CHAPTER IV

RESULTS AND DISCUSSIONS

Study on removal of mercury compounds is conducted in a batch reactor. Mercury compounds used as representative component of mercury in petroleum are mercuric chloride, phenylmercuric acetate (PMA) and diphenylmercury (DPM). Mercuric chloride is an inorganic compound while phenylmercuric acetate and diphenylmercury represent organomercury compounds. Adsorbents used are alumina adsorbent, copper adsorbents, zinc adsorbents and copper-zinc adsorbent. Experiments in this study can be classified into five parts:

Part 1. Preliminary study is performed in order to find suitable condition for studying. This part is composed studies on effect of amount of adsorbent, effect of pressure, and effect of contact time.

Part 2. Blank test is conducted to study adsorption of mercury on reactor vessel.

Part 3. Experiments are designed to study an repeatability and experimental error of each mercury compound.

Part 4. Effect of temperature on mercury removal is discussed in this section. In

addition, comparison of removal efficiency among mercury compounds is also discussed.

Part 5. Experiments are conducted in order to study effect of adsorbents on mercury compounds removal

In each experiment, 100 ml of toluene containing 1000 µg/l of mercury (as mercury compound) is used as liquid feedstock. Adsorbents used are alumina, Cu/Al_2O_3, Zn/Al_2O_3 and $CuZn/Al_2O_3$. These adsorbents are prepared by dry impregnation of metal salt solution onto alumina powder, dried and then calcined in hydrogen stream. After cooling to ambient temperature, the adsorbents are weighed and kept away from moisture and air by immersing in toluene. After each experiment, liquid product and spent adsorbent are separated by filter paper (Whatman no.1). Liquid feed and product are kept and then digested with permanganate-persulfate solution. After digestion, the samples are extracted with water to separate mercury from toluene layer into water layer. Mercury content in aqueous layer is determined by cold vapor technique AAS. Detail and result of experiments are listed in Table 1A. Fresh and used adsorbents are characterized by Micromeritics ASAP 2000 to measure total surface area and pore size distribution.

Preliminary Study

In this section, the experiments are subdivided into 3 parts. First part is performed to study the

effect of adsorbent weight on mercury removal. Second part is conducted to evaluate the effect of pressure and, finally, contact time is varied to find a suitable time for mercury removal.

Effect of Adsorbent Weight

In the first part, amount of adsorbent is varied from 0.25 to 1.50 gram. Experiments are operated at a temperature of 30°C and a pressure of 200 psig. Mercuric chloride is used for this test. Contact time is kept at 60 minutes. The effect of adsorbent weight is shown in Figure 4.1. The result shows that mercury content in product decreases when adsorbent weight increases. This is due to increasing of surface area which is a function of amount of adsorbent. When 0.25 and 0.75 gram of

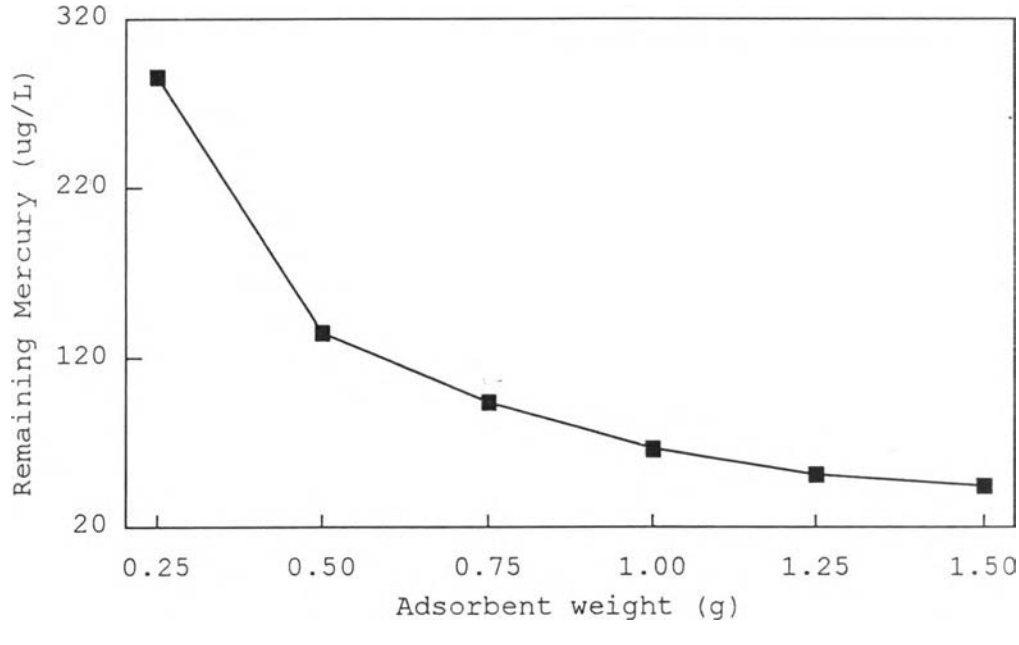

Figure 4.1 Remaining Mercury in Study on Effect of Adsorbent weight at 30°C and 200 psig

adsorbent are used, the mercury content in product is rather high. When amount of adsorbent is varied from 1.00 to 1.50, it is found that the remaining mercury is nearly constant when the adsorbent weight increases. This indicates that 1.00 gram of alumina adsorbent can remove mercury effectively. Thus, suitable adsorbent weight is 1.00 gram. This adsorbent weight is also used in the study of phenylmercury acetate and diphenylmercury.

Effect of Pressure

Experiments 7 to 15 are designed to study the effect of pressure on mercury removal. The experiments are operated at various temperatures and pressures. The temperature is varied from 30°C to 75°C and pressure is varied from 0 psig to 200 psig. Contact time is fixed at 60 minutes. Adsorbent is alumina and mercury compound is mercuric chloride. The experimental result is shown in Figure 4.2. It is found that pressure does not significantly affect removal of mercury in the selected temperature range.

In general, the removal of mercury by adsorption depends on external and internal factors. External factor relates with mass transfer of reactant from bulk solution to external surface of adsorbent. The average molar flux of reactant A from the bulk to the surface is

$$W_A = k_c(C_{Ao} - C_{AS})$$

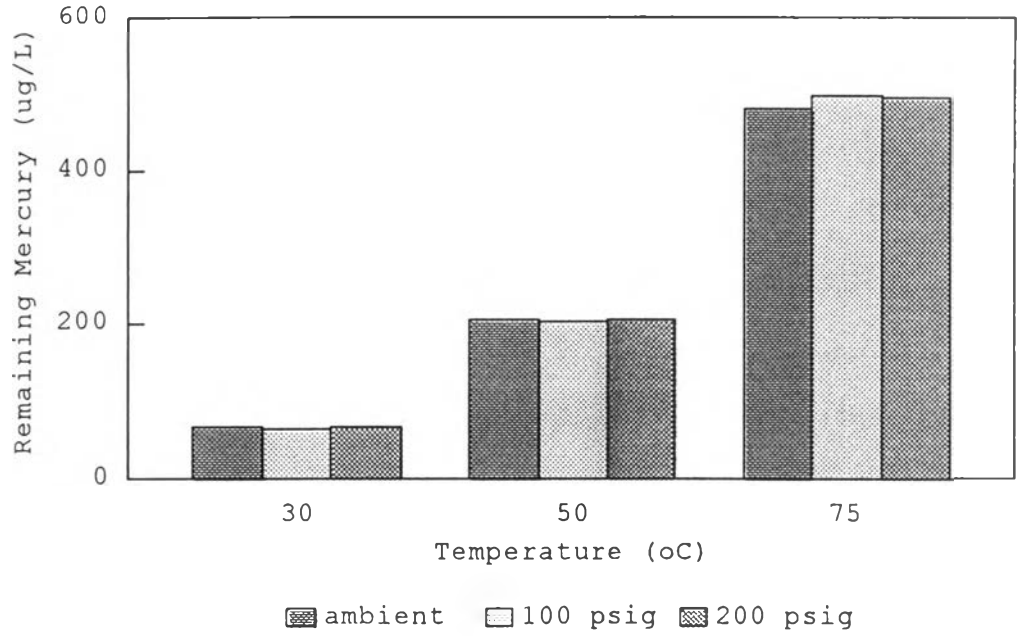

Figure 4.2 Remaining Mercury in Study on Effect of Pressure at Various Temperatures and Pressures

C_{AO} and C_{AS} are the concentration of A in bulk and at external surface of adsorbent, respectively. k_c is the mass transfer coefficient over the surface area. When C_{AO} is constant, the molar flux of A is increased when k_c is increased.

$$k_c = 0.6\left(\frac{D_{AB}^{2/3}}{\upsilon^{1.6}}\right)\left(\frac{U^{1/2}}{d_p^{1/2}}\right)$$

Term I Term II

From this equation, Term I is a function of temperature only for liquid system. Term II is a function of the flow condition and particle size.

Internal factor consists of internal mass transfer and surface adsorption. From outer surface of

adsorbent, the transfer of reactant into the pore is controlled by diffusivity of the reactant. The effective diffusivity, D_e, is defined to describe this phenomena.

$$D_e = \frac{D_A \varepsilon_p \sigma}{\tau}$$

where D_A is diffusivity of reactant A,

ε_p is pellet porosity,

σ is constriction factor,

τ is tortuosity.

ε_p, σ and τ are constant value for the same alumina support. When temperature increases, D_A increases which leads to increasing of effective diffusivity. In term of surface adsorption, reactant A will adsorb on vacant site of adsorbent as following below:

$$A + S \rightarrow A.S$$

The rate of attachment is a function of concentration of reactant A and vacant site as following;

$$\text{rate of attachment} = k_A C_A C_S$$

k_A is the contant of the attachment. C_A and C_S are defined as concentration of reactant A and of vacant site, respectively. k_A is only a function of temperature, exhibiting exponential temperature dependence.

Effect of Contact Time

Experiments 16 to 35 are conducted at the same condition, a temperature of 30°C and a pressure of 200 psig, in order to study the effect of contact time on the removal of mercury. Contact time between adsorbent and liquid feed are varied from 15 to 120 minutes. Adsorbent used in the study of mercuric chloride is Al_2O_3. Since removal of phenylmercury acetate and diphenylmercury by alumina is very low, the effect of contact time cannot be discussed. In case of organic mercury, adsorbent is 2.5Cu adsorbent. The remaining mercury is plotted as a function of time and shown in Figures 4.3 to 4.5. Figure 4.3 shows the result of mercuric chloride. The concentration curve can be divided into three parts. In initial period, 0-15 minutes, the remaining mercury decreases very rapidly and keeps at the constant value in the middle period, 30-75 minutes. In the final period, 90-120 minutes, remaining mercury is higher than the middle period and increases with increasing of the contact time. In the initial period, concentration of mercuric chloride in bulk solution is very high. Mercury in the bulk can easily transfer through the outer surface of adsorbent and is readily adsorbed on alumina. In the middle period, concentration of mercuric chloride in the bulk is very lower than the first period, thus mercury can slowly and slightly transfer to the adsorbent. The remaining mercury in this period is rather constant. The increasing of Hg concentration in final period may result from desorption of mercury from surface of adsorbent to the bulk solution.

