	539.9	531.1	504.1

Table 3.3 Amount of Mercury Remaining in Adsorption on CuS/Alumina Repeatability Study.

Temperature (°C)	Compounds	1 (ppb)	2 (ppb)	3 (ppb)	4 (ppb)
30	Mercuric chloride	90.7	90.7	90.4	89.8
	Diphenylmercury	557.6	490.2	510.6	502.9
50	Mercuric chloride	13.2	24.6	31.3	24.6
	Diphenylmercury	215.7	203.8	222.2	207.7
70	Mercuric chloride	14.2	10.0	11.0	13.2
	Diphenylmercury	99.9	130.9	99.3	113.7

Table 3.4 Average Concentration and Percent Deviation of Mercury in CuO/Alumina Adsorbent Repeatability Study.

Temperature (°C)	Compound	Average concentration (ppb)	Percent of deviation (%)
30	Mercuric chloride	99.86	22.48
	Diphenylmercury	770.5	7.17
50	Mercuric chloride	158.56	8.66
	Diphenylmercury	708.0	6.23
70	Mercuric chloride	192.22	9.46
	Diphenylmercury	574.7	18.06

Table 3.5 Average Concentration and Percent Deviation of Mercury in CuS/Alumina Adsorbent Repeatability Study.

Temperature (°C)	Compound	Average concentration (ppb)	Percent of deviation (%)
30	Mercuric chloride	84.39	13.61
	Diphenylmercury	515.31	8.20
50	Mercuric chloride	23.44	43.55
	Diphenylmercury	212.34	4.65
70	Mercuric chloride	7.34	35.61
	Diphenylmercury	110.97	17.97

Instrumental Error

After each experiment liquid feed, product and adsorbents used are analyzed for mercury content using Atomic absorption Spectroscopy techniques. The experiments are conducted to verify instrumental error, average and deviation of the experiments and to find error limits cover whole ranges of the experiments. The adsorbent was used copper oxide on alumina adsorbent. The same sample was analyzed for 3 times at the same condition. Average concentration of mercury and percent deviation are calculated and shown in Table 3.6

Table 3.6 Amount of Concentration and Percent Deviation of Mercury on CuO/alumina Repeatability Study for Analysis.

Temp. (°C)	Compounds	1 (ppb)	2 (ppb)	3 (ppb)	Average Conc.	Percent of Dev.(%)
30	Mercuric chloride	80.5	82.6	88.3	83.8	5.37
	Diphenylmercury	778.0	772.1	777.8	776..0	1.30
50	Mercuric chloride	168.5	175.6	170.1	171.4	2.45
	Diphenylmercury	709.5	723.1	731.7	716.9	1.65
70	Mercuric chloride	195.8	200.6	209.6	202.0	3.76
	Diphenylmercury	610.5	600.2	648.7	619.8	4.66

From analysis it is certain that the values of remaining mercury deviate in the range of 6% for mercuric chloride removal, 5% for diphenylmercury removal.

Digestion Error

The experiments are conducted to verify digestion error, average and deviation of the experiments and to find error limits cover whole ranges of the experiments. Feed sample was digested for 3 times at the same condition. Average concentration of mercury and percent deviation are calculated and shown in Table 3.7.

Table 3.7 Average Concentration and Percent Deviation of Mercury in Feed Repeatability Study for Digestion.

Compounds	1 (ppb)	2 (ppb)	3 (ppb)	Average Conc.	Percent of Dev.(%)
Mercuric chloride	985	973	934	964	3.11
Diphenylmercury	945	903	952	933	3.25

From analysis it is certain that the values of feed's concentration deviate in the range of 3.11% for mercuric chloride removal, 3.25% for diphenylmercury removal.

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CHAPTER IV

RESULTS AND DISCUSSIONS

This chapter covers all the results and discussions in this study. The results and discussions are divided into two sections. Section one describes the comparison of adsorbents. Section two describes the effect of temperature and type of adsorbent on mercury removal. In addition, comparison of removal efficiency among mercury compounds is also discussed.

Results and Discussions

4.1 Comparison of Adsorbents

Adsorbents used in the experiments were alumina, copper oxide and copper sulfide on alumina supports. The copper adsorbent is prepared by dry impregnation that described previously. The adsorbents are analyzed to identify the stoichiometry of copper on the adsorbent surface using X-Ray Diffractometer. X-Ray Diffraction pattern of copper oxide adsorbent is shown in Figure 4.1. Analysis indicates that copper is in the form of copper oxide (CuO). Analysis shows that the atomic ratio of Cu:O is equal to 1. For copper sulfide, X-Ray Diffraction pattern of CuS/alumina adsorbent is shown in Figure 4.2. Analysis indicates that copper is in the form of copper sulfide (CuS).

The adsorbents are also analyzed for copper content on support using Flame Atomic Absorption Spectroscopy Techniques. The adsorbents must be dissolved and decomposed before analyzed that described previously. Analysis shows that copper oxide and copper sulfide have 2.61 and 2.59 wt% of copper. The copper sulfide adsorbent is also analyzed for sulfur content on support using

Energy X-Ray Fluorescence Spectrometer. X-Ray fluorescence pattern of copper sulfide adsorbent is shown in Figure 4.3. Analysis shows that copper sulfide has 1.28 wt% of sulfur. The results of copper and sulfur contents listed in table 4.1.

Table 4.1 Copper and Sulfur Contents on Adsorbents.

Adsorbents	Cu content (%wt)	S content (%wt)
Al_2O_3	-	-
$2.5\text{CuO}/\text{Al}_2\text{O}_3$	2.61	-
$2.5\text{CuS}/\text{Al}_2\text{O}_3$	2.59	1.28

The results show that actual value copper content is more than the desired value. Chemical analysis of the adsorbents for their metal contents show that copper oxide and copper sulfide adsorbents contain approximately 2.61 wt% and 2.59 wt% of copper. The copper content in the adsorbent is slightly different which can be specified as error of analysis and method of preparation.

Chemical analysis of the copper sulfide adsorbent for their metal contents show that the adsorbent contains approximately 2.59 wt% of copper and 1.28 wt% of sulfur. Molecular weight of copper and sulfur are 63.546 and 32.016. From chemical analysis indicates that the atomic ratio of Cu:S is about to 1.

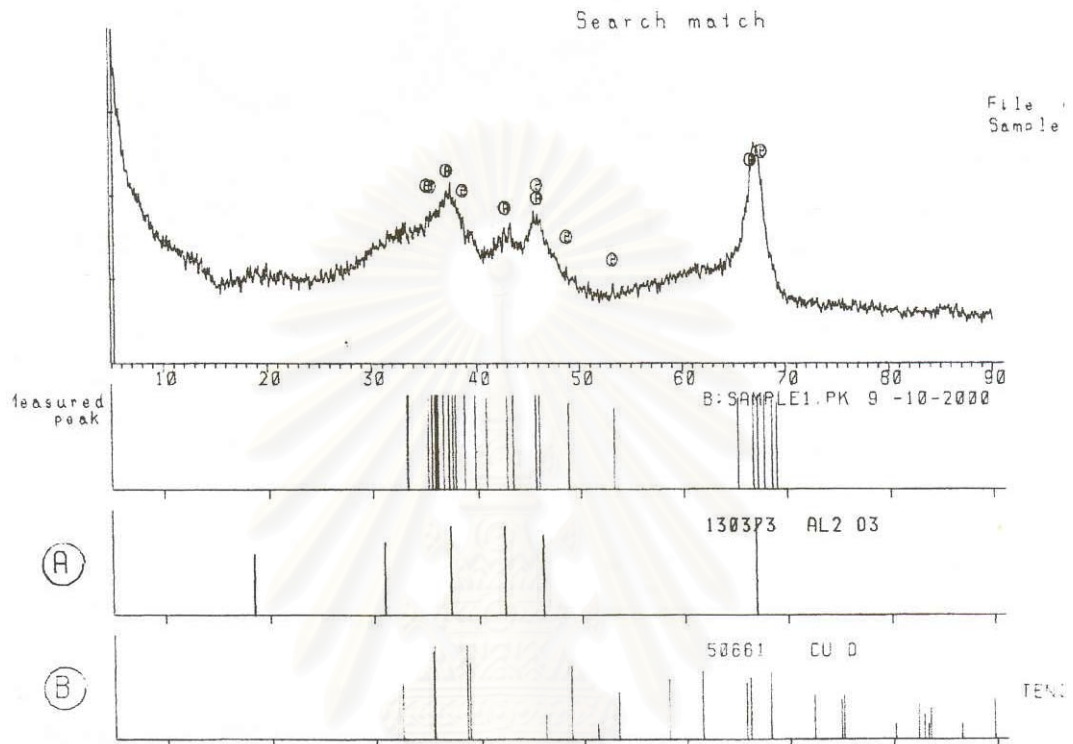


Figure 4.1 XRD Pattern of Fresh CuO/Alumina Adsorbent

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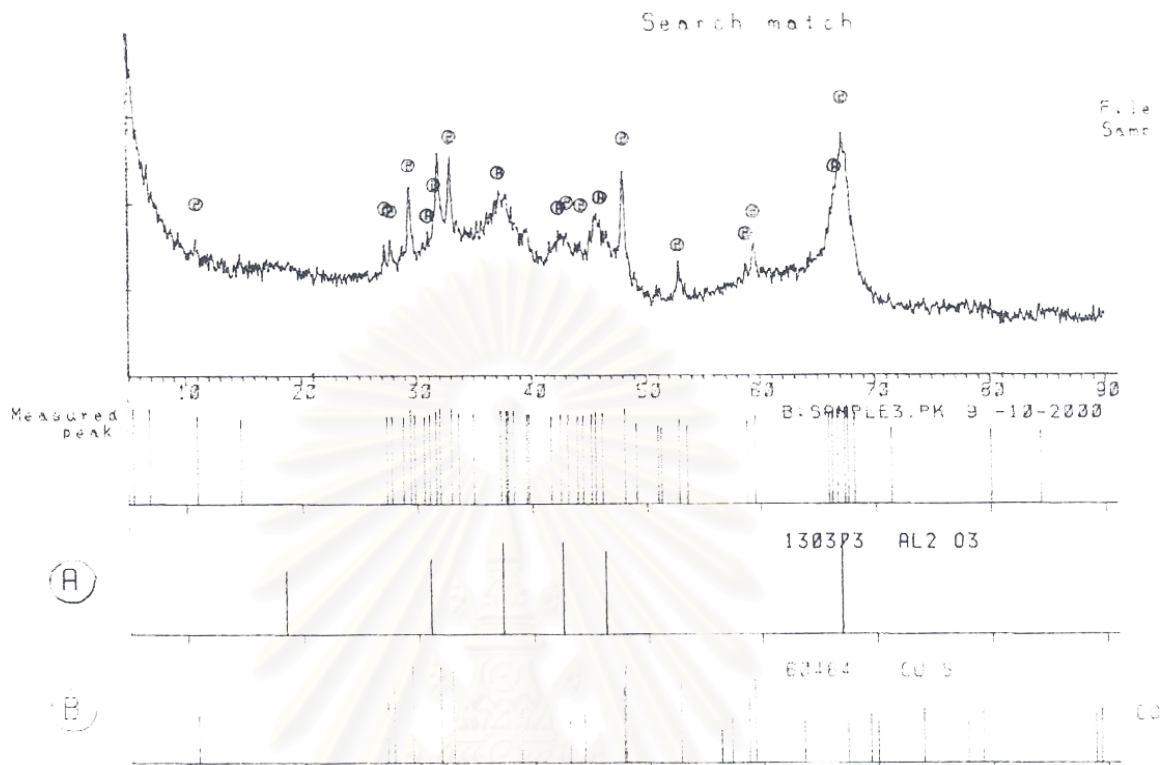


Figure 4.2 XRD pattern of fresh CuS/alumina adsorbent.

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Time : 14:08:41

Spectrum: Folder: Sulfur

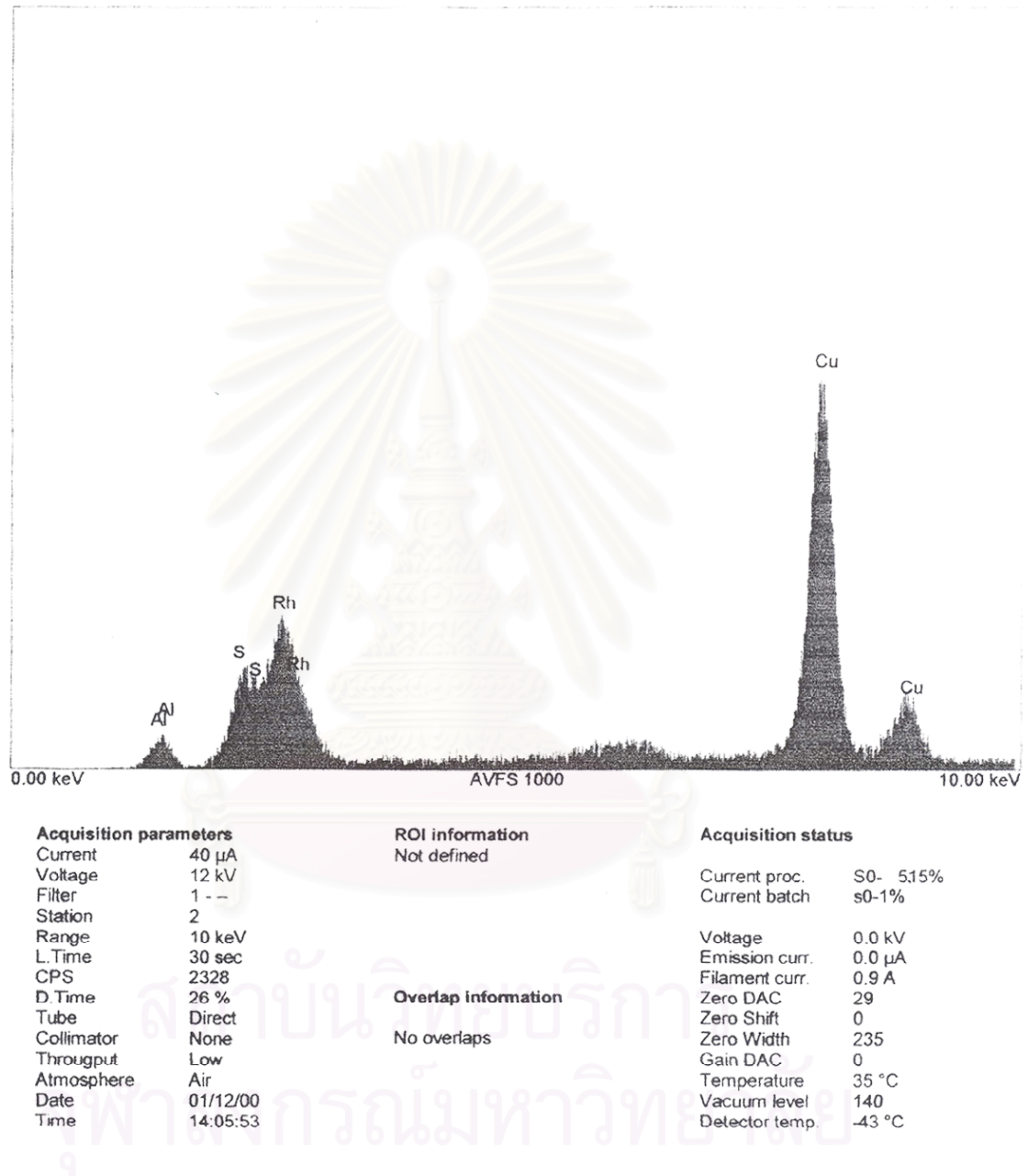


Figure 4.3 XFS Pattern of Fresh CuS/Alumina Adsorbent.

All fresh adsorbents are also analyzed for their surface area, pore volume, average pore diameter and pore size distribution by BET method.

Characterizations of fresh adsorbents were analyzed in order to study the effect of metal loading on the adsorbents. The results are shown in Table 4.2.

Table 4.2 Surface Area, Pore Volume and Average Pore Diameter of Adsorbents.

Adsorbents	Surface Area (m ² /g)	Pore Volume (cc/g)	Average Pore Diameter (°A)
Al ₂ O ₃	218.18	0.4539	83.21
CuO/Al ₂ O ₃	149.41	0.2082	55.75
CuS/Al ₂ O ₃	155.18	0.1987	51.21

Table 4.2 shows comparison of surface area, pore volume and average diameter of each adsorbent. It is clearly shown that surface area, pore volume and pore average diameter of each type of adsorbents decrease significantly when they are compared with alumina support. Reduction of average pore diameter indicates that metals, loaded on the adsorbents, deposit on the surface area inside the pore of alumina support and results in reduction of pore size. Surface area and pore volume of the adsorbents are all reduced because of the same effect.