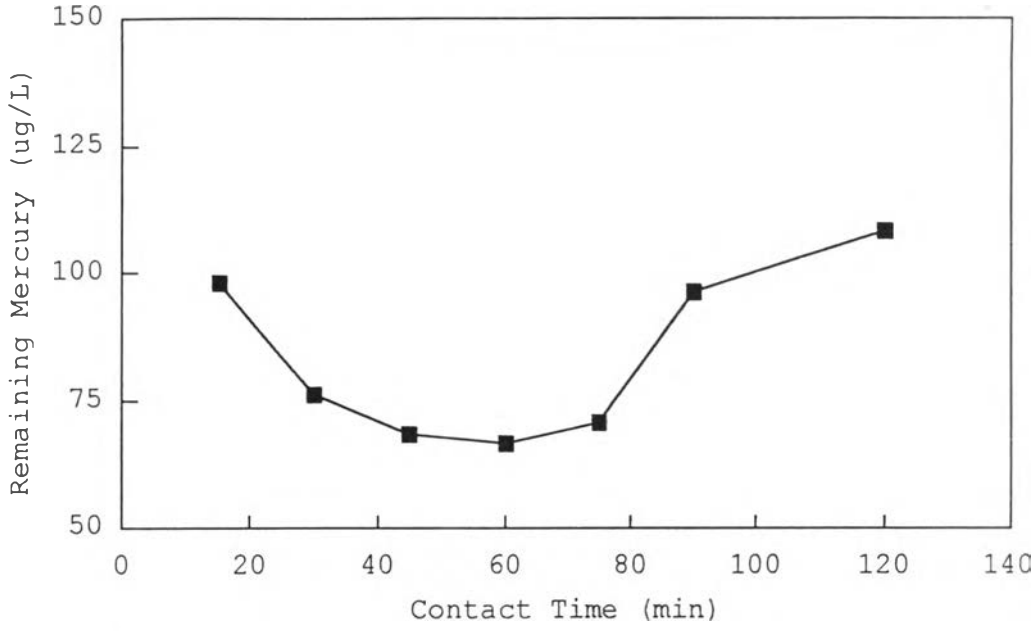

Figure 4.3 Remaining Mercury in Study on Effect of Contact Time on Mercuric Chloride Removal at 30°C and 200 psig

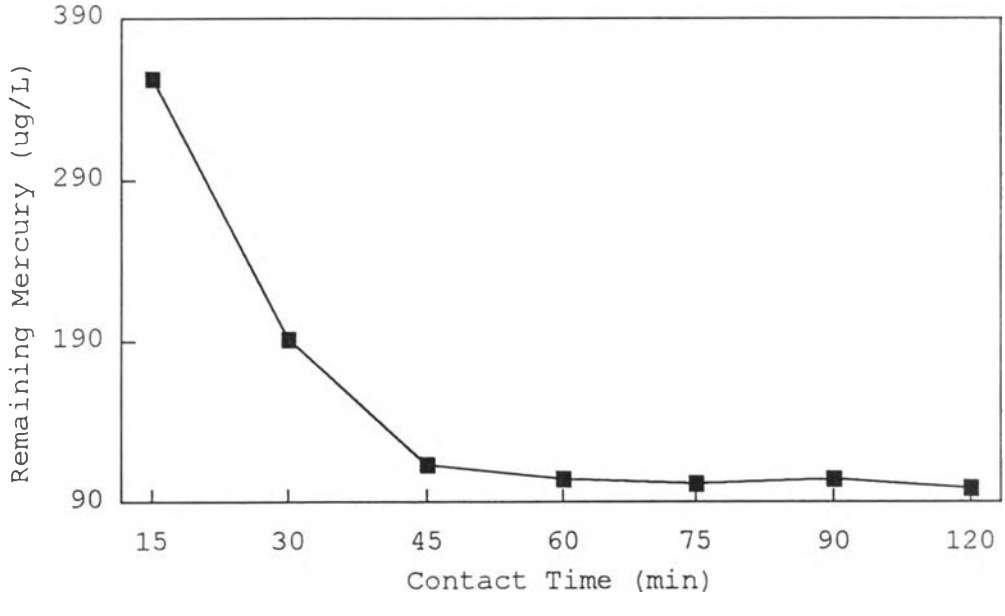

Figure 4.4 Remaining Mercury in Study on Effect of Contact Time on Phenylmercuric Acetate Removal at 30°C and 200 psig

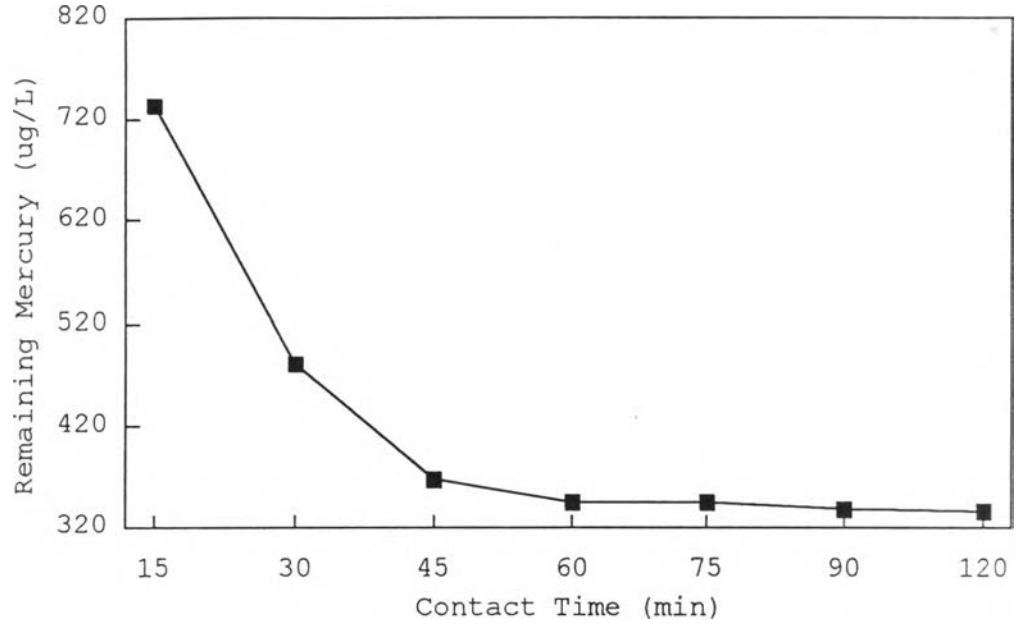

Figure 4.5 Remaining Mercury in Study on Effect of Contact Time on Diphenylmercury Removal at 30°C and 200 psig

In the case of phenylmercuric acetate and diphenylmercury, the contact time curve is divided into two parts. In first period, from 0-30 minutes, mercury in the bulk can be adsorbed rapidly on the adsorbent because of high mercury concentration in the bulk solution. In the second period, the concentration of mercury in the bulk is lower than the initial period and the deposited mercury retards transferring of mercury from the bulk to adsorbent surface. Thus, rate of mercury deposition on adsorbent is very slow and the concentration curve is nearly constant. From this set of experiments, the suitable contact time is considered. It indicates that the suitable time should be 60 minutes

because at this time, the removal of mercury is so high and constant enough for studying in this thesis.

From the preliminary study, it can be summarized that suitable adsorbent weight is 1.00 gram, operating pressure is 200 psig, contact time is 60 minutes. Temperature is varied from 30, 50 and 75°C. This condition is used for study mercury removal.

Blank Test

This section is designed to study adsorption of mercury on reactor vessel. Experiments 36 to 44 are performed with no adsorbent. The temperatures are varied at 30, 50 and 75°C and a pressure is fixed at 200 psig.

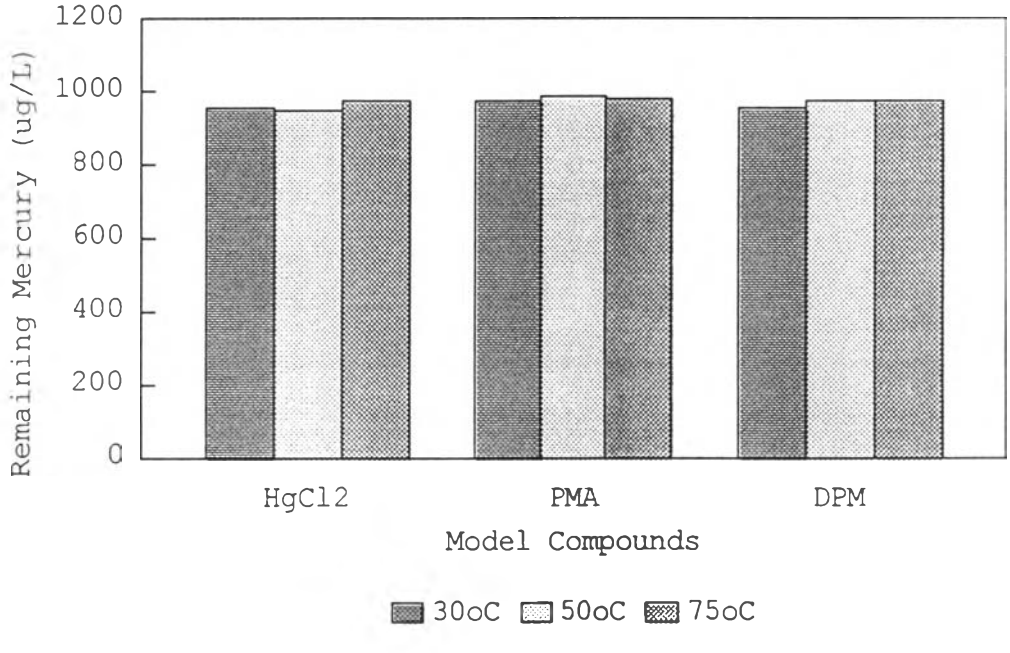

Figure 4.6 Remaining Mercury in Study on Blank Test at Various Temperatures and a Pressure of 200 psig

The initial concentration of mercury (as mercury compound) is approximately 1000 μg/l. The concentration of mercury in product is plotted with the operating temperature and shown in Figure 4.6. It is found that mercury content in product is nearly the same as the initial concentration for all selected mercury compounds. This indicates that all model compounds does not adsorb on the reactor vessel. The difference of mercury concentration between feed and product is considered as the error in analysis.

Experimental Error

Experiments 45 to 94 are conducted to study repeatability, average and deviation of the mercury compounds removal. All of model compounds are used as the feedstock.

The experiments are operated at various temperature of 30, 50 and 75°C and a pressure of 200 psig. The weight of adsorbent used is 1.0 gram for each experiment. The experiment is repeated for 5 times at the same temperature. Experimental results are illustrated in Figures 4.7 to 4.9. Average concentration of mercury and %error are calculated and shown in Tables 4.1 to 4.3. Maximum and minimum error of experiment are calculated as following equation:

$$\%\text{Maximum error} = \frac{\text{maximum conc.} - \text{average conc.}}{\text{average conc.}} * 100$$

$$\%\text{Minimum error} = \frac{\text{average conc.} - \text{minimum conc.}}{\text{average conc.}} * 100$$

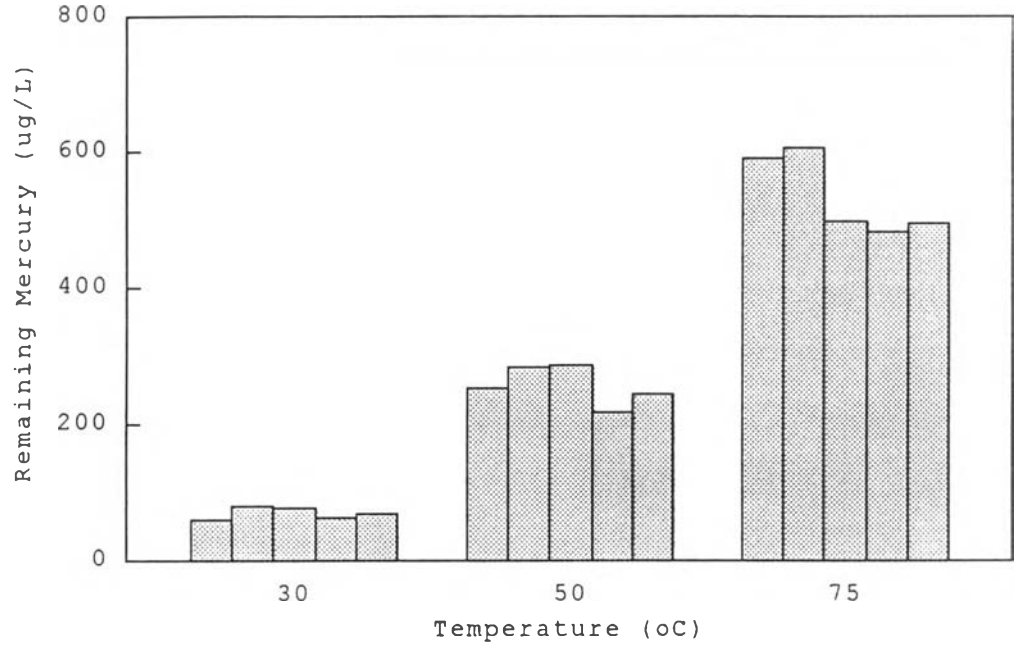

Figure 4.7 Remaining Mercury in Study on Experimental Error of Mercuric Chloride at Various Temperatures and a Pressure of 200 psig