4.2 Effect of Temperature and Type of Adsorbents

Experiments are designed to study effect of each adsorbent on mercury removal. The adsorption of mercury on different adsorbents is undertaken in order to explain the nature of metal form on selectivity of mercury adsorption. Copper oxide and copper sulfide are loaded on alumina support in order to study the effect of metal form on mercury removal. Effect of temperature and type of adsorbent on mercury removal are discussed in this section. In addition, comparison of removal efficiency among mercury compound is also discussed.

Adsorption of Mercury Compound on Alumina Adsorbent

Figure 4.4 and Figure 4.5 show the percent remove of mercuric chloride and diphenylmercury per weight and surface area of adsorbent. Table 4.3 shows percent removal of mercury per weight and per surface area of adsorbents. It can be observed that both mercuric chloride and diphenylmercury can be removed from liquid hydrocarbon by adsorption. Removal of mercuric chloride is approximately 50 to 80%. Removal of diphenylmercury is approximately 10 to 30%. The results show that mercuric chloride can be removed more effectively than diphenylmercury. This may results from polarity and complication of each compound. Mercuric chloride has the high polarities while diphenylmercury has more complicated. Diphenylmercury has the strongest metal-carbon bond of the common organic mercury compound. Diphenylmercury have two aromatic rings, which are stable, because it has high resonance energy of π electron. This indicated that the type of mercury compound strongly affect the adsorption of mercury on adsorbents. Operating temperature also has a strong effect on mercury removal. It can be observed that removal of mercuric chloride decreases with increasing of operating temperature and removal of diphenylmercury increase with increasing of operating temperature. This indicated that operating temperature strongly affect the adsorption of mercury on

adsorbents. Noraphol (1995) and Pichan (1998) also observed that mercuric chloride can be removed more effectively than diphenylmercury and operating temperature has adverse effect on removal efficiency of mercuric chloride.

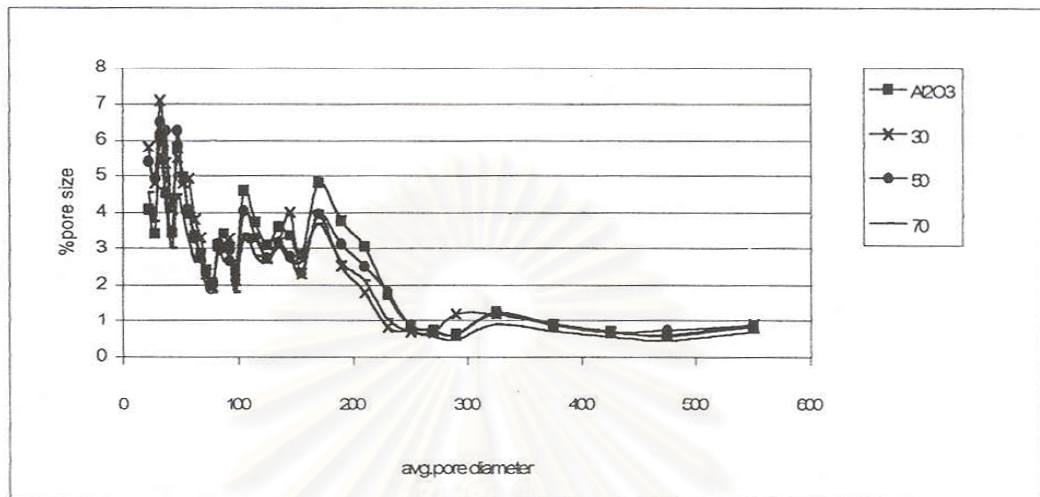


Figure 4.4. Percent Removal of Mercuric Chloride and Diphenylmercury per Weight of the Adsorbent in the Study of Adsorption on Alumina Adsorbent at Various Temperatures.

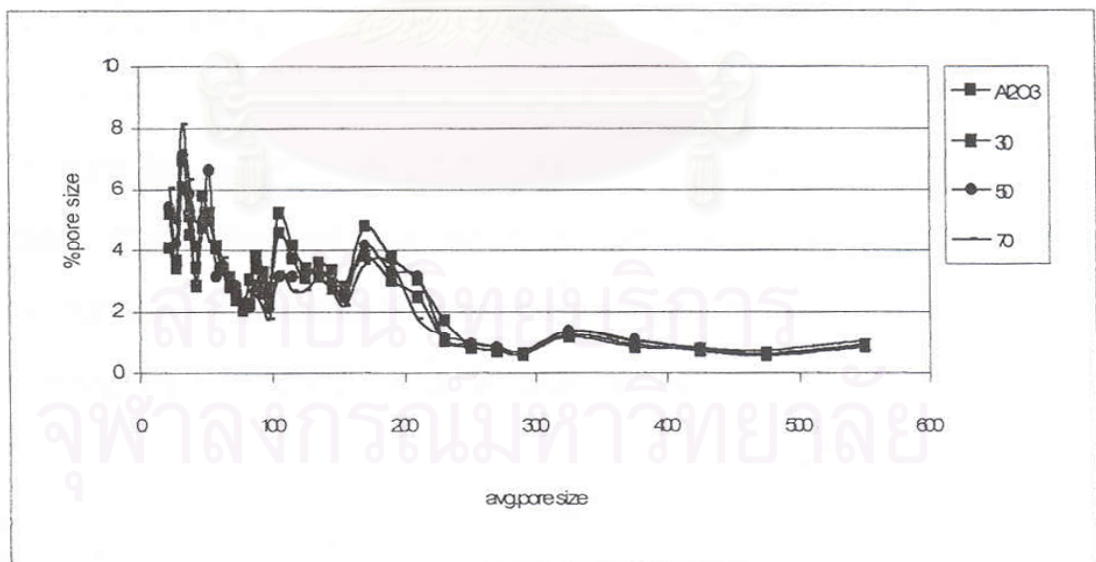


Figure 4.5. Percent Removal of Mercuric Chloride and Diphenylmercury per Surface Area of the Adsorbent in the Study of Adsorption on Alumina Adsorbent at Various Temperatures.

Table 4.3 Percent Removal of Mercuric Chloride and Diphenylmercury in the Study of Adsorption on Alumina Adsorbent at Various Temperatures.

Compound	Temperature (°C)	Percent removal per weight (%)	Percent removal per surface area (%)
Mercuric Chloride	30	83.83	0.384
	50	72.13	0.334
	70	55.47	0.254
diphenylmercury	30	9.47	0.043
	50	16.17	0.074
	70	28.50	0.131

Table 4.4 shows percent of mercury deposited on adsorbents after adsorption experiment for both mercuric chloride and diphenylmercury. It can be observed that high concentration of mercury deposited on the adsorbent when the remaining mercury in liquid hydrocarbon is low. The results are not agreement with the results obtained from percent of mercury removal in liquid hydrocarbon. It is expected that part of mercury compounds may vaporized while the samples, both liquid hydrocarbon and adsorbent, were digested with acid to prepare the sample for atomic absorption.

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Table 4.4 Percent of Mercuric Chloride and Diphenylmercury Deposited on Adsorbents

Compound	Temperature (°C)	Percent of mercury deposited on adsorbents (%)
Mercuric Chloride	30	40.25
	50	25.65
	70	20.35
diphenylmercury	30	15.23
	50	22.56
	70	25.36

The experiment is also designed to study desorption of mercury from spent alumina adsorbent. Experimental results are shown in Figure 4.6, 4.7 and Table 4.5. The results of desorption experiment shows that the adsorption of mercuric chloride and diphenylmercury on alumina can desorb approximately 50%. This indicates that the adsorption of alumina adsorbents is a reversible process.

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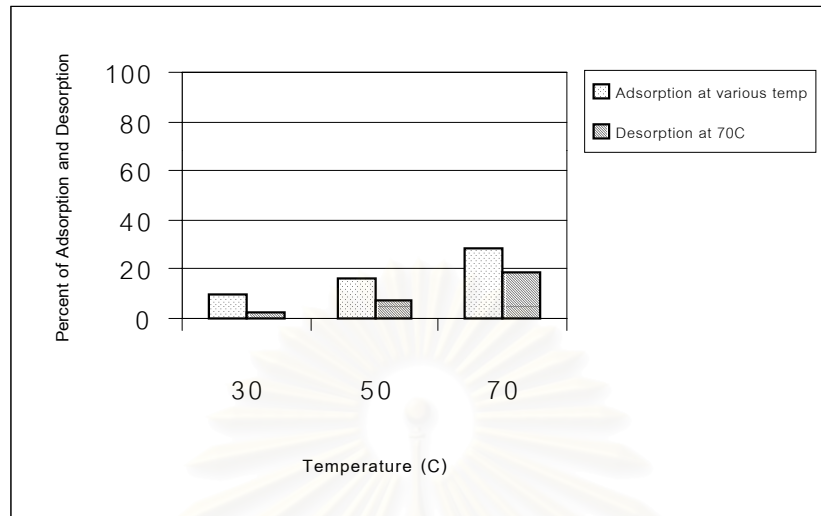


Figure 4.6 Percent of Adsorption of Adsorbent at Various Temperatures and Desorption at 70 °C of Mercuric Chloride on Alumina Adsorbent.

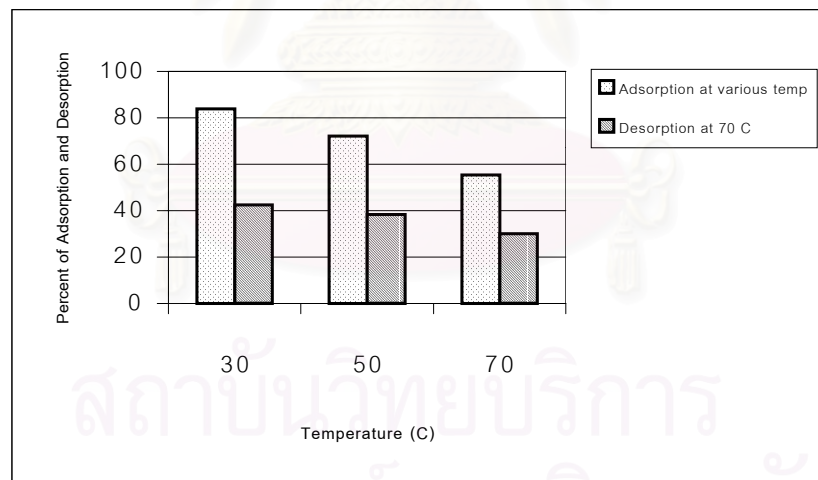


Figure 4.7 Percent of Adsorption of Adsorbent at Various Temperatures and Desorption at 70 °C of Diphenylmercury on Alumina Adsorbent.

Table 4.5 Percent of Desorption of Mercury Chloride and Diphenylmercury at 70 °C

Compounds	Percent of desorption (%)		
	30 °C	50 °C	70 °C
Mercuric chloride	50.82	53.37	54.45
Diphenylmercury	27.06	46.76	64.91

The spent alumina adsorbents are analyzed to identify the stoichiometry of mercury on the adsorbent surface using X-Ray Diffractometer. The results of X-Ray Diffraction can not detect chemical bond between mercury and alumina. The spent alumina adsorbents also are analyzed to identify the element of compounds using Energy X-Ray Fluorescence spectrometer. X-Ray fluorescence pattern is shown in Figure 4.8. The result of X-Ray fluorescence spectrometer shows that spent alumina adsorbents has chloride form in compounds. In aqueous solution, the greater part of mercuric chloride (HgCl_2) is found to be undissociate into ionic form (Hg^{2+} and Cl^-) (Remy,1995). It exists in the HgCl_2 or $(\text{HgCl}_2)_2$ forms. (Biscarini et al.,1971) Toluene has less polarity than water. Mercuric chloride also exists in HgCl_2 . From the results of desorption and X-Ray fluorescence method, this indicates that mercuric chloride is directly adsorb on alumina. In case of diphenylmercury, which is classified as organo mercury compounds, can be partially remove by adsorption on alumina adsorbent. Yamada (1995) found that the decomposition of diphenylmercury was conducted at temperatures of 165 to 300 °C. In this study, adsorption experiments were conducted at temperature less than 70 °C in which diphenylmercury were not expected to decompose. From the results of desorption , this indicates that diphenylmercury is directly adsorb on alumina.

Thus, the adsorption of mercuric chloride and diphenylmercury are a physical adsorption.

Date : 10/02/01
Time : 16:48:36

43

Spectrum: Folder: Sulfur



Acquisition parameters

Current 750 μ A
Voltage 4 kV
Filter 1 --
Station 2
Range 10 keV
L.Time 30 sec
CPS 2268
D.Time 25 %
Tube Direct
Collimator None
Throughput Low
Atmosphere Air
Date 10/02/01
Time 16:36:15

ROI information

Not defined

Overlap information

No overlaps

Acquisition status

Current proc. Sulfur 0 3-2
Current batch
Voltage 0.0 kV
Emission curr. 0.0 μ A
Filament curr. 0.9 A
Zero DAC 15
Zero Shift 4
Zero Width 250
Gain DAC 0
Temperature 32 $^{\circ}$ C
Vacuum level 64
Detector temp. -38 $^{\circ}$ C

Figure 4.8 XFS Pattern of Spent Alumina Adsorbent for Mercuric Chloride

The fresh and spent adsorbents are characterized by BET method to determine the surface area, pore volume, and pore size distribution. The results of surface area and pore volume of spent adsorbent are shown Table 4.6. The pore size distribution between fresh and spent adsorbent at various temperature are shown in Figure 4.9 and Figure 4.10.

Table 4.6 Surface Area and Pore Volume of Spent Adsorbent in the Study of Mercury Removal by Alumina Adsorbent

	Surface area (m ² /g)			Pore volume (cc/g)		
	30 °C	50 °C	70 °C	30 °C	50 °C	70 °C
Mercury chloride	212.9	195.6	185.4	0.351	0.345	0.318
Diphenylmercury	153.5	148.9	150.2	0.317	0.315	0.303

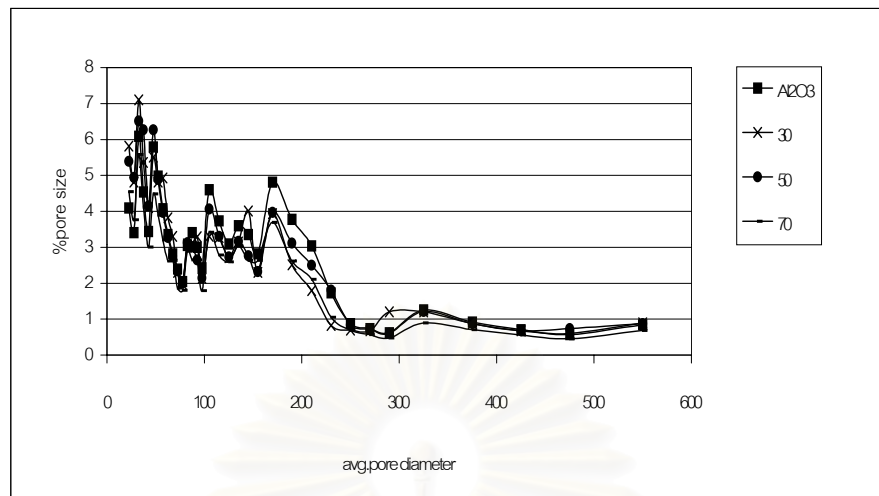


Figure 4.9 Comparison of Pore Size Distribution Between Fresh and Spent Alumina Adsorbent in the Study of Removal of Mercuric Chloride

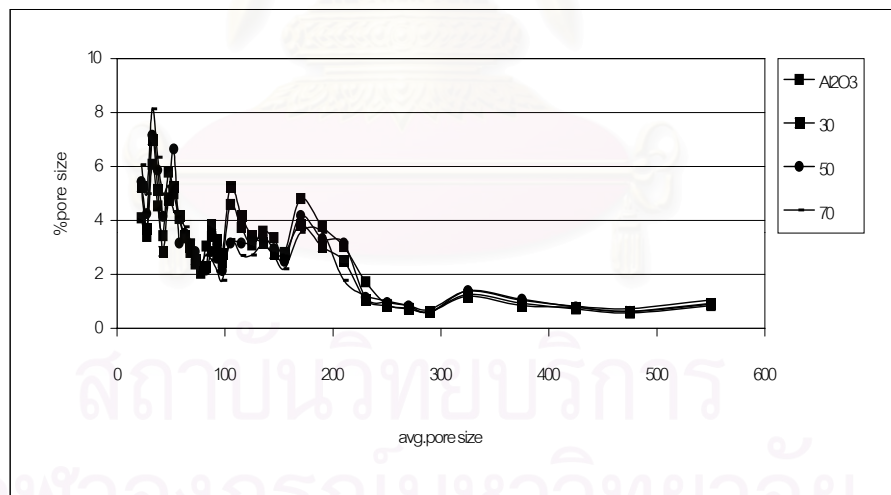


Figure 4.10 Comparison of Pore Size Distribution Between Fresh and Spent Alumina Adsorbent in the Study of Removal of Diphenylmercury

Adsorption of Mercury Compounds on CuO/Alumina Adsorbent

In this section, removals of mercury compounds by copper oxide adsorbent are studied. The spent copper oxide adsorbents are analyzed to identify the stoichiometry of mercury on the adsorbent surface using X-Ray Diffractometer. X-Ray Diffraction patterns of copper oxide adsorbent are shown in Figure 4.11 and Figure 4.12. The result of XRD can detect chemical bond between mercury and copper adsorbent. It found that mercury interacts with copper and forms copper mercury (CuHg). This indicates that the adsorption of mercury on copper oxide adsorbent is a chemical adsorption.