Table 4.1 Average and Error of experiment at various temperature and pressure of 200 psig

Model Compound	Mercuric Chloride		
Temperature (°C)	30	50	75
Avg. Conc. (μg/L)	68.73	255.76	534.49
Maximum error (%)	16.82	11.61	13.46
Minium error (%)	14.94	15.66	9.51

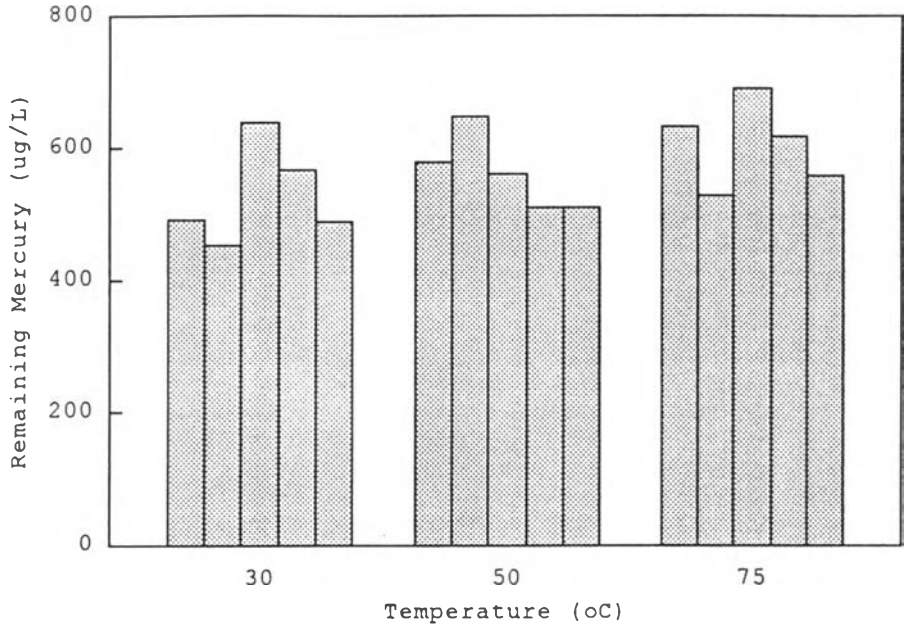

Figure 4.8 Remaining Mercury in Study on Experimental Error of Phenylmercuric Acetate at Various Temperatures and a Pressure of 200 psig

Table 4.2 Average Concentration of Phenylmercuric Acetate and Error of Experiment at Pressure of 200 psig

Model Compound	Phenylmercuric acetate		
Temperature (°C)	30	50	75
Avg. Conc. (μg/L)	527.05	561.72	605.26
Maximum error (%)	7.67	15.4	14.01
Minium error (%)	14.18	9.08	12.89

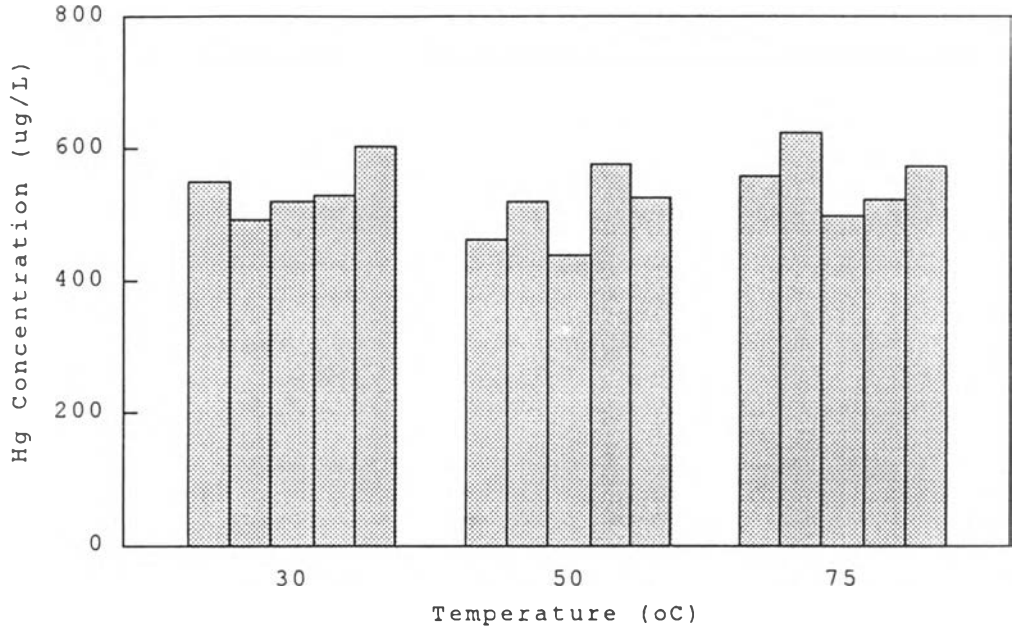

Figure 4.9 Remaining Mercury in Study on Experimental Error of Diphenylmercury at Various Temperatures and a Pressure of 200 psig

Table 4.3 Average Concentration of Diphenylmercury and Error of experiment at pressure of 200 psig

Model Compound	Diphenylmercur		
Temperature (°C)	30	50	75
Avg. Conc. (μg/L)	537.29	503.63	554.3
Maximum error (%)	11.82	14.21	12.24
Minium error (%)	8.64	12.78	10.22

Table 4.1 shows average concentration and % error in study of mercuric chloride. Average concentration of mercury is 68.73, 255.76 and 534.49 µg/L at temperature of 30, 50 and 75°C, respectively. Percent Error of this experiment is in range of 9.0 to 17.0%. Average concentration and percent error in study of phenylmercuric acetate are shown Table 4.2. Percent Error varies from 7.5 to 16.0%. Table 4.3 shown the results of diphenylmercury removal. It found that percent error is in range of 8.0 to 14.5%.

Effect of Temperature

In this section, the experiments are conducted at various temperatures and adsorbents in order to study the effect of temperature on mercury compounds removal. The temperature is varied at 30°C, 50°C and 75°C and pressureis kept at 200 psig. Amount of adsorbent is 1.00 gram. Adsorbents used are alumina, 2.5Cu adsorbent, 5.0Cu adsorbent, 2.5Zn adsorbent, 5.0Zn adsorbent and CuZn adsorbent. The weight ratio of Cu to Zn in CuZn adsorbent is fixed at 1:1 and each metal is loaded at approximately 2.5% by weight. The contact time of this study is 60 minutes for all experiments. Figures 4.10 to 4.15 show mercury content in product with a function of temperature.

In order to study effect of temperature, concentration of mercury in each experiment is plotted as function of temperature. Effect of temperature on mercury removal by using alumina adsorbent is shown in

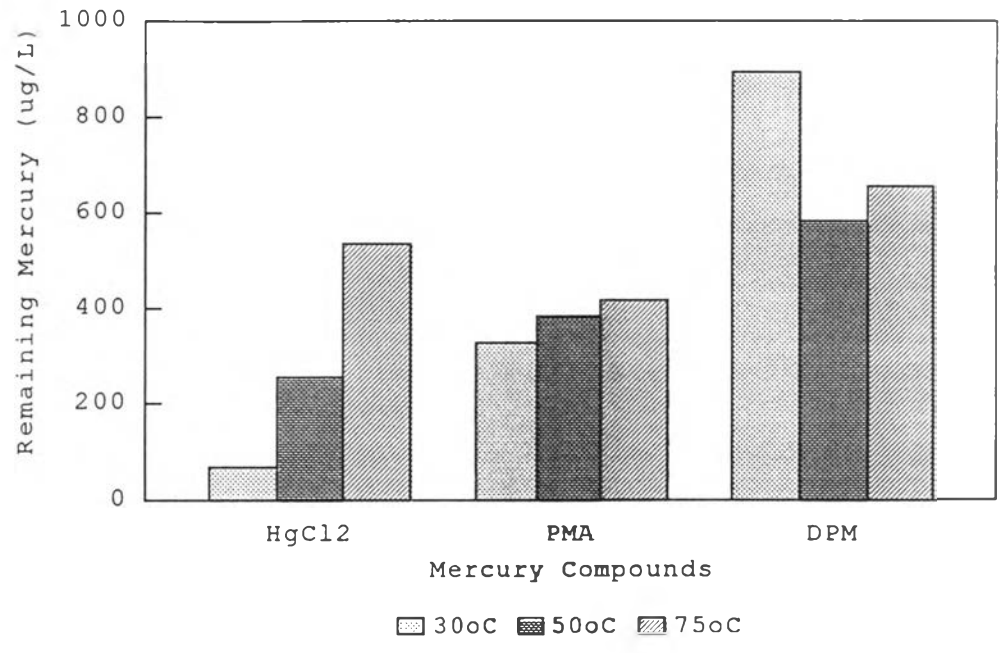

Figure 4.10 Effect of Temperature on Mercury Compounds Removal by Alumina Adsorbent at a Pressure of 200 paig

Figure 4.10. Efficiency of mercury removal is considered from remaining mercury or concentration of mercury in liquid product. If remaining mercury is high, efficiency is low. On the other hand, high efficiency is obtained when amount of mercury in liquid product is low. For mercuric chloride experiments, it found that efficiency of mercury chloride removal decreases significantly with temperature increasing. The removal of phenylmercury acetate (PMA) slightly decreases when temperature increases. In case of diphenylmercury (DPM), degree of mercury removal increases when temperature is higher than 30°C. This indicates that efficiency of mercury removal by alumina is significantly a function of nature of

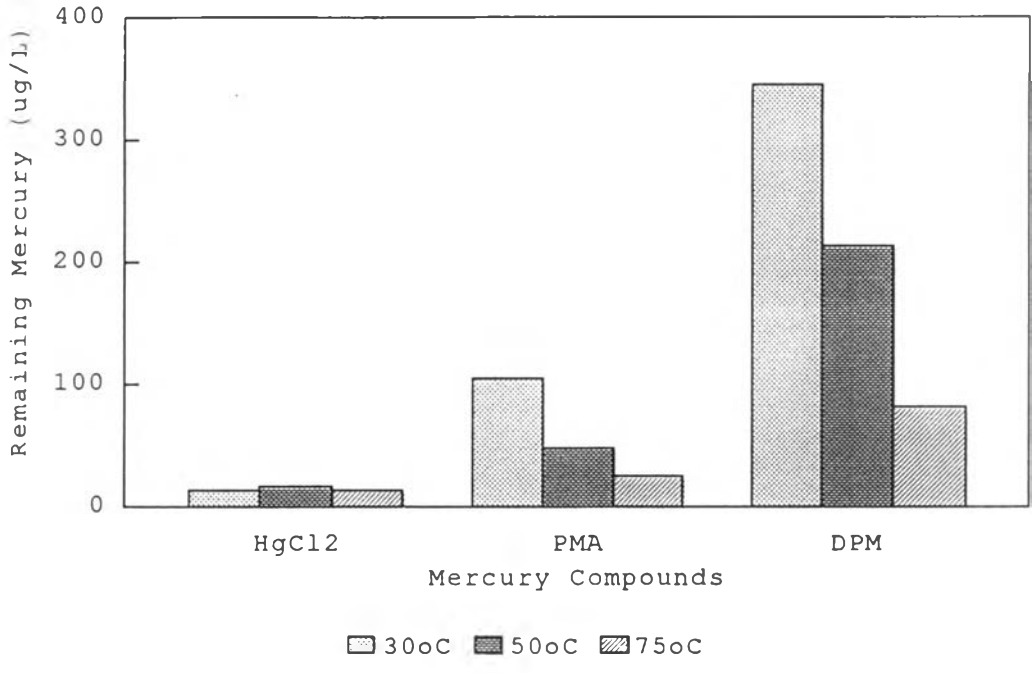

Figure 4.11 Effect of Temperature on Mercury Compounds Removal by 2.5Cu Adsorbent at a Pressure of 200 psig

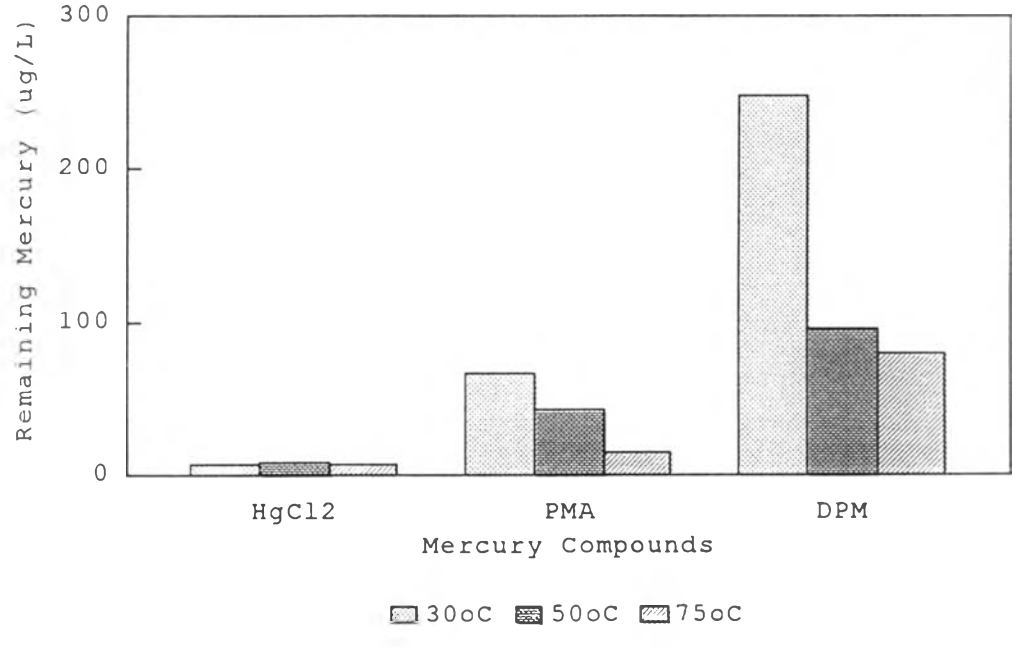

Figure 4.12 Effect of Temperature on Mercury Compounds Removal by 5.0Cu Adsorbent at a Pressure of 200 psig

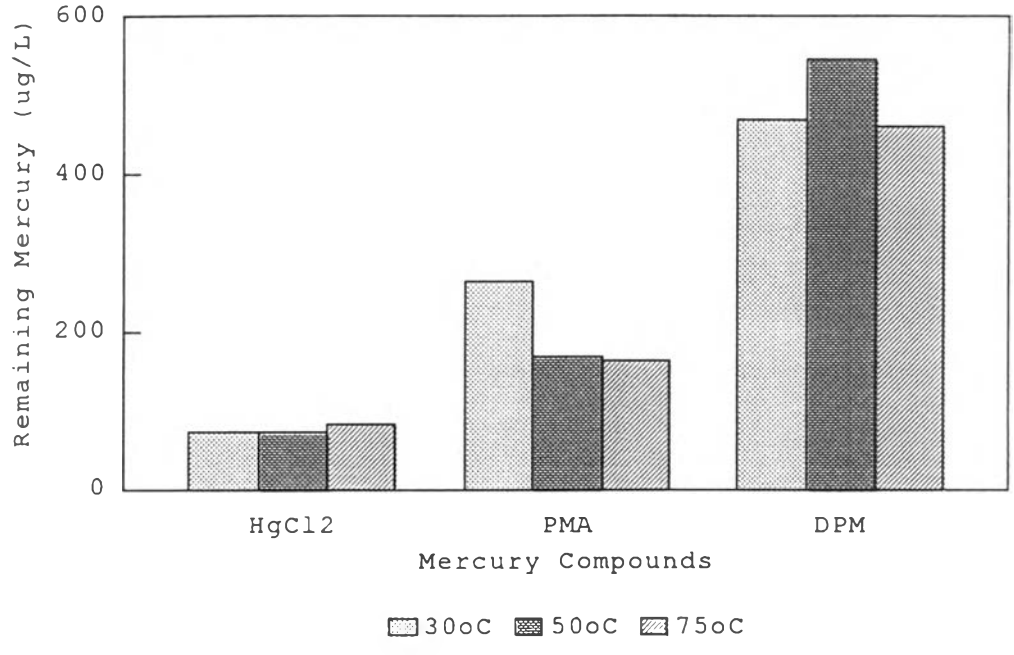

Figure 4.13 Effect of Temperature on Mercury Compounds Removal by 2.5Zn Adsorbent at a Pressure of 200 psig

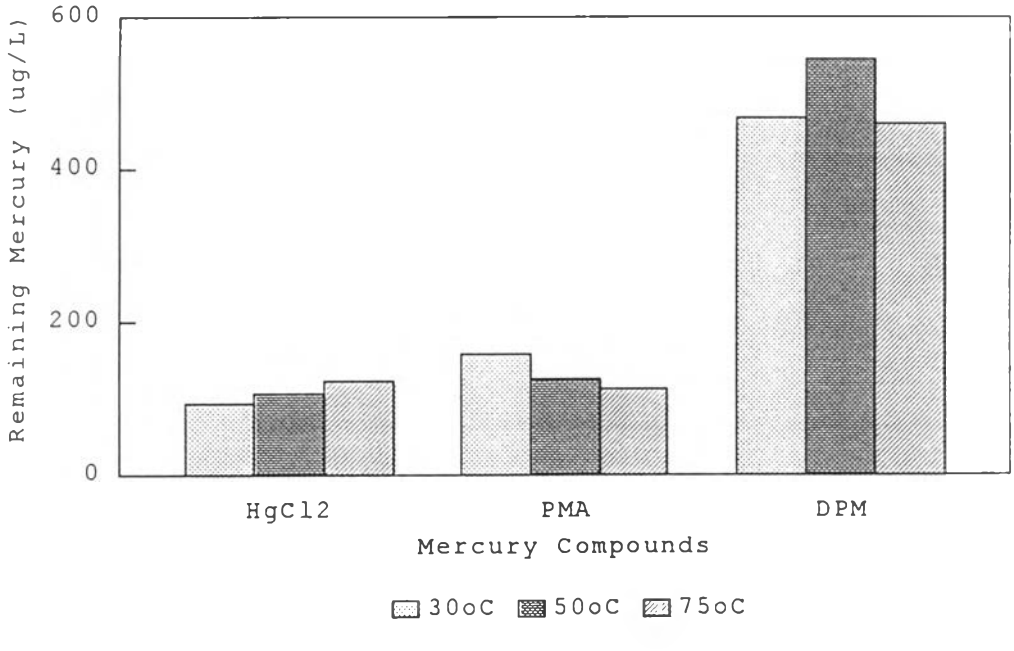

Figure 4.14 Effect of Temperature on Mercury Compounds Removal by 5.0Zn Adsorbent at a Pressure of 200 psig

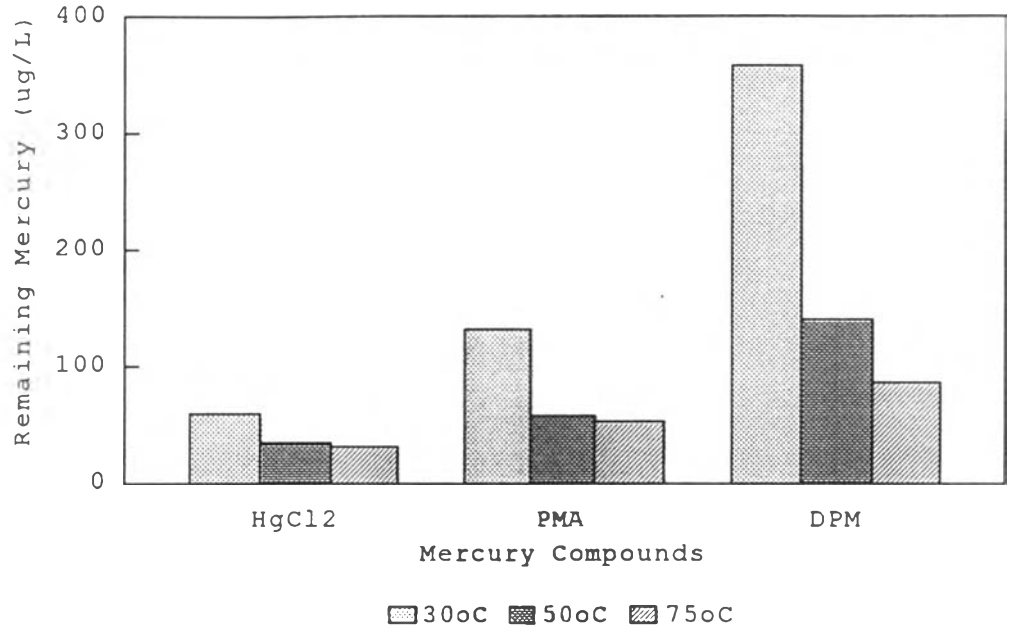

Figure 4.15 Effect of Temperature on Mercury Compounds Removal by CuZn Adsorbent at a Pressure of 200 psig

mercury compound types. However, mercuric chloride can be adsorbed by alumina adsorbent with the highest efficiency.

Removal of mercury by copper adsorbent is very different from alumina as shown in Figure 4.11 and 4.12. Temperature does not effect on removal of mercury chloride in experiments of both 2.5Cu and 5.0Cu adsorbents. Concentration of mercuric chloride is nearly constant when temperature increases. On the other hand, removal of phenylmercuric acetate and diphenylmercury significantly depend on operating temperature. It is noticeable that remaining organomercury, both PMA and DPM, decreases when temperature increases. Temperature

of 75°C is the best temperature for removing phenylmercury acetate and diphenylmercury. This indicates that mercury can adsorb and be removed very effectively on copper adsorbents, especially at temperature of 75°C. In addition, removal of each mercury compound is compared with each other at the same temperature. It is found that mercuric chloride can be removed with the highest efficiency, like in case of alumina adsorbent. Degree of phenylmercuric acetate removal is rather higher than that of diphenylmercury. This indicates that properties of mercury compounds strongly affect the adsorption of mercury on adsorbents. Polarity of each compound is one of properties which can effect on interaction between adsorbent and mercury. Polarity of mercury compounds is in the following order: $HgCl_2$ > PMA > DPM. From the experimental results, it is found that efficiency of mercury removal increases with increasing of polarity of the compounds.

Effect of temperature in experiment of zinc adsorbents is shown in Figures 4.13 and 4.14. From the Figures, it can be observed that temperature does not effect on degree of mercury compound removal. However, mercuric chloride shows the highest efficiency in adsorption on zinc adsorbent.

In study of mercury removal by CuZn adsorbent, effect of temperature can be clearly observed as shown in Figure 4.15. When temperature increases from 30°C to 75°C, efficiency of mercury removal increases, especially in case of diphenylmercury. This result indicates that

adsorption of all mercury compounds on copper-zinc adsorbent prefers to take place at high temperature.

Effect of Adsorbent

Copper and Zinc content

Copper and zinc are loaded on alumina support in order to study the effect of metal on removal of mercury. The copper and/or zinc adsorbent are prepared by dry impregnation of copper and zinc solution into alumina support. The copper and zinc content in fresh adsorbent are determined by using flame atomic absorption spectroscopy and listed in the Table 4.4. Percent error is calculated in order to determine deviation of actual value from desired value. The result shows that actual copper and/or zinc content are less than the desired value. The alumina adsorbent is analysed to measure copper and zinc content in order to use as blank experiment. The result shows that the percent of both metal is 0.01% by weight which can be specified as error of the analysis. For instance, the copper in 2.5Cu and 5.0Cu are approximately 2.30% and 4.41% by weight. This corresponds to the error of 8% and 11.8%, respectively. The zinc content in the adsorbent is slightly different from the desired value. The zinc in 2.5Zn and 5.0Zn are approximately 2.48% and 4.62% by weight, corresponding to the error of 0.8% and 7.6%, respectively. The copper and zinc content in bimetallic adsorbent, CuZn, are 2.29% and 2.39%, respectively.