Figure 4.13 and Figure 4.14 shows the percent remove of mercuric chloride and diphenylmercury per weight and surface area of adsorbent. Table 4.7 shows percent removal of mercury per weight and per surface area of adsorbents. It can be observed that both mercuric chloride and diphenylmercury can be removed from liquid hydrocarbon by adsorption. Removal of mercuric chloride is approximately 80 to 90%. Removal of diphenylmercury is approximately 20 to 40%. It is also shown that mercuric chloride can be removed more effectively than diphenylmercury. As describe in adsorption of alumina adsorbent section, this may results from polarity and complication of each compound. This indicated that type of mercury compound strongly affect the adsorption of mercury on adsorbents. Operating temperature also has a strong effect on removal of mercury. Figure 4.15 to Figure 4.18 show percent removal of mercuric chloride and dipheylmercury per weight and surface area of adsorbent by fresh alumina and copper oxide adsorbent at various temperatures. Copper oxide adsorbent can remove mercury compounds effectively than alumina adsorbent. And, it can be observed that removal of mercuric chloride increases with increasing of operating temperature and removal of diphenlymercury increase with increasing of operating temperature. Removal of mercury

increases with increasing of temperature. This indicates that it is a reactive adsorption involving chemical reaction and not a simple physisorption. The operating temperature strongly effects the adsorption of mercury on adsorbents.

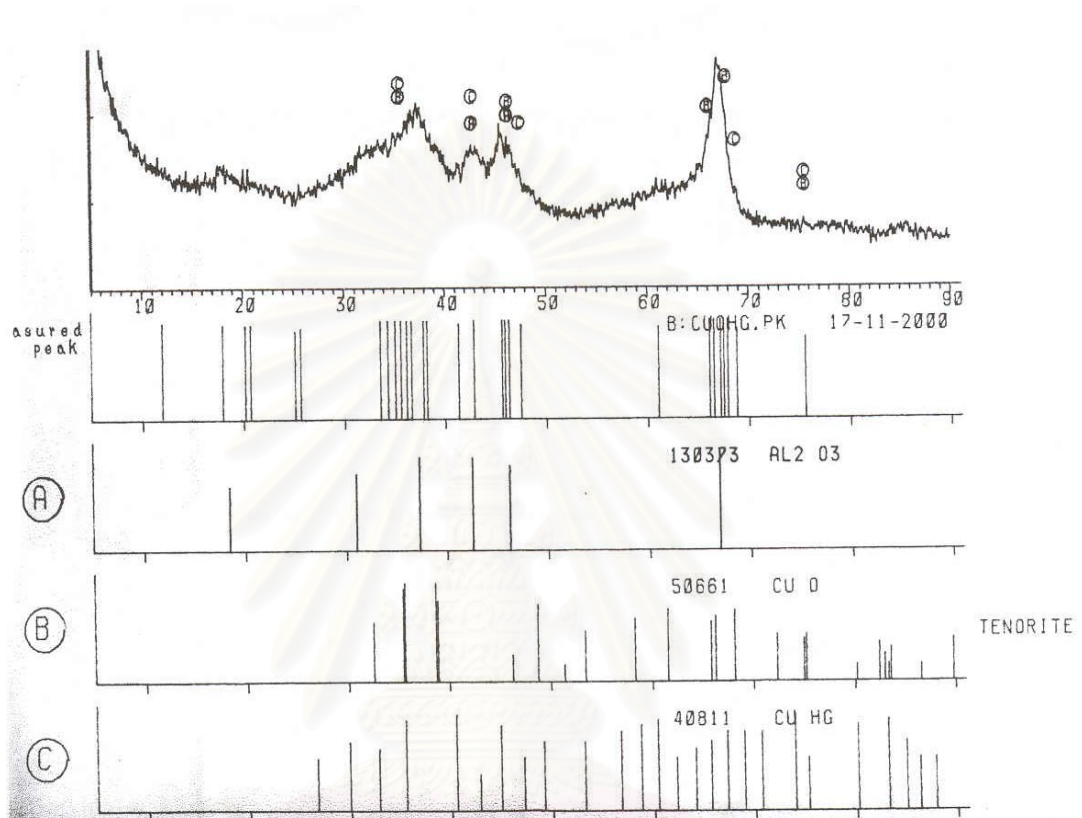


Figure 4.11 Show XRD Pattern of CuO/Alumina Adsorbent for Mercuric Chloride

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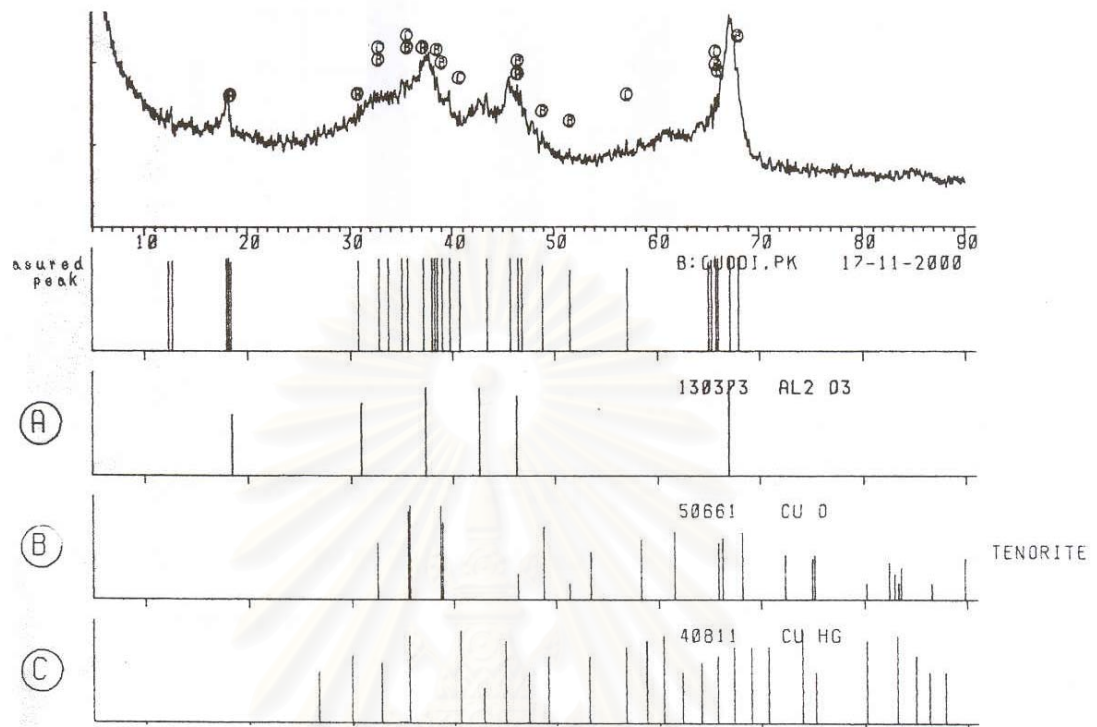


Figure 4.12 XRD Pattern of Spent CuO/Alumina Adsorbent for Diphenylmercury

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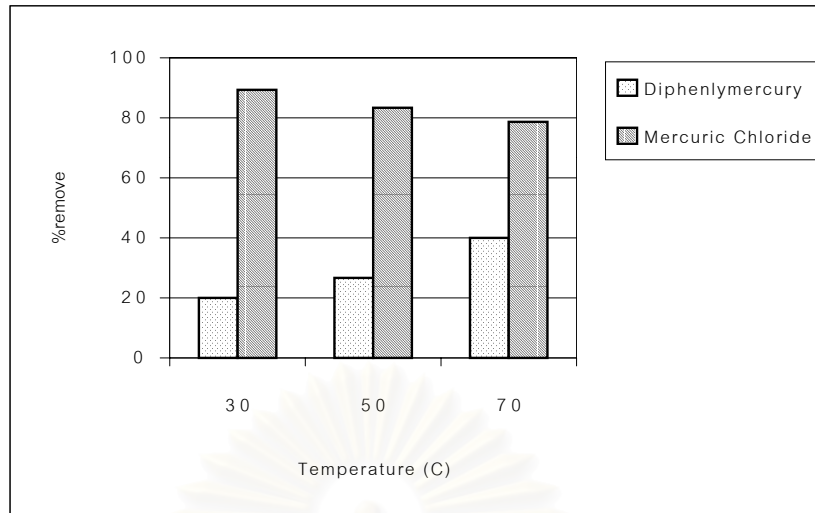


Figure 4.13 Percent Removal of Mercuric Chloride and Diphenylmercury per Weight of the Adsorbent in Study of Adsorption on CuO/Alumina Adsorbents at Various Temperatures.

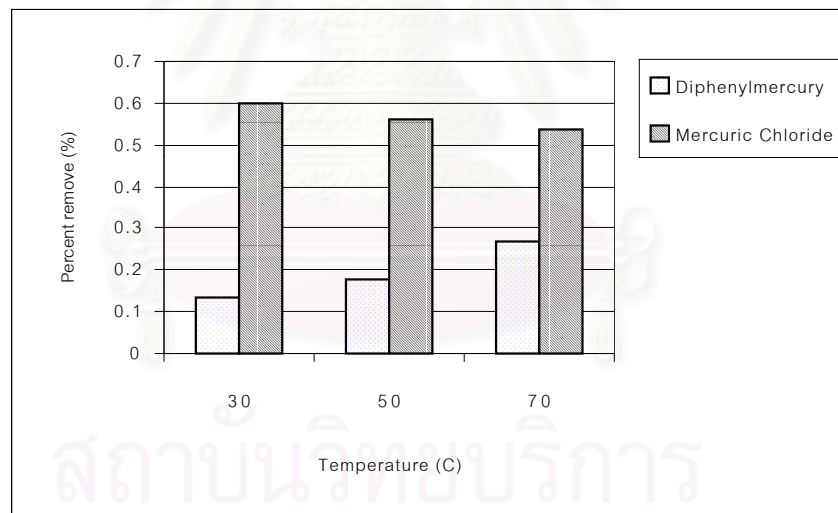


Figure 4.14 Percent Removal of Mercuric Chloride and Diphenylmercury per Surface Area of the Adsorbent in Study of Adsorption on CuO/Alumina Adsorbents at Various Temperatures.

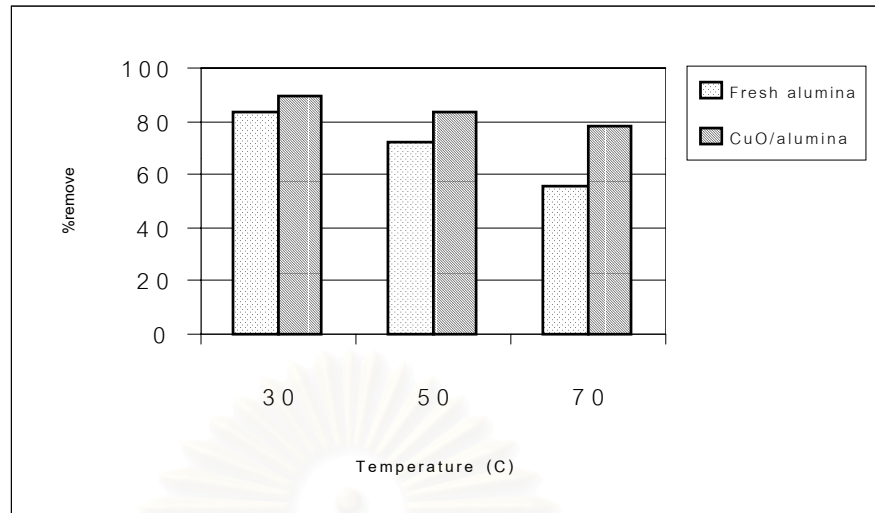


Figure 4.15 Percent Removal of Mercuric Chloride by Weight of Adsorbent in the Study of the Adsorption by Fresh Alumina and CuO/Alumina Adsorbent at Various Temperatures.

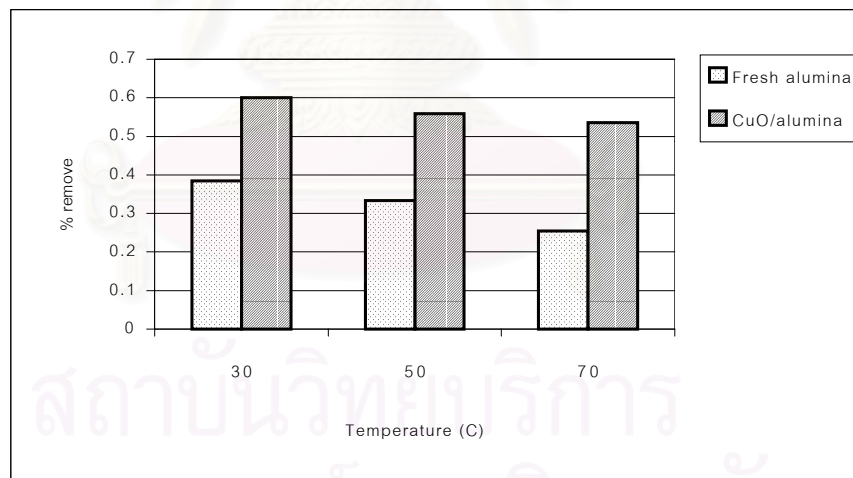


Figure 4.16 Percent Removal of Mercuric Chloride per Surface Area of the Adsorbent in the Study of Adsorption by Fresh Alumina and CuO/Alumina Adsorbent at Various Temperatures.

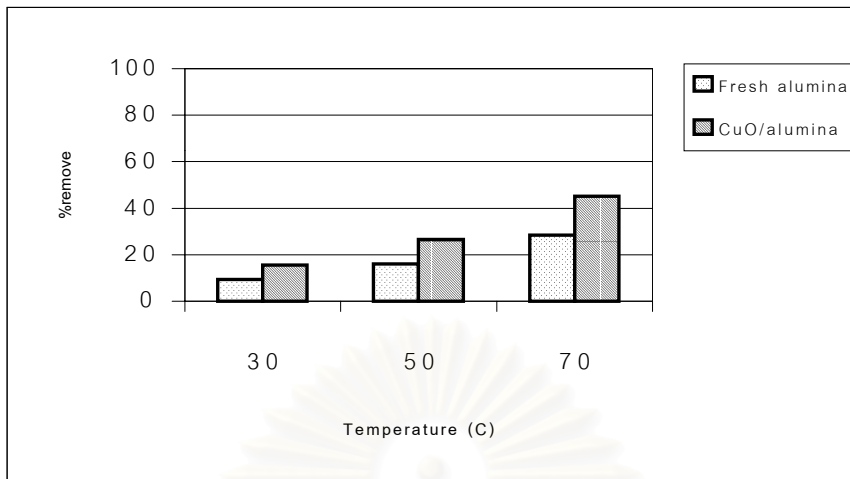


Figure 4.17 Percent Removal of Diphenylmercury per Weight of the Adsorbent in the Study of Adsorption by Fresh Alumina and CuO/Alumina Adsorbent at Various Temperatures.

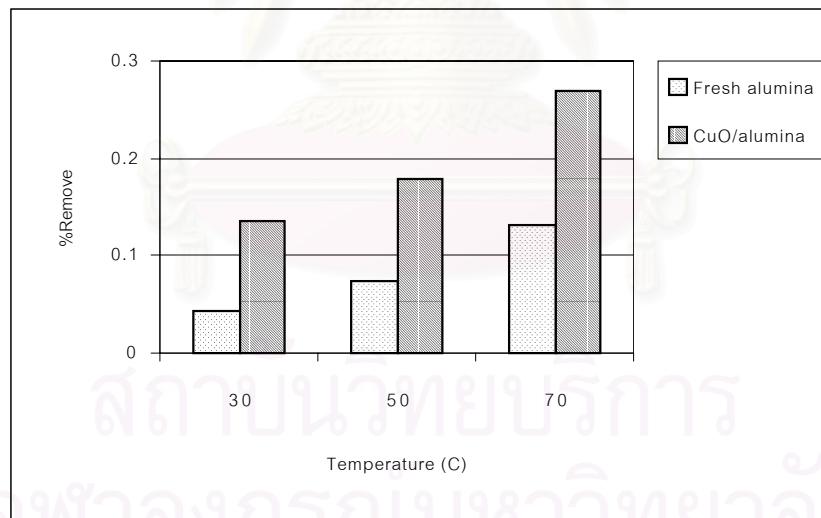


Figure 4.18 Percent Removal of Diphenylmercury per Surface Area of the Adsorbent in the Study of Adsorption by Fresh Alumina and CuO/Alumina Adsorbent at Various Temperatures.

Table 4.7 Percent Removal of Mercuric chloride and Diphenylmercury in the Study of Adsorption on Copper Oxide Adsorbent at Various Temperatures.

Compound	Temperature (°C)	Percent removal per weight	Percent removal per surface area
Mercuric Chloride	30	89.69	0.600
	50	83.60	0.559
	70	80.12	0.536
diphenylmercury	30	20.25	0.136
	50	26.72	0.179
	70	40.36	0.270

Table 4.8 shows percent of mercury deposited on adsorbents after adsorption experiment for both mercuric chloride and diphenylmercury. It can be observed that high concentration of mercury deposited on the adsorbent when the remaining mercury in liquid hydrocarbon is low. The results are not agreement with the results obtained from percent of mercury removal in liquid hydrocarbon. It is expected that part of mercury compounds may vaporized while the samples, both liquid hydrocarbon and adsorbent, were digested with acid to prepare the sample for atomic absorption.

Table 4.8 Percent of Mercuric Chloride and Diphenylmercury Deposited on the Adsorbents

Compound	Temperature (°C)	Percent of mercury deposited on adsorbents (%)
Mercuric Chloride	30	48.6
	50	45.3
	70	40.2
Diphenylmercury	30	15.6
	50	30.5
	70	32.6

The experiment is also designed to study desorption of mercury from spent Copper oxide adsorbent. Experimental results are shown in Figure 4.19, Figure 4.20 and Table 4.9. The results of desorption experiment show that the adsorption of mercuric chloride and diphenylmercury can partially desorb approximately 11%. The amounts of desorption of mercury on copper oxide adsorbents are less than the amounts of desorption of mercury on fresh alumina adsorbents. This indicates that the adsorption of copper oxide is not a reversible process and the mercury adsorption mechanism is not simple physisorption but is a chemisorption.

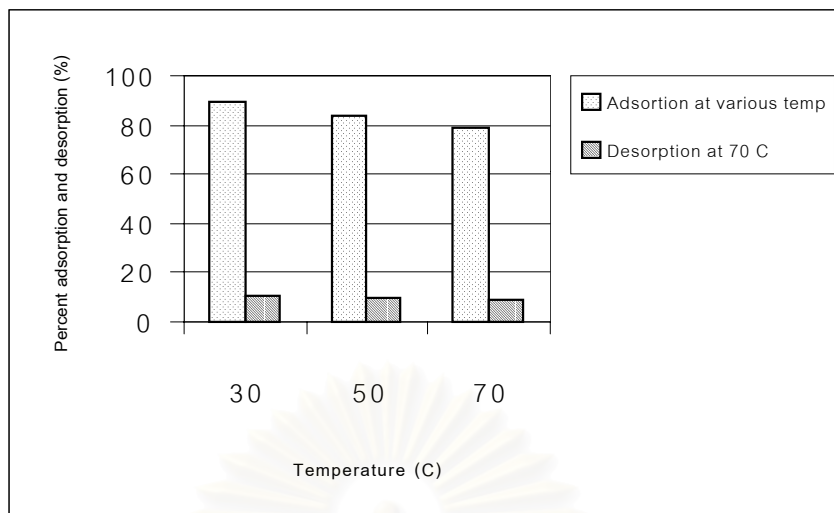


Figure 4.19 Percent of Adsorption at Various Temperatures and Desorption at 70 °C of Mercuric Chloride on CuO/Alumina Adsorbent

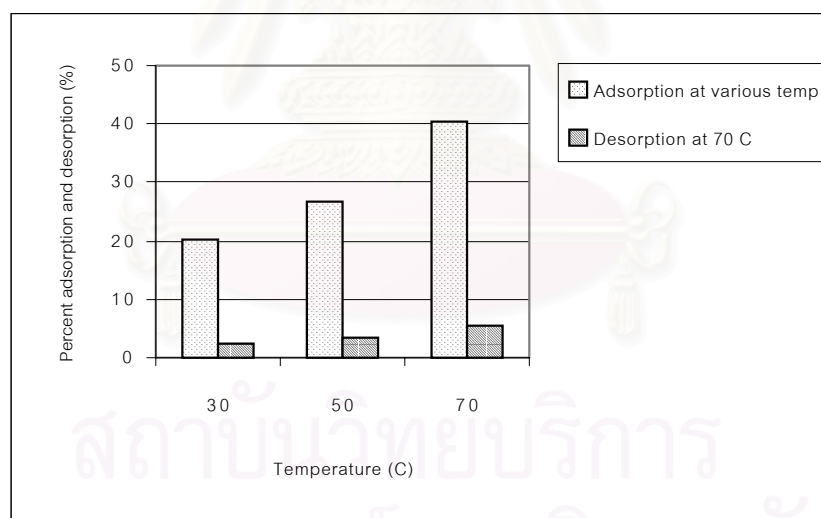


Figure 4.20 Percent of Adsorption at Various Temperature and Desorption at 70 °C of Diphenylmercury on CuO/Alumina Adsorbent

Table 4.9 Percent of Desorption of Mercury Chloride and Diphenylmercury at 70 °C

Compounds	Percent of desorption (%)		
	30 °C	50 °C	70 °C
Mercuric chloride	11.71	11.38	10.87
Diphenylmercury	11.60	12.57	13.61

The fresh and spent adsorbents are characterized by BET method to determine the surface area, pore volume, and pore size distribution. The results of surface area and pore volume of spent adsorbent are shown in Table 4.10. The pore size distributions between fresh and spent adsorbent at various temperatures are shown in Figure 4.21 and Figure 4.22. The result shows that there is slightly different of pore size distribution between fresh and spent adsorbent because amount of adsorbed mercury in each condition is rather the same. Pichan (1998) who conducted the experiment using nickel and copper adsorbents also obtained similar results.

Table 4.10 Surface Area and Pore Volume of Spent Adsorbent in the Study of Mercury Removal by CuO/Alumina Adsorbent.

	Surface area (m ² /g)			Pore volume (cc/g)		
	30 °C	50 °C	70 °C	30 °C	50 °C	70 °C
Mercury chloride	142.54	135.60	131.50	0.197	0.198	0.194
Diphenylmercury	153.34	150.60	147.56	0.210	0.256	0.275

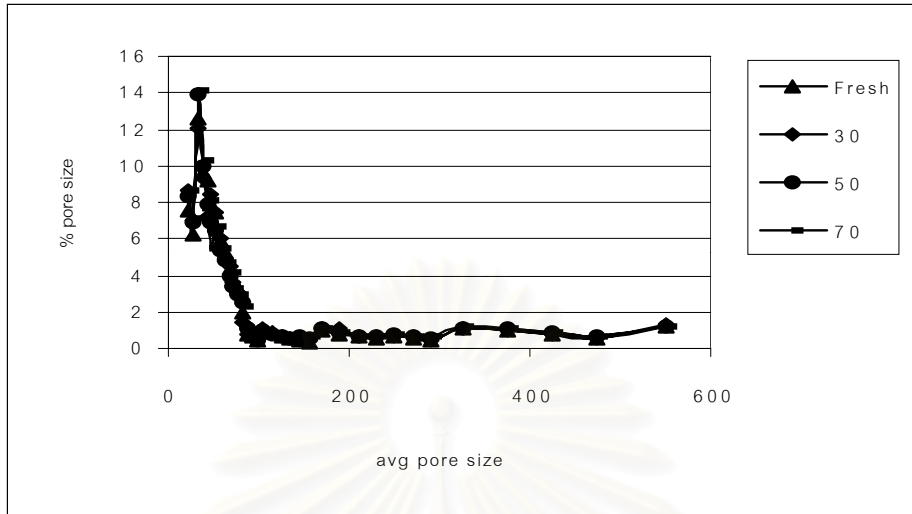


Figure 4.21 Comparison of Pore Size Distribution Between Fresh and Spent Adsorbent in the Study of Removal of Mercuric Chloride

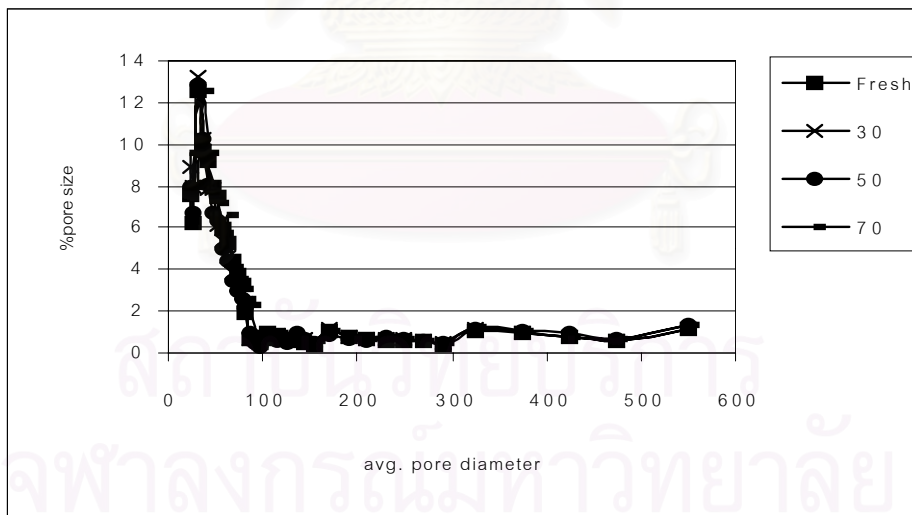


Figure 4.22 Comparison of Pore Size Distribution Between Fresh and Spent Adsorbent in the Study of Removal of Diphenylmercury

Adsorption of Mercury Compounds on CuS/Alumina Adsorbent

In this section, removal of mercury compounds by copper sulfide adsorbent are studied. The spent copper sulfide adsorbents are analyzed to identify the stoichiometry of mercury on the adsorbent surface using X-Ray Diffractometer. X-Ray Diffraction patterns of copper oxide adsorbent are shown in Figure 4.23 and Figure 4.24. The result of XRD can detect chemical bond between mercury and copper sulfide adsorbent. It found that mercury interacts with sulfur and forms mercury sulfide (HgS). This indicates that the adsorption of mercury on copper sulfide adsorbent is a chemisorption.

Figure 4.25 and 4.26 shows the percent remove of mercuric chloride and diphenylmercury. Table 4.11 shows percent removal of mercury per weight and per surface area of adsorbents. It can be observed that both mercuric chloride and diphenylmercury can be removed from liquid hydrocarbon by adsorption. Removal of mercuric chloride is approximately 90 to 99%. Removal of diphenylmercury is approximately 80 to 90%. It is also shown that mercuric chloride can be removed with higher efficiency than diphenylmercury. As describe in adsorption of alumina adsorbent section, this may results from polarity and complication of each compound. This indicates that type of mercury compound strongly affect the adsorption of mercury on adsorbents. Operating temperature also has a strong effect on removal of mercury. Figure 4.27 to 4.30 show percent removal of mercuric chloride and diphenylmercury per weight and surface area of adsorbent on fresh alumina and copper sulfide adsorbent at various temperatures. Copper sulfide adsorbent can remove mercury compounds effectively than alumina adsorbent. And, it can be observed that removal of both mercuric chloride and diphenylmercury increases with increasing of operating temperature. Removal of mercury increases with increasing of temperature. This indicates that it is a reactive adsorption involving chemical

reaction and not a simple physisorption. The operating temperature strongly effects the adsorption of mercury on adsorbents.

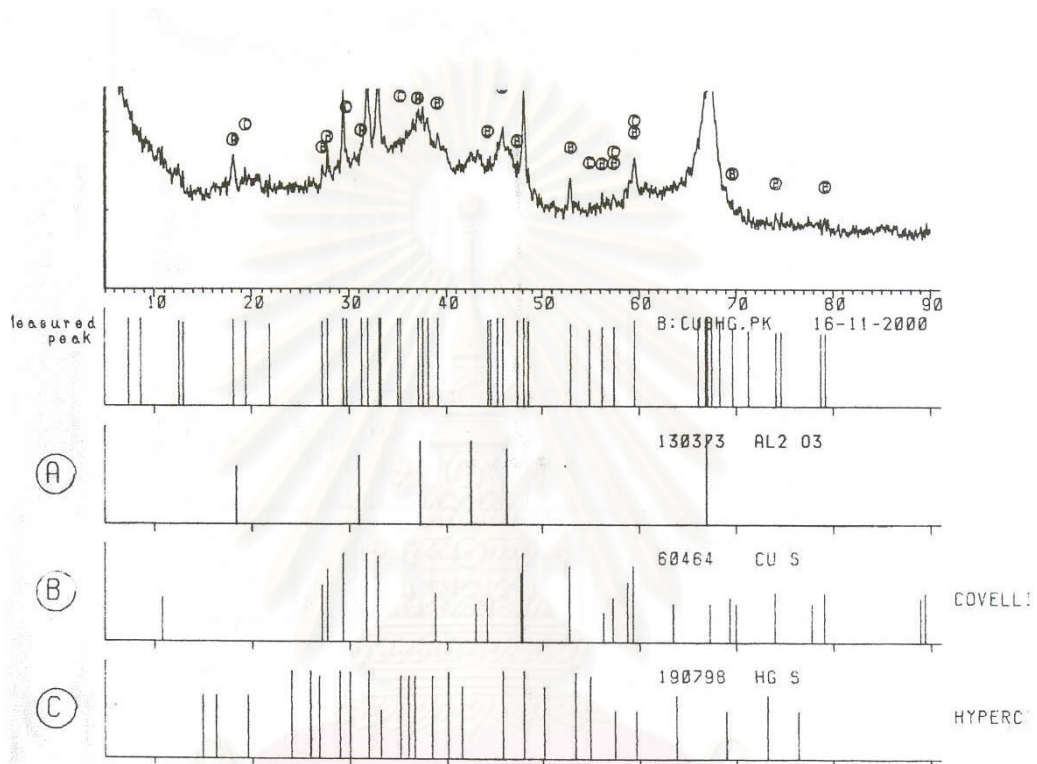


Figure 4.23 XRD Pattern of Spent CuS/Alumina Adsorbent for Mercuric Chloride

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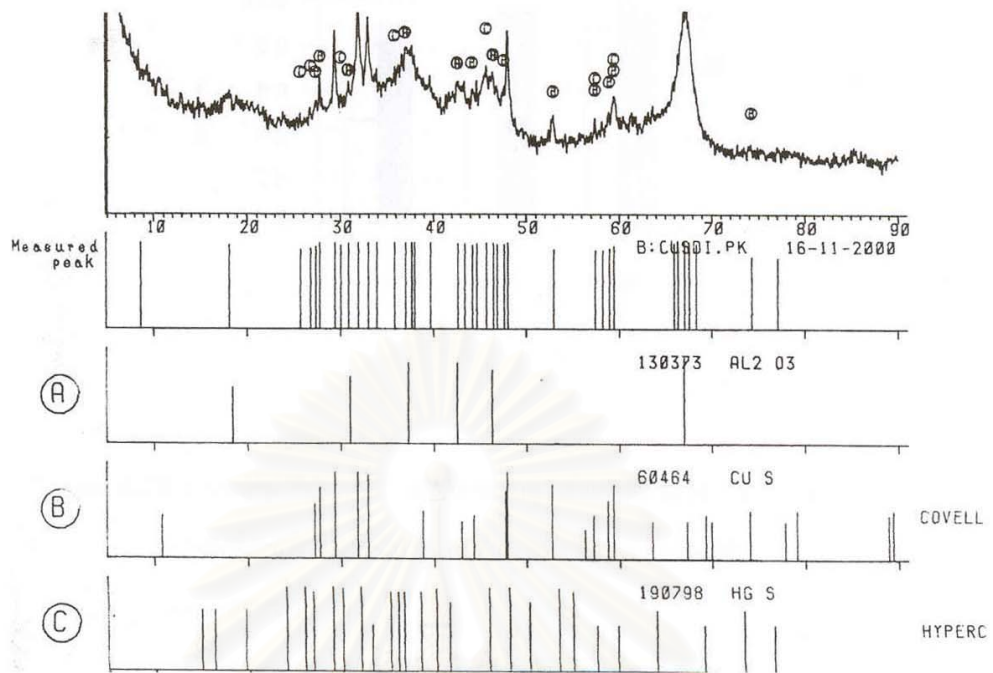