Table 4.4 Copper and Zinc Content in Adsorbents

Adsorbents	Cu Content (wt%)	% Error	Zn Content (wt%)	% Error
Alumina	0.01	-	0.01	-
2.5Cu	2.30	8.00	-	-
5.0Cu	4.41	11.80	-	-
2.5Zn	-	-	2.48	0.80
5.0Zn	-	-	4.62	7.60
CuZn	2.29	8.40	2.39	4.40

Fresh adsorbents are also analysed to determine total surface area, pore volume and pore size distribution. Figure 4.16 shows total surface area of the fresh adsobents. Surface area of alumina is 168.35 m^2/g while surface area of 2.5Cu, 5.0Cu, 2.5Zn, 5.0Zn and CuZn adsorbents are 164.16, 157.72, 162.18, 147.76 and 149.99 m^2/g, respectively. These results show that copper and zinc loading decrease surface area of alumina support. When percent of copper and zinc increases, total surface area of the fresh adsorbents decreases.

Figure 4.17 shows comparison of total pore volume among fresh alumina, fresh copper, fresh zinc and fresh copper-zinc adsorbent. It is found that pore volume alumina adsorbent is the highest. Pore volume of alumina, 2.5Cu, 5.0Cu, 2.5Zn, 5.0Zn and CuZn adsorbent are 0.241, 0.236, 0.227, 0.237, 0.219 and 0.224 cc/g, respectively. Total pore volume decreases with increasing of percent copper and zinc loading.

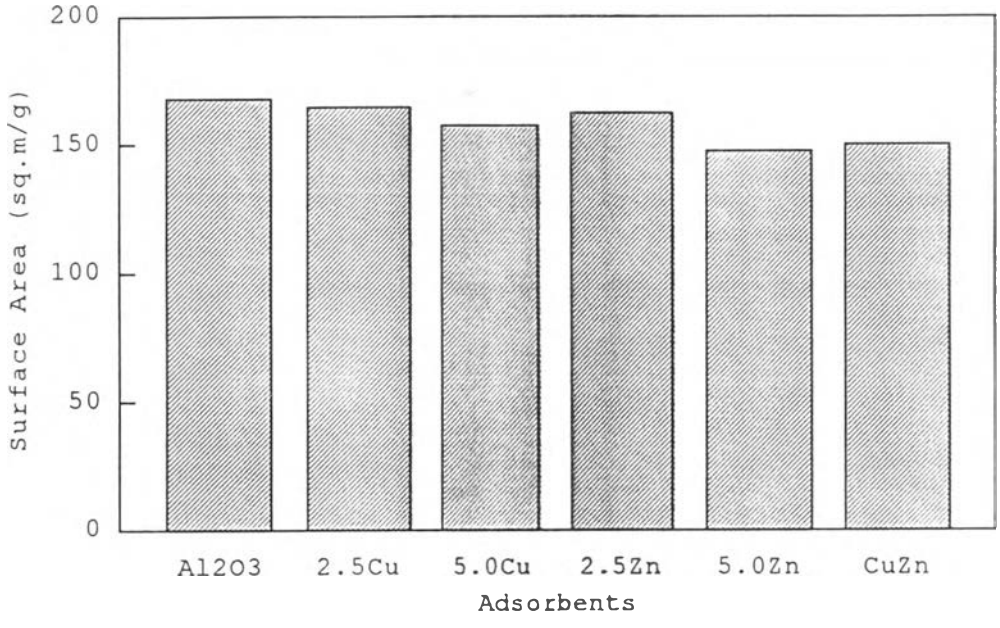

Figure 4.16 Comparison of Total Surface Area among Fresh Adsorbents

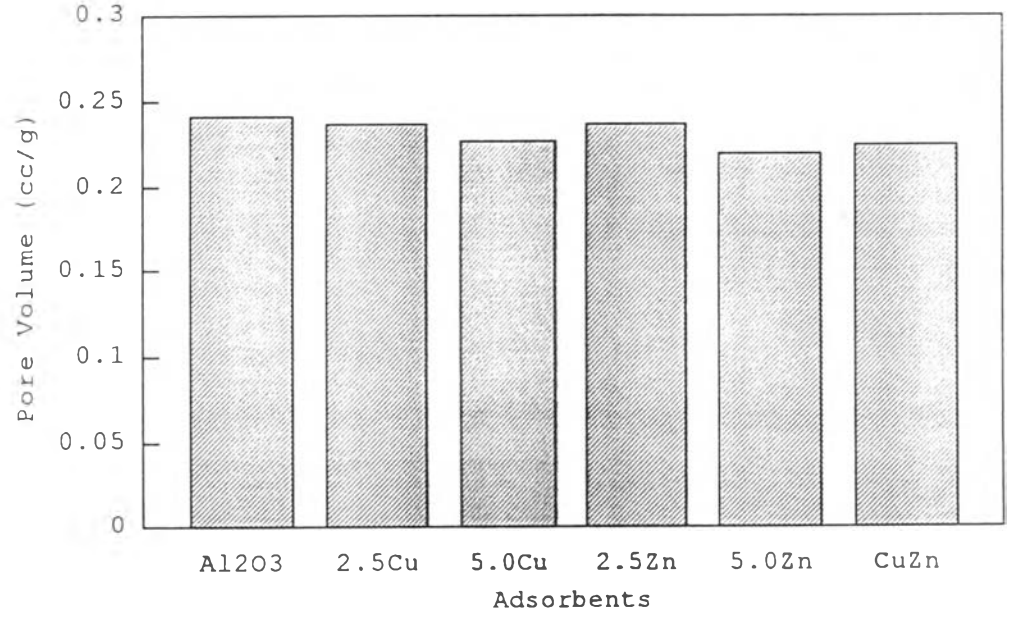

Figure 4.17 Comparison of Pore Volume among Fresh Adsorbents

In addition, pore size distribution of fresh adsorbents is also analyzed and shown in Figures 4.18 to 4.20. Comparison of pore size distribution between fresh alumina and fresh copper adsorbents is shown in Figure 4.18. It is found that pore size distribution of 2.5Cu and 5.0Cu adsorbents are slightly different from that of fresh alumina adsorbent. Figures 4.19 and 4.20 show pore size distribution of fresh zinc adsorbents, both 2.5Zn and 5.0Zn, and fresh copper-zinc adsorbent. Results of the analysis data show that there are no significant variation of pore size distribution of fresh fresh zinc adsorbents and fresh copper-zinc adsorbent. It can be concluded that copper and/or zinc loading on alumina support disperse entirely on pore diameter of the support. In addition, it also indicates that adsorbent

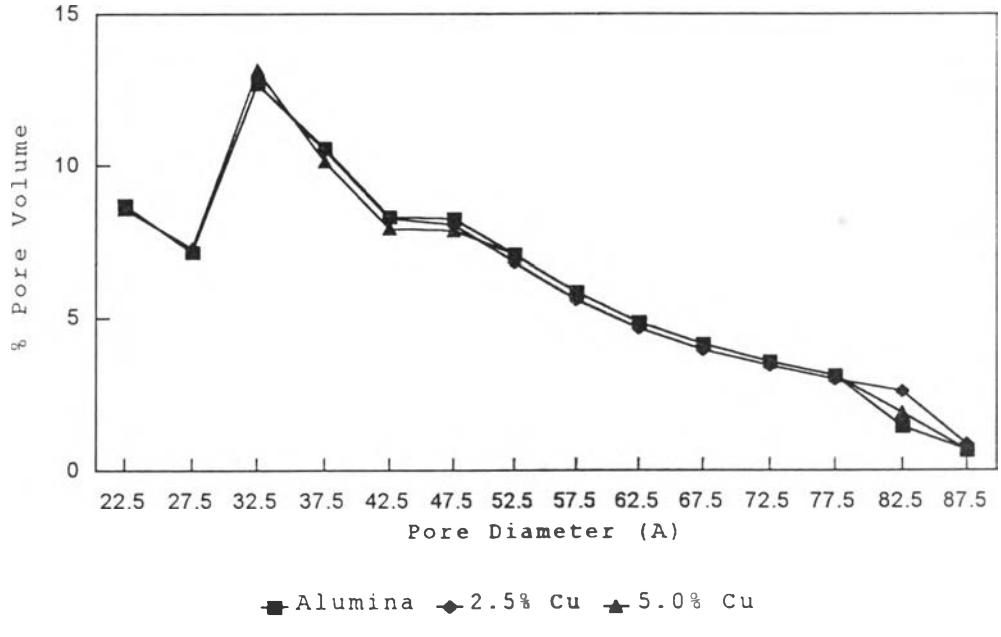

Figure 4.18 Comparison of Pore Size Distribution between Fresh Alumina and Fresh Copper Adsorbents

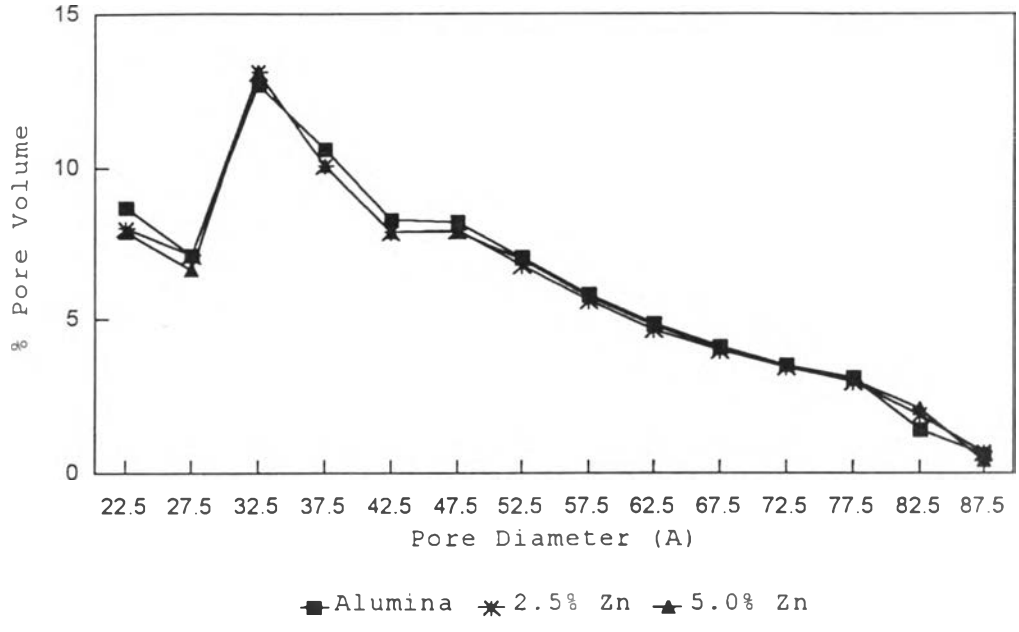

Figure 4.19 Comparison of Pore Size Distribution between Fresh Alumina and Fresh Zinc Adsorbents

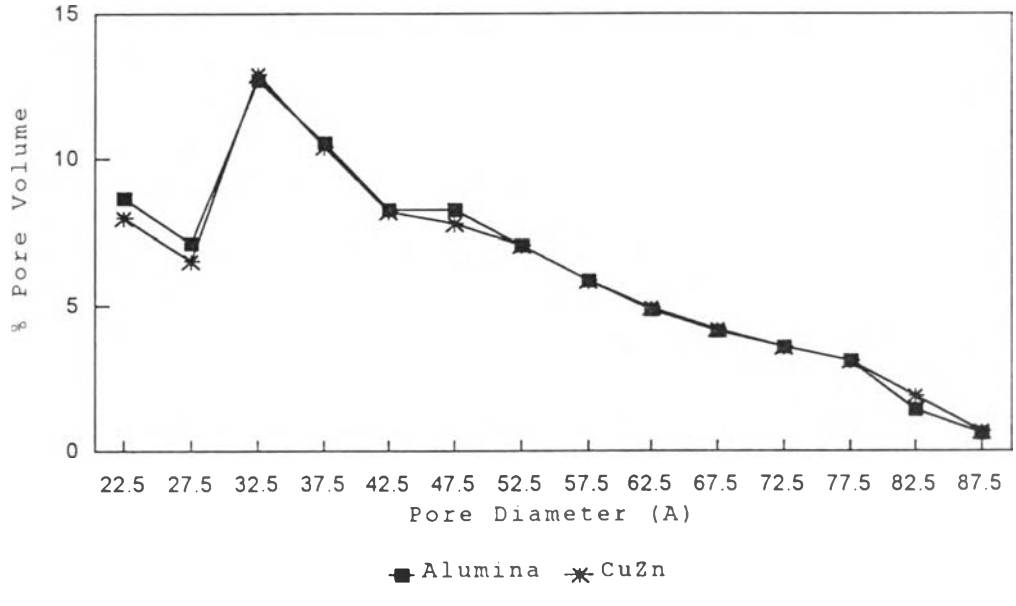

Figure 4.20 Comparison of Pore Size Distribution between Fresh Alumina and Fresh Copper-Zinc Adsorbents

preparation by dry imprenation does not effect on pore size distribution of alumina support.