Figure 4.24 XRD Pattern of Spent CuS/Alumina Adsorbent for Diphenylmercury

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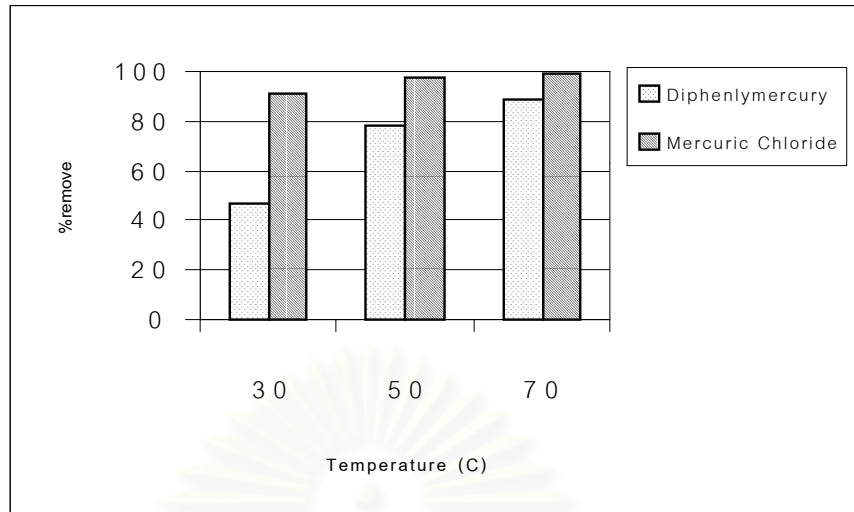


Figure 4.25 Percent Removal of Mercuric Chloride and Diphenylmercury per Weight of Adsorbent in the Study of Adsorption on CuS/Alumina Adsorbents at Various Temperatures.

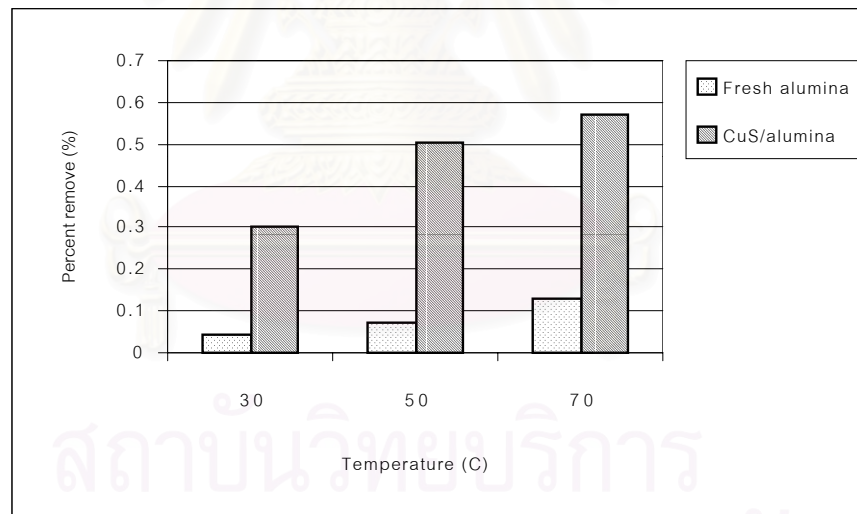


Figure 4.26 Percent Removal of Mercuric Chloride and Diphenylmercury per Surface Area of Adsorbent in the Study of Adsorption on CuS/Alumina Adsorbents at Various Temperatures.

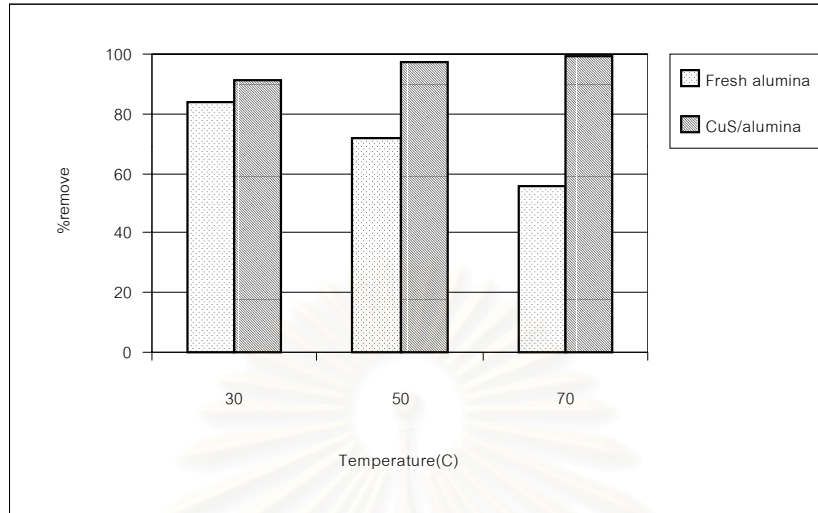


Figure 4.27 Percent Removal of Mercury Chloride per Weight of Adsorbent in the Study of Adsorption on Fresh Alumina and CuS/Alumina Adsorbent at Various Temperatures.

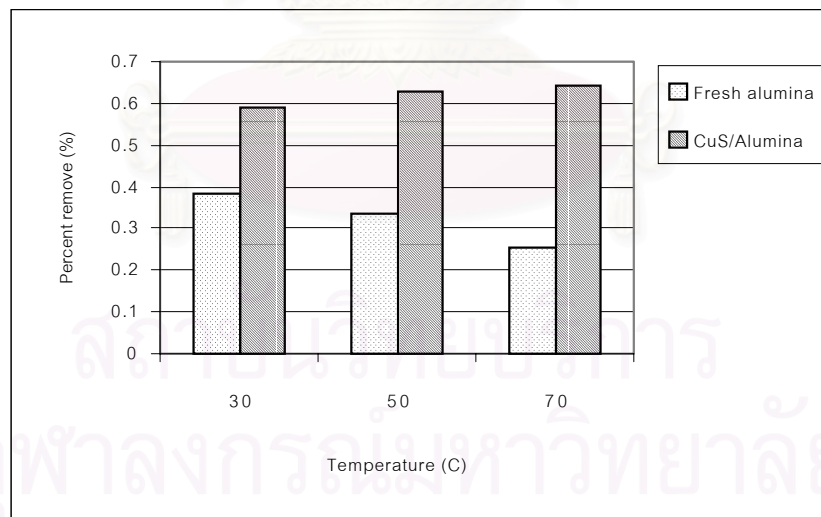


Figure 4.28 Percent Removal of Mercury Chloride per Surface Area of Adsorbent in the Study of Adsorption on Fresh Alumina and CuS/Alumina Adsorbent at Various Temperatures.

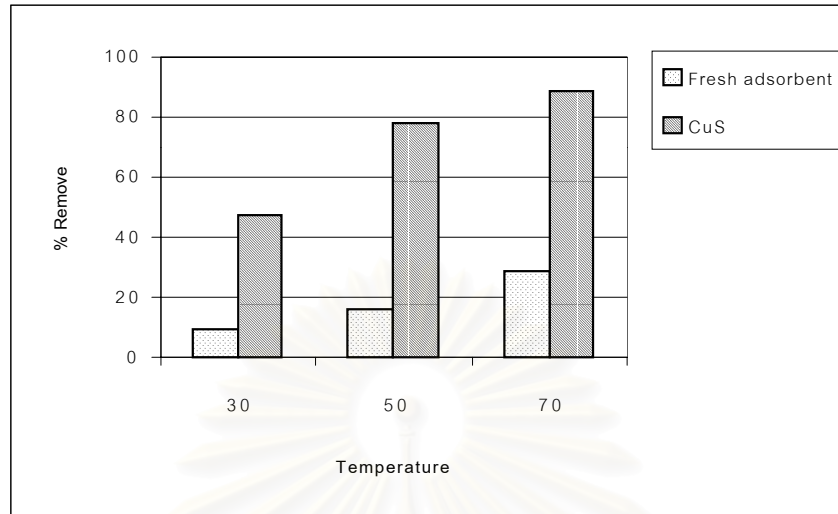


Figure 4.29 Percent Removal of Diphenylmercury per Weight of Adsorbent in the Study of Adsorption on Fresh Alumina and CuS/Alumina Adsorbent at Various T Temperatures.

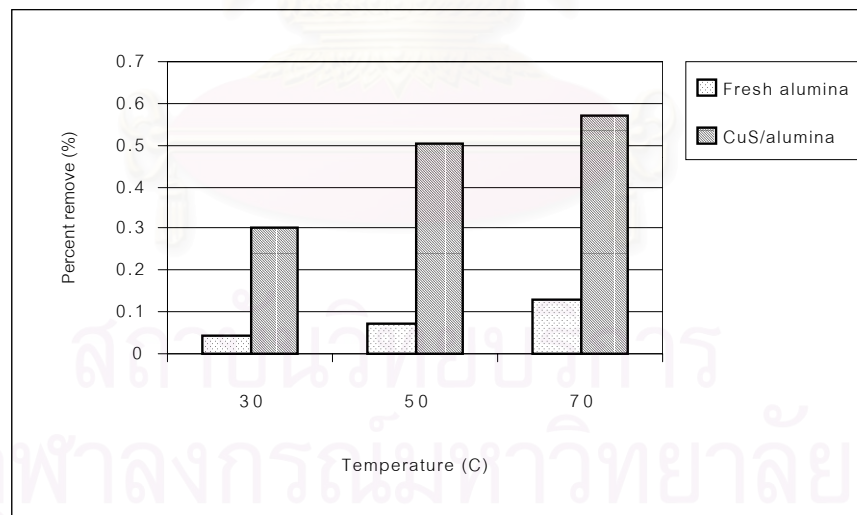


Figure 4.30 Percent Removal of Diphenylmercury per Surface Area of Adsorbent in the Study of Adsorption on Fresh Alumina and CuS/Alumina Adsorbent at Various Temperatures.

Table 4.11 Percent Removal of Mercuric Chloride and Diphenylmercury in the Study of Adsorption on Copper Sulfide Adsorbent at Various Temperatures.

Compound	Temperature (°C)	Percent removal per weight (%)	Percent removal per surface area (%)
Mercuric Chloride	30	91.47	0.589
	50	97.63	0.629
	70	99.43	0.641
diphenylmercury	30	47.04	0.303
	50	78.20	0.504
	70	88.75	0.572

Table 4.12 shows percent of mercury deposited on adsorbents after adsorption experiment for both mercuric chloride and diphenylmercury. It can be observed that high concentration of mercury deposited on the adsorbent when the remaining mercury in liquid hydrocarbon is low. The results are not agreement with the results obtained from percent of mercury removal in liquid hydrocarbon. It is expected that part of mercury compounds may vaporized while the samples, both liquid hydrocarbon and adsorbent, were digested with acid to prepare the sample for atomic absorption.

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Table 4.12 Percent of Mercuric Chloride and Diphenylmercury Deposited on Adsorbents

Compound	Temperature (°C)	Percent of mercury deposited on adsorbents (%)
Mercuric Chloride	30	40.3
	50	48.5
	70	50.5
Diphenylmercury	30	38.9
	50	40.6
	70	43.5

The experiment is also designed to study desorption of mercury from spent copper sulfide adsorbent. Experimental results are shown in Figure 4.31, 4.32 and Table 4.13. The results of desorption experiment shows that the adsorption of mercuric chloride and diphenylmercury can partially desorb approximately 5%. The amounts of desorption of mercury by copper oxide adsorbents are less than the amounts of desorption of mercury by fresh alumina adsorbents. This indicates that the adsorption of copper oxide is not a reversible process and the mercury adsorption mechanism is not simple physisorption but is a chemisorption.

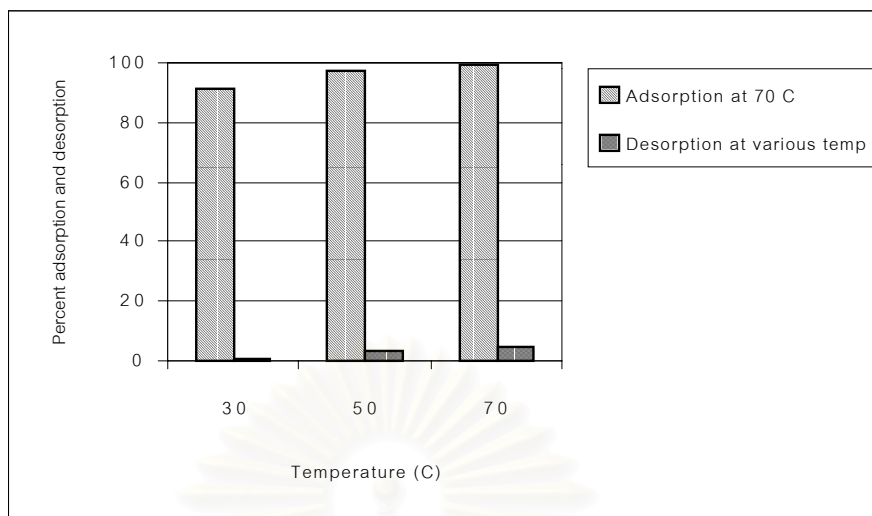


Figure 4.31 Percent of Adsorption at Various Temperatures and Desorption at 70 °C of Mercuric Chloride on CuS/Alumina Adsorbents.

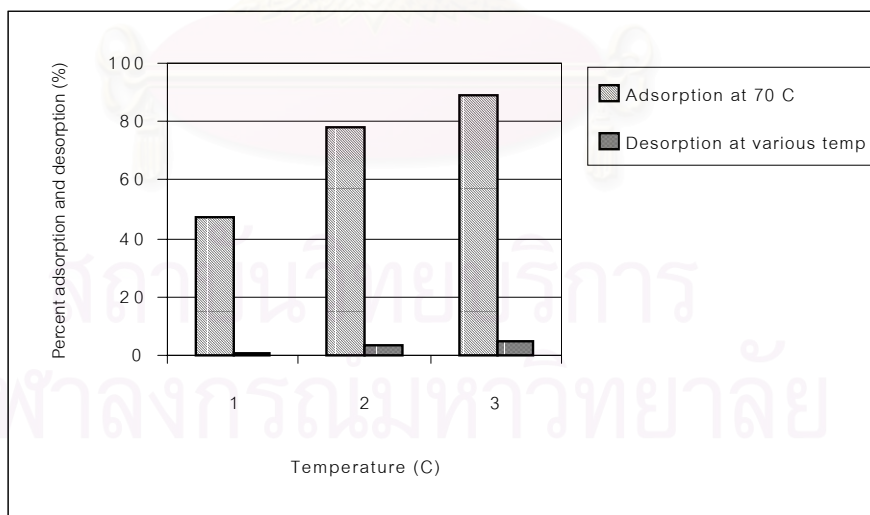


Figure 4.32 Percent of Adsorption at Various Temperatures and Desorption at 70 °C of Diphenylmercury on CuS/Alumina Adsorbents.

Table 4.13 Percent of Desorption of Mercury Chloride and Diphenylmercury at 70 °C.

Compounds	Percent of desorption (%)		
	30 °C	50 °C	70 °C
Mercuric chloride	1.09	3.58	4.53
Diphenylmercury	2.12	4.47	5.18

The fresh and spent adsorbents are characterized by BET method to determine the surface area, pore volume, and pore size distribution. The results of surface area and pore volume of spent adsorbent are shown in Table 4.14. The pore size distribution between fresh and spent adsorbent at various temperature are shown in Figure 4.33 and Figure 4.34. The result shows that there is slightly different of pore size distribution between fresh and spent adsorbent because amount of adsorbed mercury in each condition is rather the same.

Table 4.14 Surface Area and Pore Volume of Spent Adsorbent in the Study of Mercury Removal on CuS/Alumina Adsorbent.

	Surface area (m ² /g)			Pore volume (cc/g)		
	30 °C	50 °C	70 °C	30 °C	50 °C	70 °C
Mercury chloride	140.73	158.65	113.99	0.184	0.178	0.168
Diphenylmercury	168.56	170.25	166.76	0.194	0.185	0.197

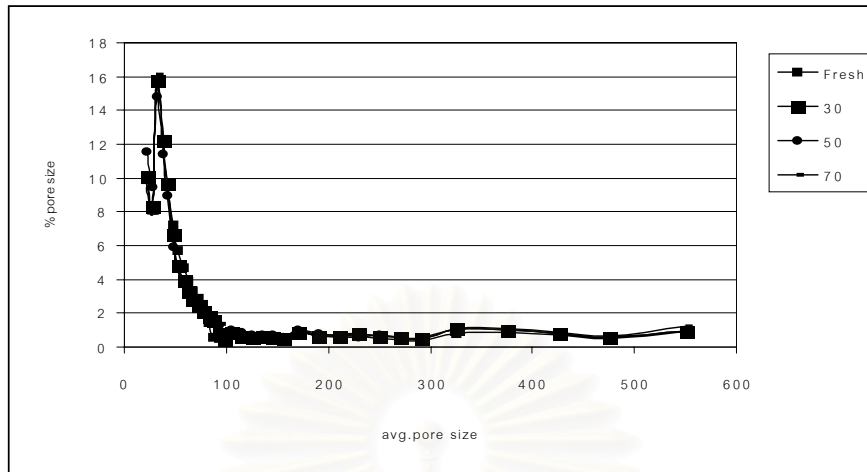


Figure 4.33 Comparison of Pore Size Distribution Between Fresh and Spent Adsorbent in the Study of Removal of Mercuric Chloride.

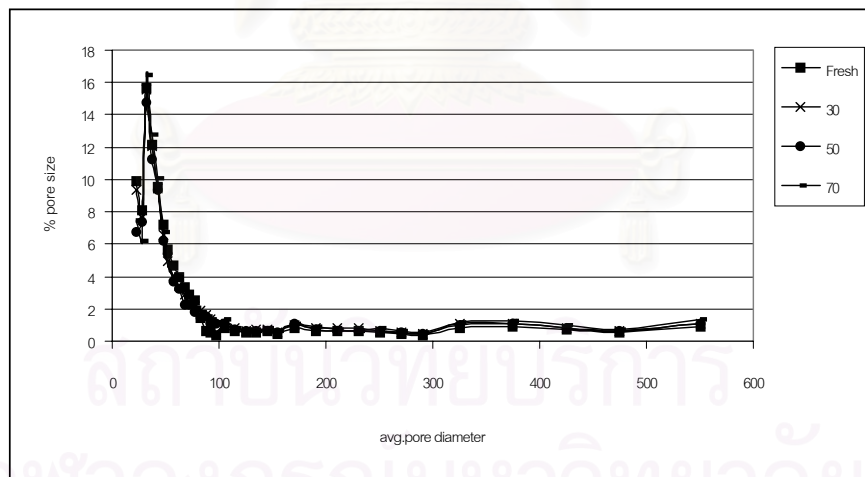
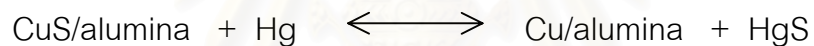


Figure 4.34 Comparison of Pore Size Distribution Between Fresh and Spent Adsorbent in the Study of Removal of Diphenylmercury.

4.3 Effect of Type of Mercury Compounds and Adsorbents

Figure 4.35 to 4.38 show percent removal of mercuric chloride and diphenylmercury per weight and surface area of the adsorbent on fresh alumina, copper oxide and copper sulfide adsorbent at various temperatures. It is shown that mercuric chloride can be removed more effectively than diphenylmercury. It is also shown that copper sulfide adsorbent can remove mercuric chloride and diphenylmercury more effectively than other adsorbent. From the periodic table, Sulfide form is more reactivity than oxide form. And, sulfide form is more reactivity to mercury compound. The mechanisms of mercury adsorption by use of copper sulfide are not well-known. Since mercury in the spent adsorbent is mainly in the form of HgS, the reaction involved is :



In the chemisorption of mercury, chemical bonds are formed between the mercury and the copper sulfide on alumina. In this mechanism, sulfur is the real active component for reaction with mercury. The presence of copper makes the sulfur insoluble in oil and reaction with mercury. (Y.Yan, 1996) This indicates that sulfur in adsorbent is active specie for mercury removal. Removal of mercury depends on type of mercury compounds. Mercuric chloride can be removed more effectively than diphenylmercury by every adsorbent. In addition, it is also depends on type of adsorbents. Efficiency of adsorbent on mercury removal was in the following order : copper sulfide > copper oxide > alumina adsorbents

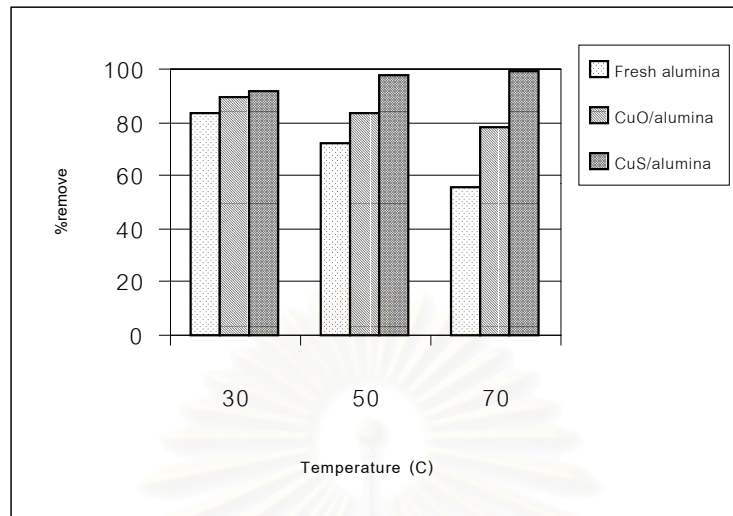


Figure 4.35 Percent Removal of Mercuric Chloride per Weight of the Adsorbent in the Study of Adsorption on Fresh Alumina, CuO/Alumina and CuS/Alumina Adsorbent at Various Temperatures.

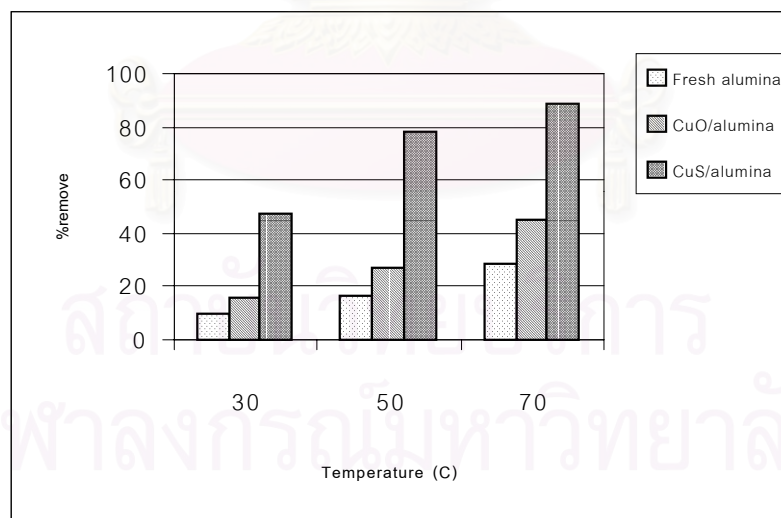


Figure 4.36 Percent Removal of Diphenylmercury per Weight of the Adsorbent in the Study of Adsorption on Fresh Alumina, CuO/Alumina and CuS/Alumina Adsorbent at Various Temperatures.

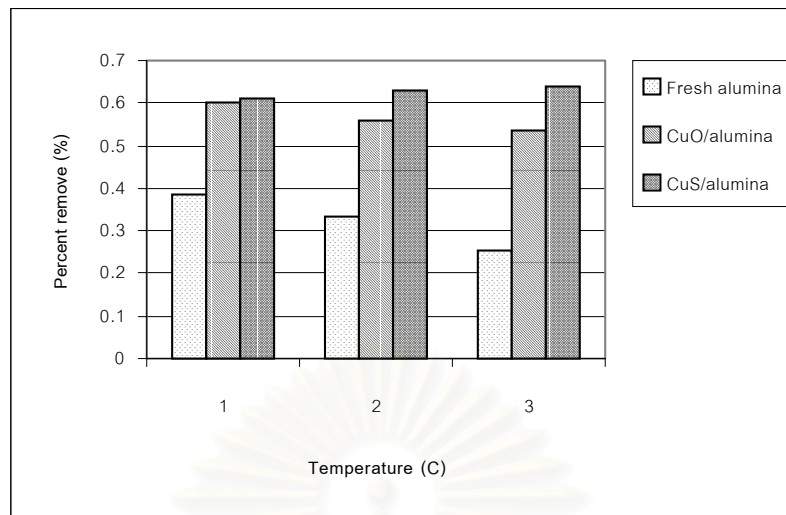


Figure 4.37 Percent Removal of Mercuric Chloride per Surface Area of the adsorbent in the Study of Adsorption on Fresh Alumina, CuO/Alumina and CuS/Alumina Adsorbent at Various Temperatures.

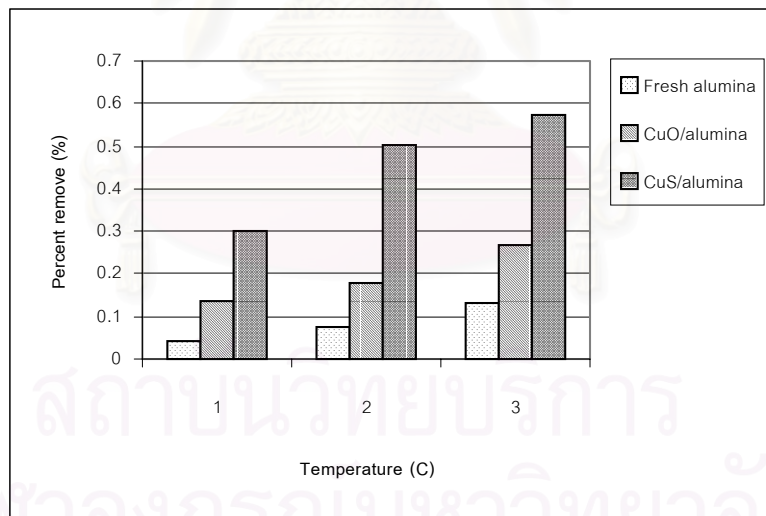


Figure 4.38 Percent Removal of Diphenylmercury per Surface Area of the adsorbent in the Study of Adsorption on Fresh Alumina, CuO/Alumina and CuS/Alumina Adsorbent at Various Temperatures.

CHAPTER V

CONCLUSIONS

Conclusions

The following conclusions are drawn from this study

1. Alumina, copper oxide, copper sulfide adsorbents can be used in the removal of mercury compounds from liquid hydrocarbon. Copper sulfide adsorbents can remove mercury more effectively than other adsorbent.
2. Removal of mercury depends on temperature. Removal of mercuric chloride and diphenylmercury increase with increasing of operating temperature for copper oxide and copper sulfide adsorbent.
3. Removal of mercury depends on type of mercury. Mercuric chloride can be removed more effectively than diphenylmercury by all adsorbent.
4. In addition, it is also depends on type of adsorbents. Efficiency of adsorbent on mercury removal was in the following order: copper sulfide > copper oxide > alumina.
5. The adsorption of mercuric chloride and diphenylmercury on copper oxide and copper sulfide adsorbent is a chemical adsorption. Formation of copper mercury (CuHg) and mercury sulfide (HgS) were detected on spent copper oxide and copper sulfide adsorbent.

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APPENDICES

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Appendix A

Table 1A Conditions and Result of each experiment of adsorption

Exp.no.	Type of mercury	Type of adsorbent	Temp (C)	Ini. Conc. ppb	Remaining Hg ppb	% remove
1	HgCl ₂	-	30	950.1	935.2	1.57
2	HgCl ₂	-	50	950.1	930.3	2.08
3	HgCl ₂	-	70	950.1	940.2	1.04
4	DPM	-	30	962.2	952.8	1.00
5	DPM	-	50	963.2	948.8	1.50
6	DPM	-	70	964.2	950.2	1.45
7	DPM	alumina	30	950.8	870.9	8.4
8	DPM	alumina	30	997.2	893.5	10.4
9	DPM	alumina	30	985.2	890.6	9.6
10	DPM	alumina	70 (desorp)	985.2	959.6	2.6
11	DPM	alumina	50	950.8	811.9	14.6
12	DPM	alumina	50	997.2	812.7	18.5
13	DPM	alumina	50	985.2	833.5	15.4
14	DPM	alumina	70 (desorp)	985.2	910.7	7.6
15	DPM	alumina	70	950.8	678.8	28.6
16	DPM	alumina	70	997.2	705.0	29.3
17	DPM	alumina	70	985.2	713.3	27.6
18	DPM	alumina	70 (desorp)	985.2	802.9	18.5
19	HgCl ₂	alumina	30	945.8	155.1	83.6
20	HgCl ₂	alumina	30	963.4	142.6	85.2
21	HgCl ₂	alumina	30	985.6	170.5	82.7
22	HgCl ₂	alumina	70 (desorp)	985.6	565.7	42.6
25	HgCl ₂	alumina	50	985.6	270.1	72.6
26	HgCl ₂	alumina	70 (desorp)	985.6	606.1	38.5
27	HgCl ₂	alumina	70	945.8	390.6	58.7
28	HgCl ₂	alumina	70	963.4	459.5	52.3
29	HgCl ₂	alumina	70	945.8	390.6	58.7
30	HgCl ₂	alumina	70	945.8	451.1	52.3
31	HgCl ₂	alumina	70	945.8	421.8	55.4
32	HgCl ₂	alumina	70 (desorp)	945.8	660.2	30.2
33	DPM	CuO/alumina	30	1052.0	825.8	21.5
34	DPM	CuO/alumina	30	952.1	776.0	18.5
35	DPM	CuO/alumina	30	945.6	741.4	21.6
36	DPM	CuO/alumina	30	940.0	756.7	19.5
37	DPM	CuO/alumina	30	942.3	752.9	20.1
38	DPM	CuO/alumina	70 (desorp)	942.3	920.2	2.4
39	DPM	CuO/alumina	50	1052.0	752.2	28.5

Table 1A Conditions and Result of each experiment of adsorption. (continue)