Effect of Alumina Adsorbent

In this study, alumina support is neutral activated alumina. The activated alumina is prepared by dehydration and calcination of aluminum hydroxide with CO_2 stream at approximately 900°C. Therefore, surface of each alumina particles is coated with a thin layer of aluminum oxycarbonated, $[Al_2(OH)_5]_2CO_3.H_2O$. This alumina is used as support and adsorbent. Alumina adsorbent is prepared by reduction of activated neutral alumina in hydrogen gas at temperature of 400°C for 6 hours.

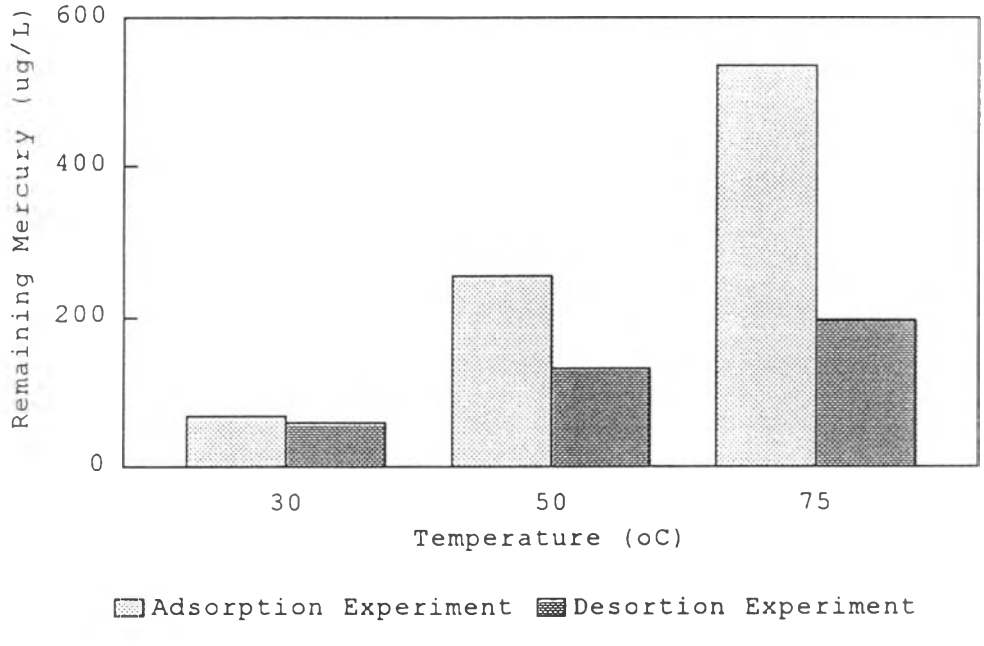

Figure 4.21 Remaining Mercury in Study on Adsorption and Desorption of Mercuric Chloride at Various Temperatures and at 200 psig

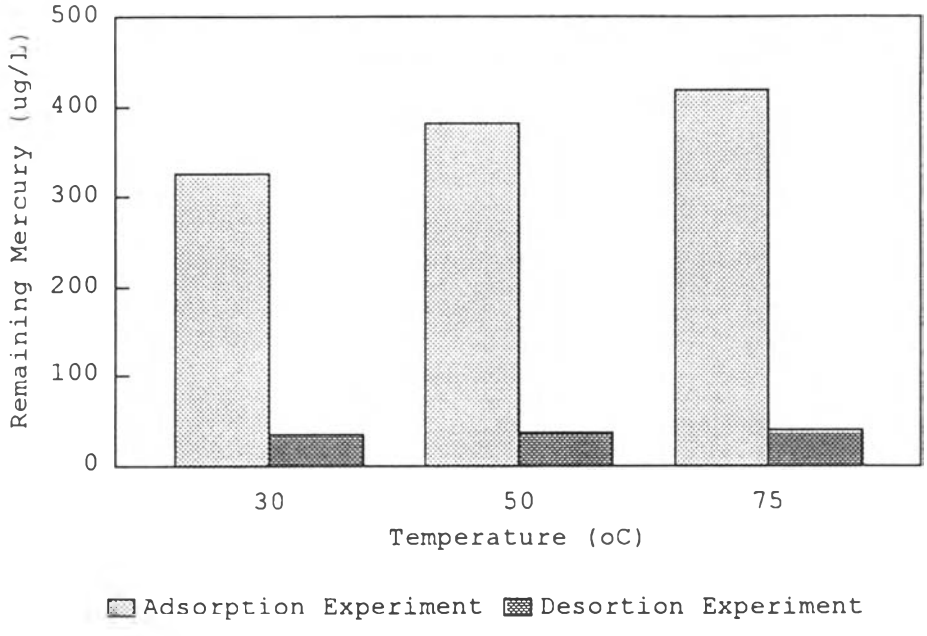

Figure 4.22 Remaining Mercury in Study on Adsorption and Desorption of Phenylmercuric Acetate at Various Temperatures and a Pressure of 200 psig

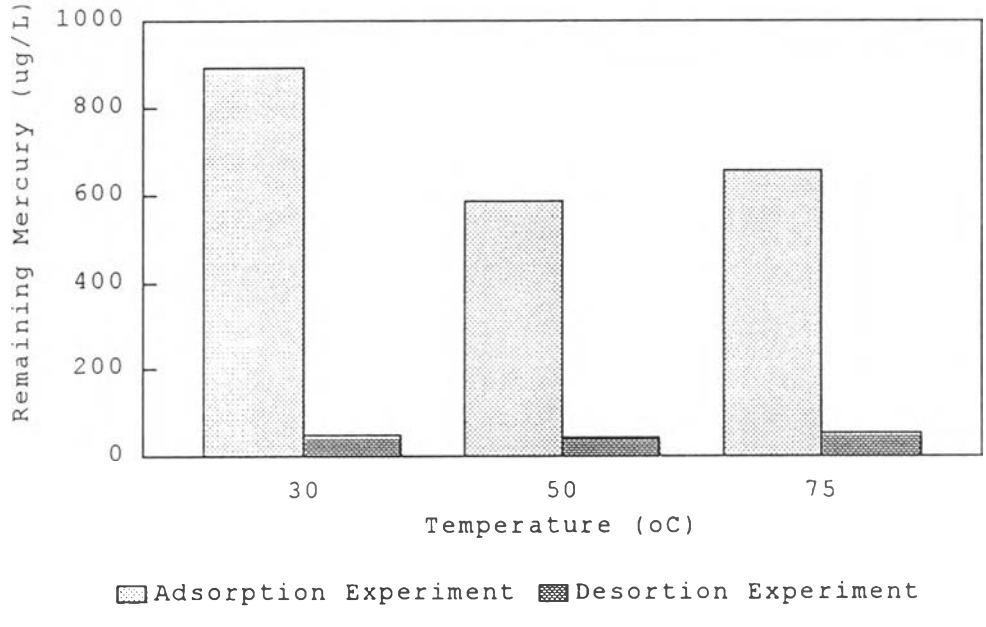

Figure 4.23 Remaining Mercury in Study on Adsorption and Desorption of Diphenylmercury at Various Temperatures and a Pressure of 200 psig

The experiment result of mercury removal by alumina adsorbent is shown in Figures 4.21 to 4.23. Figure 4.21 shows the result of study on mercury chloride. The removal of mercury chloride by alumina is very strongly a function of temperature. The efficiency of mercury removal decreases significantly with temperature increasing. The experiment is also designed to study desorption of mercury from spent alumina adsorbent. The result of desorption experiment shows that concentration of mercury chloride in toluene increases when temperature increases from 30°C to 75°C. This indicates that the adsorption of mercuric chloride on alumina adsorbent is an reversible process or phsical adsorption. In the study of phenylmercury acetate (in Figure 4.22) and diphenylmercury (in Figure 4.23), mercury concentration is rather constant at various operating temperature. However, the desorption organic mercury from spent alumina takes place sparingly with respect to adsorption. This cannot defined as reversible process as shown in the desorption study of each mercury compounds.

Total surface area of fresh and spent alumina are shown in Figures 4.24 and pore volume is shown in Figures 4.25. It is found that both surface area and pore volume of spent alumina is less than fresh alumina for all mercury compounds. Decreasing of surface area and pore volume result from deposit of mercury on adsorbent. Figures 4.26 to 4.28 show the pore size distribution of fresh and spent alumina. From the data it is apparent that there is slight difference of pore size distribution

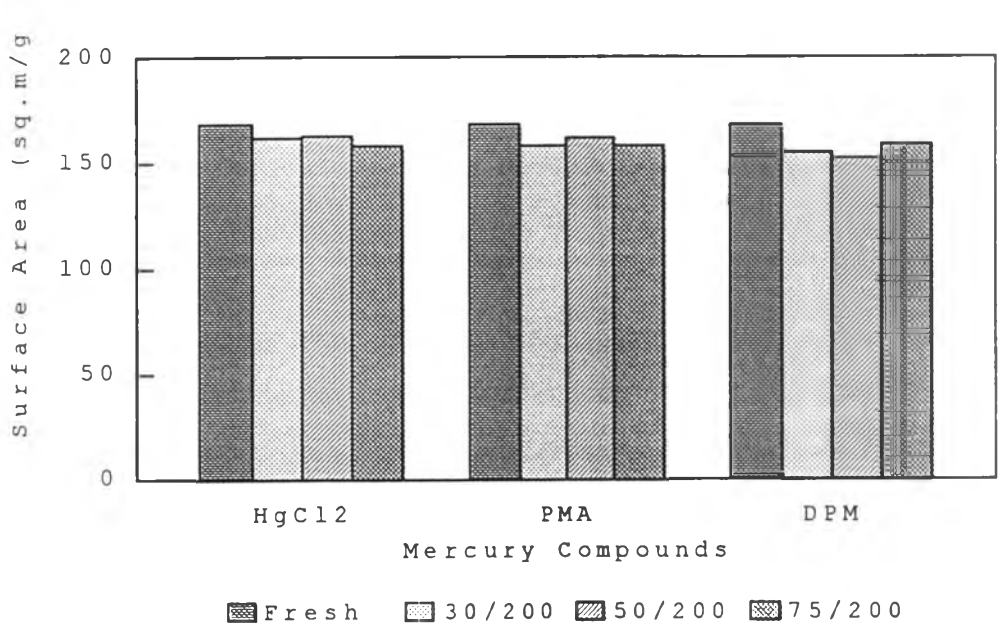

Figure 4.24 Comparison of Surface Area between Fresh and Spent Alumina Adsorbents at Various Temperatures and a Pressure of 200 psig