Exp.no.	Type of mercury	Type of adsorbent	Temp (C)	Ini. Conc. ppb	Remaining Hg ppb	% remove
40	DPM	CuO/alumina	50	952.1	716.9	24.7
41	DPM	CuO/alumina	50	945.6	703.5	25.6
42	DPM	CuO/alumina	50	940.0	678.7	27.8
43	DPM	CuO/alumina	50	942.3	688.8	26.9
44	DPM	CuO/alumina	70 (desorp)	942.3	910.6	3.4
45	DPM	CuO/alumina	70	1052.0	678.5	35.5
46	DPM	CuO/alumina	70	952.1	619.8	34.9
47	DPM	CuO/alumina	70	945.6	539.9	42.9
48	DPM	CuO/alumina	70	940.0	531.1	43.5
49	DPM	CuO/alumina	70	942.3	504.1	46.5
50	DPM	CuO/alumina	70 (desorp)	942.3	890.7	5.5
51	HgCl ₂	CuO/alumina	30	945.1	98.7	89.6
52	HgCl ₂	CuO/alumina	30	985.3	83.8	91.5
53	HgCl ₂	CuO/alumina	30	978.6	96.3	90.2
54	HgCl ₂	CuO/alumina	30	945.2	98.3	89.6
55	HgCl ₂	CuO/alumina	30	978.6	122.3	87.5
56	HgCl ₂	CuO/alumina	70 (desorp)	978.6	875.8	10.5
57	HgCl ₂	CuO/alumina	50	945.1	149.3	84.2
58	HgCl ₂	CuO/alumina	50	985.3	171.4	82.6
59	HgCl ₂	CuO/alumina	50	978.6	144.8	85.2
60	HgCl ₂	CuO/alumina	50	945.2	156.0	83.5
61	HgCl ₂	CuO/alumina	50	978.6	171.3	82.5
62	HgCl ₂	CuO/alumina	70 (desorp)	978.6	885.4	9.5
63	HgCl ₂	CuO/alumina	70	945.1	183.3	80.6
64	HgCl ₂	CuO/alumina	70	985.3	202.0	79.5
65	HgCl ₂	CuO/alumina	70	978.6	181.0	81.5
66	HgCl ₂	CuO/alumina	70	945.2	184.3	80.5
67	HgCl ₂	CuO/alumina	70	978.6	210.4	78.5
68	HgCl ₂	CuO/alumina	70 (desorp)	978.6	895.0	8.5
69	DPM	S/alumina	30	950.2	859.9	9.5
70	DPM	S/alumina	50	950.2	783.0	17.6
71	DPM	S/alumina	70	950.2	659.4	30.6
72	HgCl ₂	S/alumina	30	985.6	172.5	82.5
73	HgCl ₂	S/alumina	50	985.6	279.9	71.6
74	HgCl ₂	S/alumina	70	985.6	435.6	55.8
75	DPM	CuS/alumina	30	1052.0	557.6	47.0
76	DPM	CuS/alumina	30	952.1	490.2	48.5
77	DPM	CuS/alumina	30	945.6	510.6	46.0
78	DPM	CuS/alumina	30	940.0	502.9	46.5

Table 1A Conditions and Result of each experiment of adsorption. (continue)

Exp.no.	Type of mercury	Type of adsorbent	Temp (C)	Ini. Conc. ppb	Remaining Hg ppb	% remove
79	DPM	CuS/alumina	70 (desorp)	940.0	930.6	1.0
80	DPM	CuS/alumina	50	1052.0	215.7	79.5
81	DPM	CuS/alumina	50	952.1	203.8	78.6
82	DPM	CuS/alumina	50	945.6	222.2	76.5
83	DPM	CuS/alumina	50	940.0	207.7	77.9
84	DPM	CuS/alumina	70 (desorp)	940.0	907.1	3.5
85	DPM	CuS/alumina	70	1052.0	99.9	90.5
86	DPM	CuS/alumina	70	952.1	130.9	86.3
87	DPM	CuS/alumina	70	945.6	99.3	89.5
88	DPM	CuS/alumina	70	940.0	113.7	87.9
89	DPM	CuS/alumina	70 (desorp)	940.0	896.8	4.6
90	HgCl ₂	CuS/alumina	30	945.1	90.7	90.4
91	HgCl ₂	CuS/alumina	30	985.3	72.9	92.6
92	HgCl ₂	CuS/alumina	30	978.6	84.2	91.4
93	HgCl ₂	CuS/alumina	30	945.1	89.8	90.5
94	HgCl ₂	CuS/alumina	70 (desorp)	945.1	935.6	1.0
95	HgCl ₂	CuS/alumina	50	945.1	13.2	98.6
96	HgCl ₂	CuS/alumina	50	985.3	24.6	97.5
97	HgCl ₂	CuS/alumina	50	978.6	31.3	96.8
98	HgCl ₂	CuS/alumina	50	945.1	24.6	97.4
99	HgCl ₂	CuS/alumina	70 (desorp)	945.1	912.0	3.5
100	HgCl ₂	CuS/alumina	70	945.1	14.2	98.5
101	HgCl ₂	CuS/alumina	70	985.3	1.0	99.9
102	HgCl ₂	CuS/alumina	70	978.6	1.0	99.9
103	HgCl ₂	CuS/alumina	70	945.1	13.2	98.6
104	HgCl ₂	CuS/alumina	70 (desorp)	945.1	902.6	4.5

สถาบันวิจัยชีววิทยา
จุฬาลงกรณ์มหาวิทยาลัย

Appendix B

Table 1B pore size distribution of alumina in study of mercuric chloride removal

Pore diameter (Å)	fresh		30		50		70	
	Pore vol.(cc/g)	%Pore vol.	Pore vol.(cc/g)	%Pore vol.	Pore vol.(cc/g)	%Pore vol.	Pore vol.(cc/g)	%Pore vol.
550	0.004292	0.841712	0.003397	0.892665	0.003297	0.873757	0.003235	0.681099
475	0.002898	0.568332	0.002275	0.597825	0.002792	0.739924	0.002154	0.453504
425	0.003628	0.711494	0.002582	0.678499	0.002545	0.674465	0.002654	0.558774
375	0.004681	0.918000	0.003335	0.876372	0.003325	0.881178	0.003345	0.704258
325	0.006425	1.260019	0.004574	1.201957	0.004575	1.212447	0.004265	0.897955
290	0.003174	0.622459	0.004575	1.202220	0.002258	0.598406	0.002245	0.472663
270	0.003778	0.740911	0.002564	0.673769	0.002691	0.713158	0.002720	0.572670
250	0.004474	0.877405	0.002653	0.697156	0.003186	0.844340	0.003250	0.684257
230	0.008803	1.726373	0.003152	0.828284	0.006827	1.809263	0.005014	1.055650
210	0.015498	3.039342	0.006845	1.798731	0.009444	2.502809	0.010024	2.110458
190	0.019275	3.780057	0.009541	2.507187	0.011752	3.114466	0.012450	2.621229
170	0.024556	4.815723	0.014987	3.938289	0.014978	3.969407	0.017546	3.694144
155	0.014374	2.818912	0.008745	2.298014	0.008747	2.318093	0.012530	2.638072
145	0.017127	3.358808	0.015242	4.005298	0.010452	2.769945	0.012540	2.640178
135	0.018364	3.601399	0.011951	3.140488	0.011951	3.167204	0.014450	3.042310
125	0.015787	3.096018	0.010325	2.713207	0.010333	2.738408	0.012350	2.600175
115	0.019028	3.731617	0.012456	3.273192	0.012453	3.300242	0.013250	2.789662
105	0.023446	4.598039	0.012574	3.304200	0.015341	4.065607	0.016240	3.419178
97.5	0.012352	2.422374	0.008094	2.126944	0.008094	2.145038	0.008540	1.798016
92.5	0.015296	2.999727	0.012546	3.296842	0.010007	2.652013	0.012560	2.644389
87.5	0.017388	3.409993	0.011526	3.028806	0.011374	3.014290	0.012560	2.644389
82.5	0.015563	3.052089	0.011756	3.089245	0.011771	3.119501	0.013760	2.897037
77.5	0.010430	2.045447	0.007458	1.959816	0.007575	2.007495	0.008560	1.802227
72.5	0.012202	2.392957	0.008745	2.298014	0.008847	2.344595	0.008886	1.870863
67.5	0.014355	2.815186	0.012563	3.301309	0.010391	2.753779	0.012550	2.642283
62.5	0.017104	3.354298	0.014526	3.817147	0.012364	3.276655	0.012426	2.616176
57.5	0.020759	4.071087	0.018745	4.925817	0.014982	3.970467	0.015240	3.208637
52.5	0.025426	4.986341	0.018326	4.815712	0.018456	4.891132	0.018520	3.899210
47.5	0.029520	5.789223	0.020966	5.509452	0.023654	6.268684	0.021282	4.480723
42.5	0.017524	3.436665	0.015632	4.107782	0.015648	4.146967	0.014295	3.009676
37.5	0.023122	4.534499	0.020388	5.357565	0.023650	6.267624	0.019526	4.111014
32.5	0.031034	6.086136	0.027025	7.101638	0.024568	6.510908	0.026520	5.583534
27.5	0.017358	3.404110	0.018332	4.817289	0.018652	4.943075	0.017882	3.764885
22.5	0.020872	4.093247	0.022145	5.819270	0.020356	5.394662	0.021625	4.552938

Table 2B pore size distribution of alumina in study of diphenylmercury removal

Pore diameter (Å)	fresh		30		50		70	
	Pore vol.(cc/g)	%Pore vol.	Pore vol.(cc/g)	%Pore vol.	Pore vol.(cc/g)	%Pore vol.	Pore vol.(cc/g)	%Pore vol.
550	0.004292	0.841712	0.004159	0.923346	0.003564	0.898888	0.003678	1.044937
475	0.002898	0.568332	0.002845	0.631623	0.002458	0.619940	0.002563	0.728160
425	0.003628	0.711494	0.003458	0.767716	0.003124	0.787914	0.002865	0.813960
375	0.004681	0.918000	0.003759	0.834541	0.004256	1.073419	0.003654	1.038118
325	0.006425	1.260019	0.005364	1.190870	0.005548	1.399279	0.004865	1.382169
290	0.003174	0.622459	0.002758	0.612308	0.002356	0.594214	0.002456	0.697761
270	0.003778	0.740911	0.003254	0.722426	0.003256	0.821206	0.002985	0.848052
250	0.004474	0.877405	0.003758	0.834319	0.003785	0.954627	0.003526	1.001753
230	0.008803	1.726373	0.004758	1.056331	0.004526	1.141517	0.004256	1.209149
210	0.015498	3.039342	0.011254	2.498518	0.012545	3.164014	0.006254	1.776790
190	0.019275	3.780057	0.013586	3.016249	0.013154	3.317612	0.012546	3.564377
170	0.024556	4.815723	0.017245	3.828589	0.016582	4.182199	0.012546	3.564377
155	0.014374	2.818912	0.012456	2.765376	0.009856	2.485813	0.007785	2.211755
145	0.017127	3.358808	0.012458	2.765820	0.011725	2.957199	0.009583	2.722575
135	0.018364	3.601399	0.014256	3.164997	0.013524	3.410931	0.010859	3.085092
125	0.015787	3.096018	0.015426	3.424750	0.012545	3.164014	0.009584	2.722859
115	0.019028	3.731617	0.018854	4.185806	0.012543	3.163510	0.009525	2.706097
105	0.023446	4.598039	0.023654	5.251461	0.012546	3.164266	0.011625	3.302716
97.5	0.012352	2.422374	0.012485	2.771814	0.008459	2.133471	0.006254	1.776790
92.5	0.015296	2.999727	0.014859	3.298870	0.010256	2.586698	0.007458	2.118852
87.5	0.017388	3.409993	0.017256	3.831031	0.011265	2.841181	0.008954	2.543873
82.5	0.015563	3.052089	0.010256	2.276951	0.008546	2.155414	0.009548	2.712631
77.5	0.010430	2.045447	0.009854	2.187702	0.008569	2.161215	0.008546	2.427958
72.5	0.012202	2.392957	0.011452	2.542476	0.011254	2.838407	0.009442	2.682516
67.5	0.014355	2.815186	0.013658	3.032234	0.011758	2.965522	0.011546	3.280272
62.5	0.017104	3.354298	0.015486	3.438071	0.013965	3.522157	0.013265	3.768648
57.5	0.020759	4.071087	0.018752	4.163161	0.012546	3.164266	0.014526	4.126904
52.5	0.025426	4.986341	0.023658	5.252349	0.026354	6.646826	0.015246	4.331459
47.5	0.029520	5.789223	0.021548	4.783905	0.019165	4.833665	0.018546	5.269004
42.5	0.017524	3.436665	0.012845	2.851738	0.016452	4.149411	0.017542	4.983763
37.5	0.023122	4.534499	0.023256	5.163101	0.023265	5.867739	0.022354	6.350875
32.5	0.031034	6.086136	0.031524	6.998692	0.028365	7.154027	0.028659	8.142155
27.5	0.017358	3.404110	0.016582	3.681396	0.016854	4.250801	0.017586	4.996264
22.5	0.020872	4.093247	0.023654	5.251461	0.021524	5.428636	0.021356	6.067338

Table 3B pore size distribution of CuO/alumina in study of mercuric chloride removal

Pore diameter (Å)	fresh		30		50		70	
	Pore vol.(cc/g)	%Pore vol.	Pore vol.(cc/g)	%Pore vol.	Pore vol.(cc/g)	%Pore vol.	Pore vol.(cc/g)	%Pore vol.
550	0.003145	1.155608	0.003085	1.304225	0.002845	1.215339	0.002854	1.243080
475	0.001524	0.559983	0.001425	0.602438	0.001525	0.651456	0.001568	0.682954
425	0.002045	0.751421	0.001865	0.788453	0.002051	0.876155	0.001985	0.864581
375	0.002654	0.975194	0.002456	1.038307	0.002505	1.070097	0.002563	1.116333
325	0.002865	1.052724	0.002684	1.134697	0.002645	1.129902	0.002845	1.239160
290	0.001145	0.420722	0.001165	0.492519	0.001174	0.501514	0.001425	0.620669
270	0.001452	0.533527	0.001452	0.613852	0.001425	0.608738	0.001425	0.620669
250	0.001672	0.614365	0.001678	0.709397	0.001685	0.719806	0.001785	0.777470
230	0.001526	0.560718	0.001452	0.613852	0.001452	0.620272	0.001452	0.632429
210	0.001745	0.641188	0.001675	0.708128	0.001524	0.651029	0.001524	0.663789
190	0.002154	0.791472	0.002654	1.122014	0.001985	0.847961	0.001985	0.864581
170	0.002759	1.013775	0.002653	1.121591	0.002456	1.049165	0.002563	1.116333
155	0.000974	0.357890	0.001123	0.474763	0.001384	0.591223	0.001485	0.646802
145	0.001264	0.464448	0.001152	0.487023	0.001624	0.693747	0.001452	0.632429
135	0.001458	0.535732	0.001236	0.522535	0.001254	0.535689	0.001245	0.542269
125	0.001725	0.633839	0.001624	0.686568	0.001524	0.651029	0.001526	0.664660
115	0.002356	0.865696	0.001954	0.826079	0.001824	0.779184	0.001852	0.806652
105	0.002654	0.975194	0.002652	1.121168	0.002287	0.976970	0.002256	0.982617
97.5	0.001325	0.486862	0.001255	0.530568	0.001145	0.489126	0.001523	0.663354
92.5	0.001758	0.645965	0.001526	0.645137	0.001485	0.634369	0.001452	0.632429
87.5	0.001957	0.719086	0.001842	0.778730	0.002654	1.133747	0.001685	0.733914
82.5	0.005264	1.934220	0.003256	1.376517	0.005952	2.542601	0.005264	2.292773
77.5	0.008954	3.290085	0.007152	3.023603	0.006854	2.927921	0.006859	2.987486
72.5	0.010256	3.768496	0.008624	3.645910	0.007854	3.355105	0.007526	3.278003
67.5	0.011958	4.393884	0.010625	4.491860	0.009142	3.905319	0.009526	4.149117
62.5	0.014256	5.238268	0.011756	4.970005	0.011253	4.807105	0.010842	4.722311
57.5	0.016245	5.969113	0.014256	6.026913	0.012653	5.405163	0.012563	5.471904
52.5	0.020311	7.463136	0.017652	7.462617	0.015262	6.519687	0.015246	6.640504
47.5	0.021538	7.913989	0.019952	8.434973	0.016272	6.951143	0.012563	5.471904
42.5	0.025142	9.238254	0.017235	7.286325	0.018542	7.920851	0.018523	8.067825
37.5	0.026253	9.646483	0.022014	9.306711	0.023452	10.018326	0.023562	10.262597
32.5	0.034256	12.587130	0.028426	12.017469	0.032562	13.909975	0.032561	14.182176
27.5	0.017035	6.259393	0.016625	7.028439	0.016258	6.945162	0.016252	7.078675
22.5	0.020526	7.542137	0.020358	8.606615	0.019582	8.365123	0.019854	8.647552

Table 4B pore size distribution of CuO/alumina in study of diphenylmercury removal