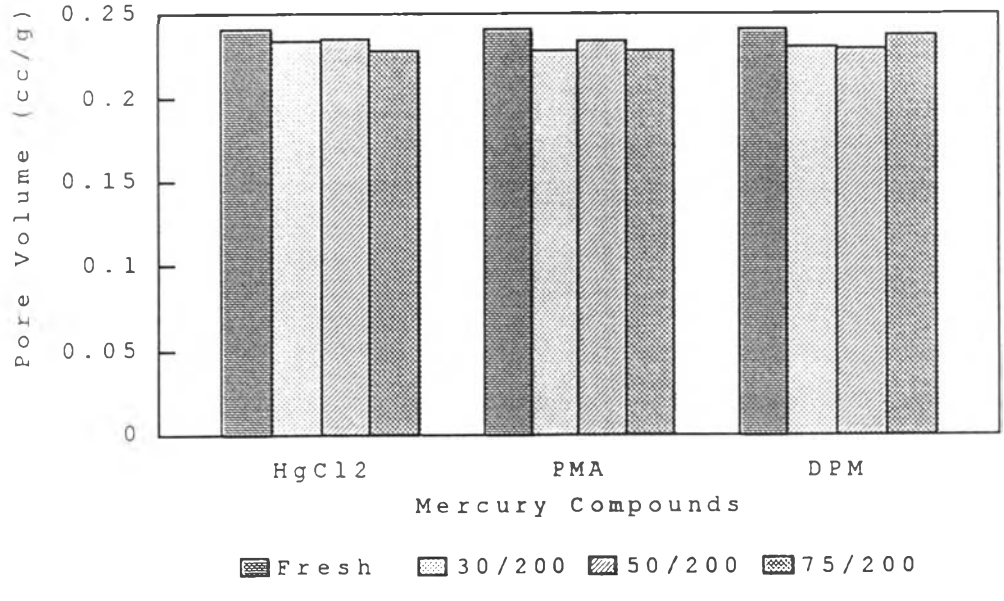

Figure 4.25 Comparison of Pore Volume between Fresh and Spent Alumina Adsorbents at Various Temperatures and a Pressure of 200 psig

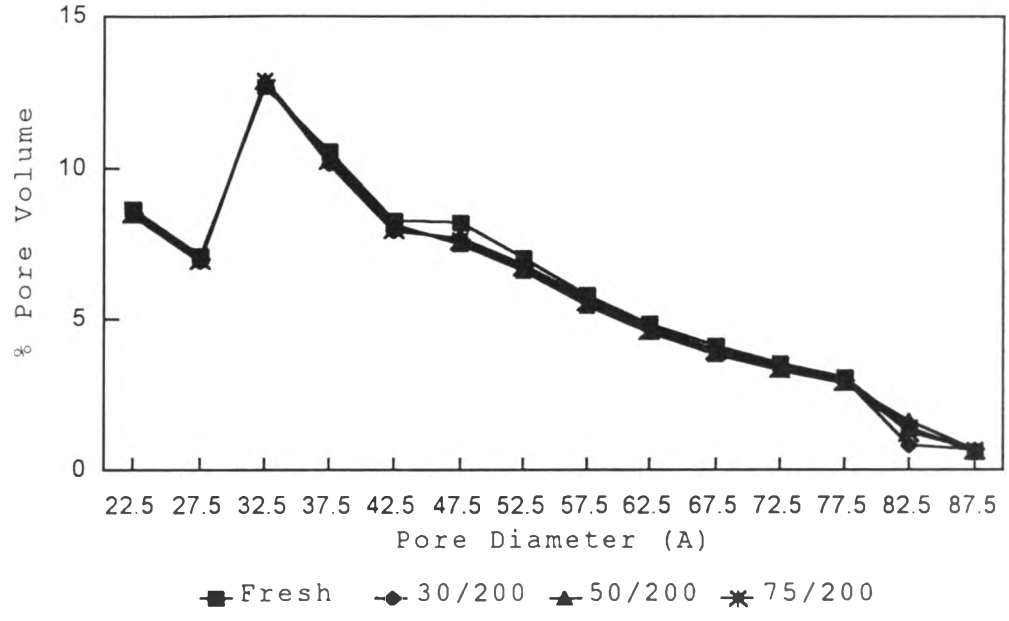

Figure 4.26 Comparison of Pore Size Distribution between Fresh and Spent Alumina Adsorbents in Study of Mercuric Chloride Removal at Various Temperatures and a Pressure of 200 psig

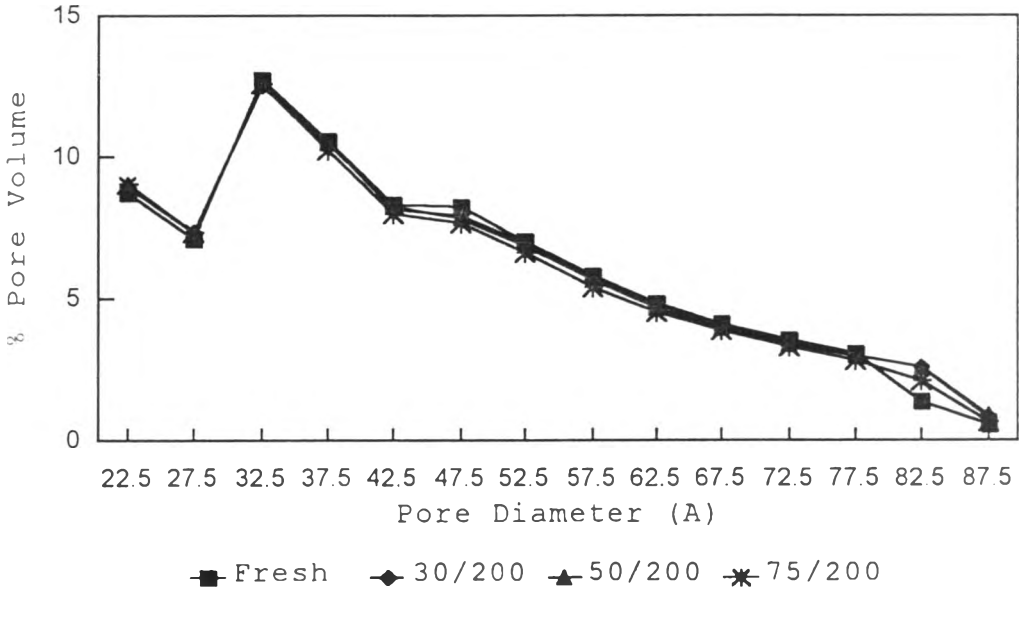

Figure 4.27 Comparison of Pore Size Distribution between Fresh and Spent Alumina Adsorbents in Study of Phenylmercuric Acetate Removal at Various Temperatures and a Pressure of 200 psig

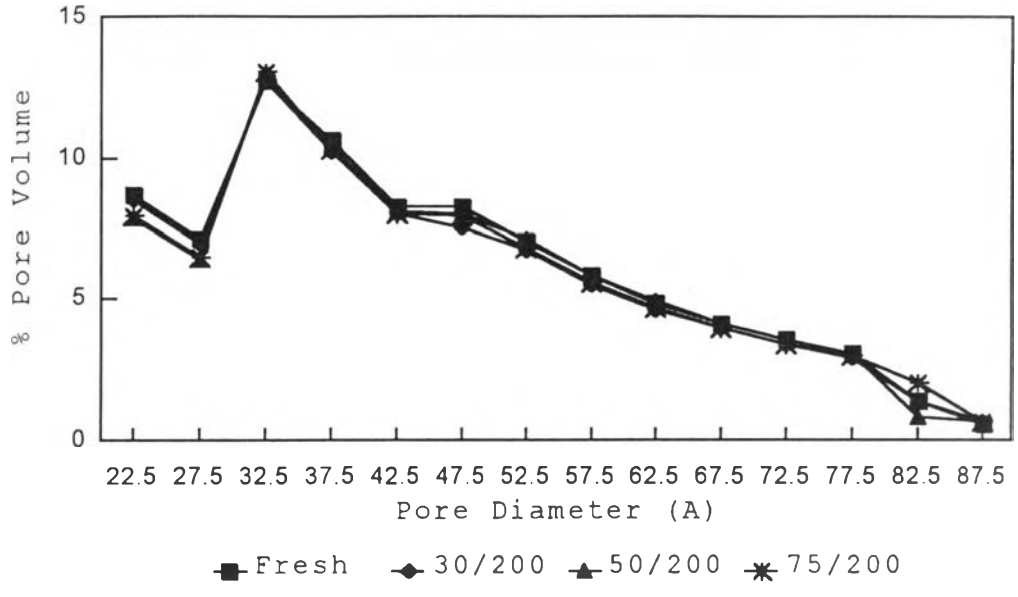

Figure 4.28 Comparison of Pore Size Distribution between Fresh and Spent Alumina Adsorbents in Study of Diphenylmercury Removal at Various Temperatures and a Pressure of 200 psig

between fresh and spent alumina adsorbents. This may result from that amount of adsorbed mercury on adsorbent is not sufficiency high. Thus, variation of pore size distribution cannot be observed.

Effect of Copper Adsorbent

The effect of copper is studied by using adsorbents containing copper as an active metal. Percent of copper loading is varied at 2.5% and 5.0% by weight. Results of mercury removal by copper adsorbents are shown in Figures 4.29, 4.30 and 4.31 for mercuric chloride, phenylmercuric acetate and diphenylmercury, respectively. It is found that efficiency of mercury removal increases

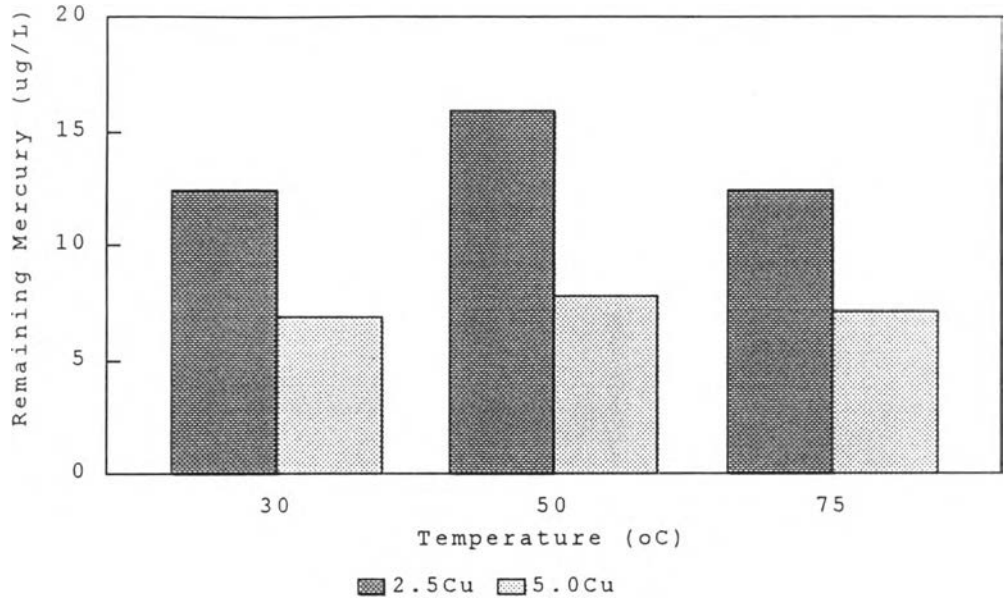

Figure 4.29 Remaining Mercury in Study of Mercuric Chloride Removal by Copper Adsorbents at Various Temperatures and a pressure of 200 psig

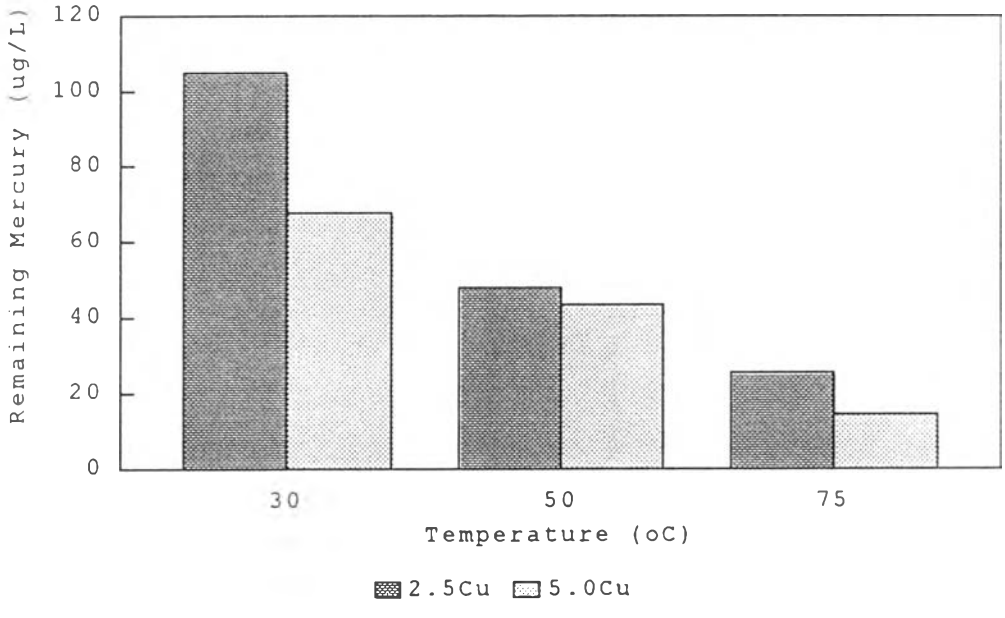

Figure 4.30 Remaining Mercury in Study of Phenylmercuric Acetate Removal by Copper Adsorbents at Various Temperatures and a Pressure of 200 psig