Pore diameter (Å)	fresh		30		50		70	
	Pore vol.(cc/g)	%Pore vol.	Pore vol.(cc/g)	%Pore vol.	Pore vol.(cc/g)	%Pore vol.	Pore vol.(cc/g)	%Pore vol.
550	0.003145	1.155608	0.002456	1.157530	0.002698	1.363239	0.003124	1.336991
475	0.001524	0.559983	0.001245	0.586777	0.001385	0.699810	0.001458	0.623986
425	0.002045	0.751421	0.001625	0.765874	0.001874	0.946890	0.001854	0.793464
375	0.002654	0.975194	0.002045	0.963822	0.002152	1.087357	0.002458	1.051960
325	0.002865	1.052724	0.002423	1.141976	0.002356	1.190434	0.002874	1.229998
290	0.001145	0.420722	0.000956	0.450569	0.000952	0.481024	0.001162	0.497306
270	0.001452	0.533527	0.001256	0.591961	0.001138	0.575006	0.001365	0.584185
250	0.001672	0.614365	0.001325	0.624482	0.001352	0.683135	0.001548	0.662504
230	0.001526	0.560718	0.001524	0.718272	0.001450	0.732653	0.001854	0.793464
210	0.001745	0.641188	0.001358	0.640035	0.001125	0.568437	0.001652	0.707013
190	0.002154	0.791472	0.001675	0.789439	0.001385	0.699810	0.001847	0.790468
170	0.002759	1.013775	0.002356	1.110399	0.001772	0.895352	0.002354	1.007451
155	0.000974	0.357890	0.001235	0.582064	0.000994	0.502246	0.001325	0.567066
145	0.001264	0.464448	0.001362	0.641920	0.001246	0.629576	0.001454	0.622274
135	0.001458	0.535732	0.001125	0.530220	0.001961	0.990849	0.001254	0.536680
125	0.001725	0.633839	0.001356	0.639092	0.000915	0.462329	0.001758	0.752378
115	0.002356	0.865696	0.001756	0.827615	0.001102	0.556816	0.002184	0.934695
105	0.002654	0.975194	0.001895	0.893126	0.001354	0.684146	0.001147	0.490886
97.5	0.001325	0.486862	0.001125	0.530220	0.000654	0.330452	0.001425	0.609863
92.5	0.001758	0.645965	0.001365	0.643334	0.000910	0.459803	0.002165	0.926564
87.5	0.001957	0.719086	0.001425	0.671612	0.001874	0.946890	0.005314	2.274254
82.5	0.005264	1.934220	0.005175	2.439013	0.004412	2.229285	0.006124	2.620913
77.5	0.008954	3.290085	0.006135	2.891467	0.005145	2.599653	0.007154	3.061727
72.5	0.010256	3.768496	0.006958	3.279353	0.005856	2.958906	0.008277	3.542342
67.5	0.011958	4.393884	0.008142	3.837380	0.006854	3.463173	0.009680	4.142789
62.5	0.014256	5.238268	0.009685	4.564607	0.008745	4.418653	0.015462	6.617336
57.5	0.016245	5.969113	0.011368	5.357816	0.009854	4.979006	0.013522	5.787066
52.5	0.020311	7.463136	0.012985	6.119919	0.012563	6.347803	0.016854	7.213075
47.5	0.021538	7.913989	0.016589	7.818509	0.013250	6.694929	0.017524	7.499818
42.5	0.025142	9.238254	0.016582	7.815210	0.015958	8.063220	0.022456	9.610586
37.5	0.026253	9.646483	0.021685	10.220289	0.020254	10.233893	0.029323	12.549485
32.5	0.034256	12.587130	0.028168	13.275771	0.025482	12.875484	0.018976	8.121237
27.5	0.017035	6.259393	0.016859	7.945762	0.013214	6.676739	0.018564	7.944911
22.5	0.020526	7.542137	0.018957	8.934564	0.015685	7.925280	0.022475	9.618718

Table 5B pore size distribution of CuS/alumina in study of mercuric chloride removal

Pore diameter (Å)	fresh		30		50		70	
	Pore vol.(cc/g)	%Pore vol.	Pore vol.(cc/g)	%Pore vol.	Pore vol.(cc/g)	%Pore vol.	Pore vol.(cc/g)	%Pore vol.
550	0.002111	0.905049	0.002245	0.950417	0.002496	0.973327	0.003362	1.198907
475	0.001260	0.540200	0.001438	0.608775	0.001520	0.592731	0.001893	0.675054
425	0.001615	0.692399	0.001842	0.779808	0.001947	0.759242	0.002427	0.865481
375	0.002084	0.893473	0.002377	1.006299	0.002513	0.979956	0.003132	1.116888
325	0.001838	0.788006	0.002602	1.101553	0.002687	1.047808	0.003131	1.116532
290	0.000855	0.366564	0.001114	0.471610	0.001263	0.492513	0.001311	0.467510
270	0.001036	0.444164	0.001343	0.568557	0.001518	0.591951	0.001590	0.567003
250	0.001228	0.526481	0.001592	0.673971	0.001798	0.701139	0.001885	0.672201
230	0.001462	0.626803	0.001896	0.802669	0.001541	0.600920	0.002245	0.800579
210	0.001422	0.609654	0.001534	0.649417	0.001648	0.642645	0.002063	0.735677
190	0.001522	0.652527	0.001596	0.675664	0.002062	0.804087	0.002124	0.757430
170	0.001951	0.836452	0.002048	0.867018	0.002642	1.030260	0.002725	0.971750
155	0.001107	0.474604	0.001153	0.488121	0.001503	0.586102	0.001539	0.548816
145	0.001369	0.586931	0.001439	0.609199	0.001852	0.722196	0.001914	0.682543
135	0.001255	0.538056	0.001515	0.641373	0.001914	0.746373	0.001961	0.699303
125	0.001223	0.524337	0.001316	0.557127	0.001795	0.699969	0.001752	0.624773
115	0.001480	0.634520	0.001594	0.674818	0.002170	0.846202	0.002121	0.756360
105	0.001832	0.785433	0.001974	0.835690	0.002682	1.045859	0.002626	0.936446
97.5	0.000936	0.401291	0.001002	0.424195	0.001383	0.539307	0.001405	0.501031
92.5	0.001200	0.514476	0.001876	0.794202	0.003312	1.291530	0.003758	1.340123
87.5	0.001366	0.585645	0.003826	1.619731	0.003979	1.551630	0.004262	1.519852
82.5	0.003369	1.444392	0.004321	1.829289	0.004497	1.753627	0.004817	1.717768
77.5	0.005828	2.498639	0.004979	2.107852	0.005187	2.022695	0.005556	1.981300
72.5	0.006722	2.881923	0.005753	2.435524	0.005997	2.338559	0.006424	2.290833
67.5	0.007799	3.343666	0.006686	2.830508	0.006975	2.719934	0.007472	2.664556
62.5	0.009179	3.935313	0.007881	3.336410	0.008227	3.208158	0.008813	3.142763
57.5	0.010987	4.710457	0.009450	4.000643	0.009873	3.850023	0.010577	3.771815
52.5	0.013298	5.701252	0.011455	4.849457	0.011976	4.670098	0.012830	4.575247
47.5	0.016779	7.193662	0.015744	6.665199	0.015246	5.945250	0.018281	6.519103
42.5	0.022295	9.558537	0.022800	9.652346	0.023070	8.996256	0.027556	9.826618
37.5	0.028306	12.135633	0.028923	12.244509	0.029285	11.419825	0.034944	12.461219
32.5	0.036574	15.680373	0.037295	15.788783	0.037963	14.803853	0.045256	16.138534
27.5	0.018886	8.096996	0.019619	8.305675	0.024315	9.481750	0.022384	7.982255
22.5	0.023073	9.892089	0.023984	10.153591	0.029604	11.544221	0.026286	9.373730

Table 6B pore size distribution of CuS/alumina in study of diphenylmercury removal

	fresh		30		50		70	
Pore diameter (Å)	Pore vol.(cc/g)	%Pore vol.	Pore vol.(cc/g)	%Pore vol.	Pore vol.(cc/g)	%Pore vol.	Pore vol.(cc/g)	%Pore vol.
550	0.002111	0.905049	0.002575	1.116531	0.002562	1.094577	0.002634	1.336411
475	0.001260	0.540200	0.001501	0.650840	0.001425	0.608810	0.001461	0.741267
425	0.001615	0.692399	0.001924	0.834255	0.001842	0.786968	0.001873	0.950303
375	0.002084	0.893473	0.002484	1.077073	0.002451	1.047154	0.002418	1.226820
325	0.001838	0.788006	0.002439	1.057561	0.002265	0.967688	0.002299	1.166443
290	0.000855	0.366564	0.001046	0.453550	0.001054	0.450306	0.001070	0.542885
270	0.001036	0.444164	0.001268	0.549810	0.001285	0.548997	0.001294	0.656536
250	0.001228	0.526481	0.001503	0.651707	0.001542	0.658797	0.001534	0.778305
230	0.001462	0.626803	0.001790	0.776152	0.001452	0.620346	0.001201	0.609351
210	0.001422	0.609654	0.001782	0.772683	0.001452	0.620346	0.001357	0.688500
190	0.001522	0.652527	0.001802	0.781355	0.001752	0.748516	0.001699	0.862021
170	0.001951	0.836452	0.002310	1.001626	0.002452	1.047581	0.002178	1.105051
155	0.001107	0.474604	0.001309	0.567588	0.001325	0.566087	0.001235	0.626601
145	0.001369	0.586931	0.001622	0.703306	0.001526	0.651961	0.001528	0.775261
135	0.001255	0.538056	0.001750	0.758808	0.001526	0.651961	0.001261	0.639793
125	0.001223	0.524337	0.001542	0.668618	0.001425	0.608810	0.001348	0.683934
115	0.001480	0.634520	0.001865	0.808672	0.001758	0.751080	0.001631	0.827520
105	0.001832	0.785433	0.002307	1.000325	0.002452	1.047581	0.002597	1.317639
97.5	0.000936	0.401291	0.001182	0.512520	0.002451	1.047154	0.002270	1.151729
92.5	0.001200	0.514476	0.003148	1.364986	0.002546	1.087741	0.002709	1.374464
87.5	0.001366	0.585645	0.003771	1.635122	0.003586	1.532066	0.003074	1.559654
82.5	0.003369	1.444392	0.004260	1.847154	0.003458	1.477380	0.003476	1.763617
77.5	0.005828	2.498639	0.004913	2.130298	0.004256	1.818314	0.004012	2.035567
72.5	0.006722	2.881923	0.005679	2.462439	0.005264	2.248967	0.004641	2.354702
67.5	0.007799	3.343666	0.006605	2.863957	0.005264	2.248967	0.005401	2.740303
62.5	0.009179	3.935313	0.007789	3.377344	0.007526	3.215374	0.006374	3.233973
57.5	0.010987	4.710457	0.009346	4.052466	0.008562	3.657990	0.007654	3.883406
52.5	0.013298	5.701252	0.011335	4.914905	0.012650	5.404528	0.009289	4.712956
47.5	0.016779	7.193662	0.015155	6.571274	0.014526	6.206021	0.013278	6.736853
42.5	0.022295	9.558537	0.021841	9.470352	0.021947	9.376535	0.019811	10.051498
37.5	0.028306	12.135633	0.027726	12.022114	0.026254	11.216638	0.025132	12.751211
32.5	0.036574	15.680373	0.035942	15.584607	0.034526	14.750730	0.032437	16.457546
27.5	0.018886	8.096996	0.017628	7.643577	0.017256	7.372374	0.012152	6.165555
22.5	0.023073	9.892089	0.021486	9.316423	0.015745	6.726821	0.014767	7.492326

Appendix C

Table 1C Properties of Toluene *

Formula	C_7H_8
Chemical Name	Toluene
Physical properties	
Molecular Weight	92.13
Form	liquid
Color	colorless
Boiling point ($^{\circ}C$)	110.8
Melting Point ($^{\circ}C$)	-95
Specific Gravity	0.866
Solubility	soluble in ether and alcohol
Purity	>99%
Supplier	Merck

* From Encyclopedia of Chemical Engineering

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Table 2C Properties of Mercuric Chloride *

Formula	Hg ₇ Cl ₈
Chemical Name	Mercuric Chloride
Physical properties	
Molecular Weight	271.52
Form	liquid
Color	white
Boiling point (°C)	302
Melting Point (°C)	277
Specific Gravity	5.44
Solubility	soluble in water
Purity	>99%
Supplier	Carlo Erba

* From Merck Index

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Table 3C Properties of Diphenylmercury *

Formula	$C_{12}H_{10}Hg$
Chemical Name	Diphenylmercury
Physical properties	
Molecular Weight	354.8
Form	solid
Color	white
Boiling point (°C)	-
Melting Point (°C)	121-124
Specific Gravity	2.32
Solubility	moderately soluble in toluene
Purity	>97%
Supplier	Fluka

* From Supplier

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Table 4C Properties of Aluminum oxide, activated, neutral Brockmann *

Formula	Al_2O_3
Chemical Name	Neutral Alumina
Physical properties	
Form	solid
Color	white
Standard grade	150 mesh
Surface area	$155 \text{ m}^2/\text{g}$
PH of aqueous suspension	7.0+/-0.5

* From Catalogue Handbook's Aldrich

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Table 5C Properties of Copper nitrate *

Formula	$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$
Chemical Name	Copper nitrate trihydrate
Physical properties	
Molecular Weight	241.6
Form	solid
Color	blue
Boiling point ($^{\circ}\text{C}$)	-
Melting Point ($^{\circ}\text{C}$)	114.5
Specific Gravity	2.32
Solubility	soluble in ether and alcohol
Purity	>99%

* From Merck Index

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Table 6C Properties of Nitric Acid *

Formula	HNO_3
Chemical Name	Nitric Acid
Physical properties	
Molecular Weight	63.02
Form	liquid
Color	colorless
Boiling point ($^{\circ}\text{C}$)	86
Melting Point ($^{\circ}\text{C}$)	-41.59
Specific Gravity	1.502
Solubility	soluble in water
Purity	69.0-70.597%

* From Merck Index

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Table 7C Properties of Hydrochloric Acid *

Formula	HCl
Chemical Name	Hydrochloric
Physical properties	
Molecular Weight	36.47
Form	liquid
Color	colorless
Melting Point (°C)	-15.65
Specific Gravity	1.05
Solubility	soluble in water and alcohol
Purity	37%

* From Encyclopedia of Chemical Engineering

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Table 8C Properties of Sulfuric Acid *

Formula	H ₂ SO ₄
Chemical Name	Sulfuric Acid
Physical properties	
Molecular Weight	97.09
Form	liquid
Color	colorless
Melting Point (°C)	-
Specific Gravity	2.03
Solubility	soluble in water
Purity	95.7%

* From Merck Index



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Table 9C Properties of Hydrogen Peroxide *

Formula	H ₂ O ₂
Chemical Name	Hydrogen Peroxide
Physical properties	
Molecular Weight	34.02
Form	liquid
Color	colorless
Melting Point (°C)	151.4
Specific Gravity	1.13
Solubility	soluble in water, acid and ether
Purity	35-35.6%

* From Encyclopedia of Chemical Engineering

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Table 10C Properties of Potassium Permanganated *

Formula	KMnO ₄
Chemical Name	Potassium Permanganated
Physical properties	
Molecular Weight	158.03
Form	solid
Color	dark purple
Specific Gravity	2.71
Solubility	soluble in water,
Purity	>99%

* From Merck Index



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Table 11C Properties of Potassium Persulfate *

Formula	K_2SO_4
Chemical Name	Potassium Persulfate
Physical properties	
Molecular Weight	270.32
Form	solid
Color	white
Specific Gravity	-
Solubility	soluble in water,
Purity	>99%

* From Merck Index



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Table 12C Properties of Hydroxylamine Hydrochloride *

Formula	$\text{NH}_2\text{OH}\cdot\text{HCl}$
Chemical Name	Hydroxylamine Hydrochloride
Physical properties	
Molecular Weight	69.4
Form	solid
Color	white
Boiling point ($^{\circ}\text{C}$)	58
Melting Point ($^{\circ}\text{C}$)	33
Specific Gravity	1.20
Solubility	soluble in water,
Purity	>99%

* From Merck Index

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Table 13C Properties of Sodium Chloride *

Formula	NaCl ₂
Chemical Name	Sodium Chloride
Physical properties	
Molecular Weight	58.54
Form	solid
Color	white
Boiling point (°C)	58.54
Melting Point (°C)	-
Specific Gravity	2.17
Solubility	soluble in water
Purity	>99%

* From Merck Index

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VITA

Wasan Chokelarb was born on January 29, 1976 in Uttaradit, Thailand. He received his Bachelor of Science Degree in Industrial Chemistry from the Faculty of Science at Chiangmai University in 1997.



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