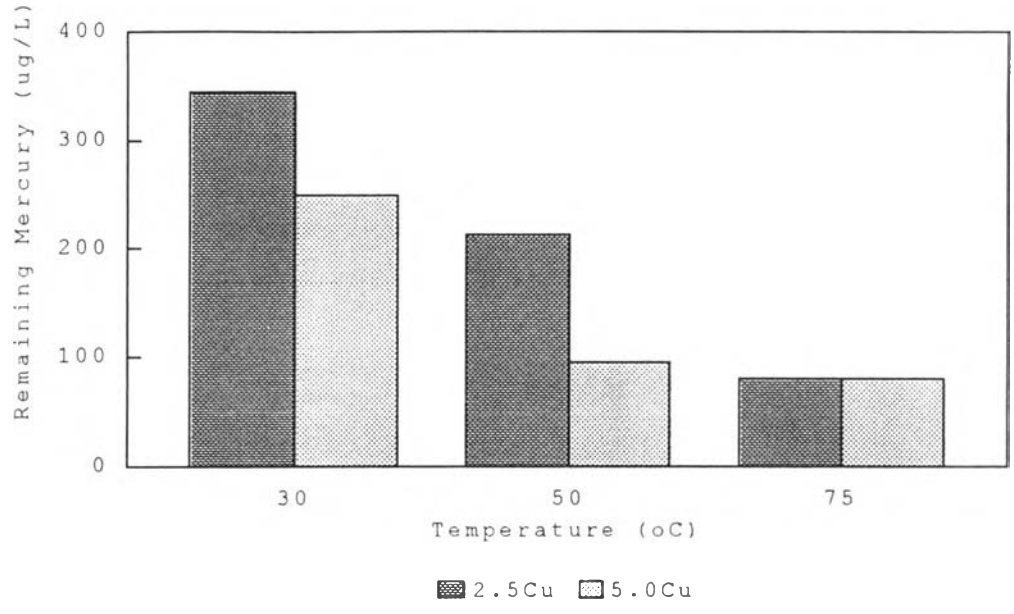

Figure 4.31 Remaining Mercury in Study of Diphenylmercury Removal by Copper Adsorbents at Various Temperatures and a Pressure of 200 psig

with percent of copper loading increase. For instance, mercuric chloride concentration in toluene decreases from 1000 µg/L to 12.4 and 6.9 µg/L in study of 2.5Cu and 5.0Cu, respectively. This corresponds to mercury removal efficiency of 98.76% and 99.31%. In case of phenylmercuric acetate and diphenylmercury, 5.0Cu adsorbent, like in study of mercuric chloride, shows higher efficiency than 2.5Cu adsorbent. However, removal efficiency of organomercury compounds is less than inorganic compound. This may result from polarity and complication of each compound. Mercuric chloride is the highest polarity while molecule of phenylmercuric acetate and diphenylmercury are more complicated.

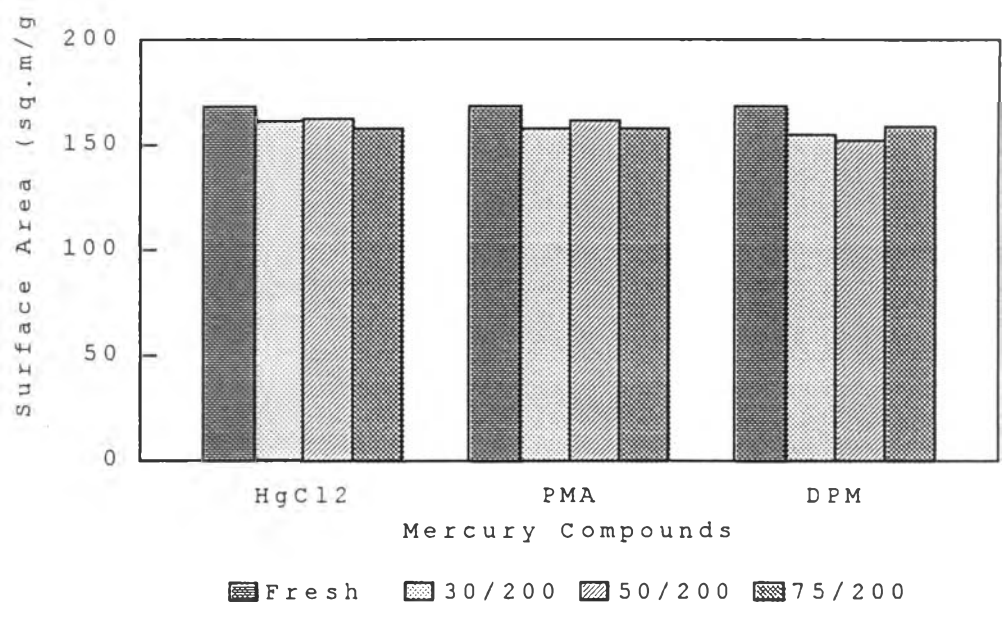

Figure 4.32 Comparison of Surface Area between Fresh and Spent 2.5Cu Adsorbent at Various Temperatures and a Pressure of 200 psig

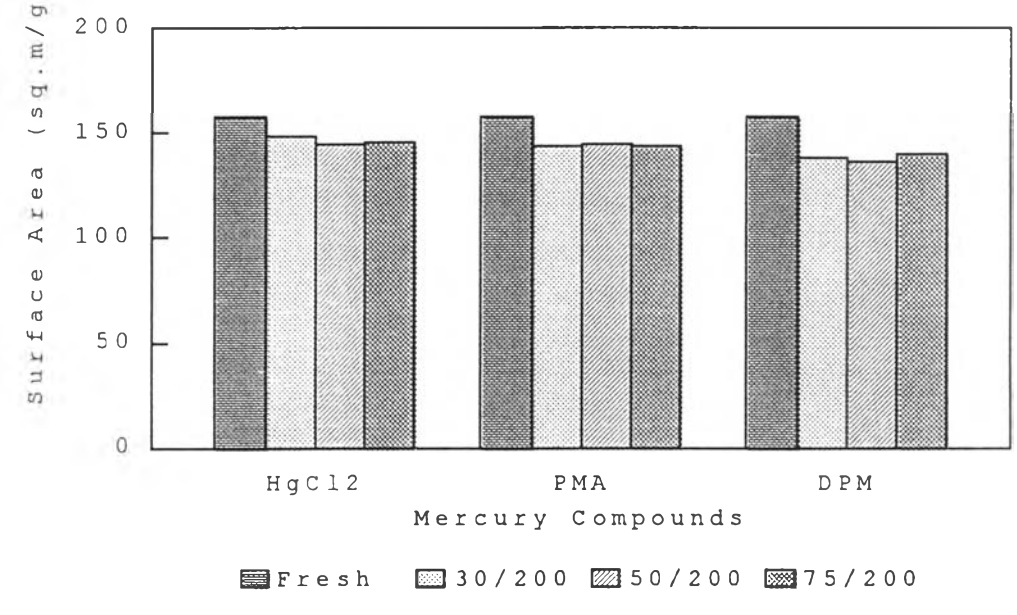

Figure 4.33 Comparison of Surface Area between Fresh and Spent 5.0Cu Adsorbent at Various Temperatures and a Pressure of 200 psig

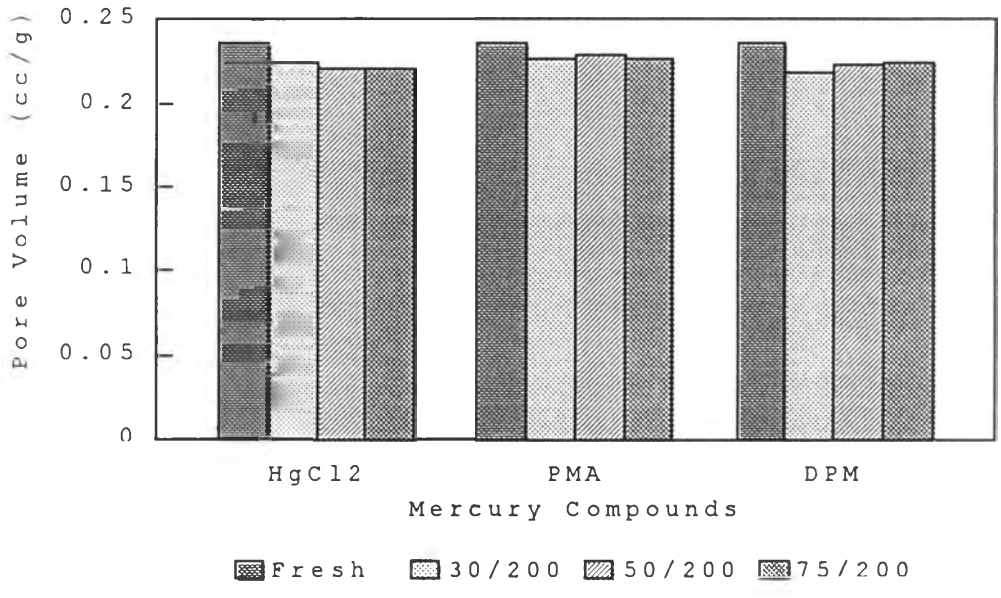

Figure 4.34 Comparison of Pore Volume between Fresh and Spent 2.5Cu Adsorbent at Various Temperatures and a Pressure of 200 psig

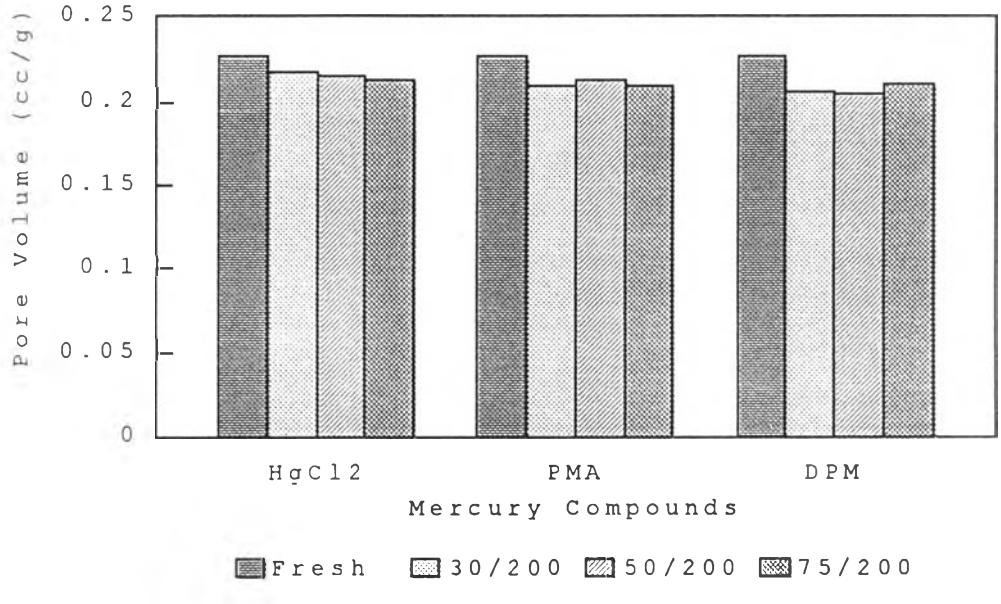

Figure 4.35 Comparison of Pore Volume between Fresh and Spent 5.0Cu Adsorbent at Various Temperatures and a Pressure of 200 psig

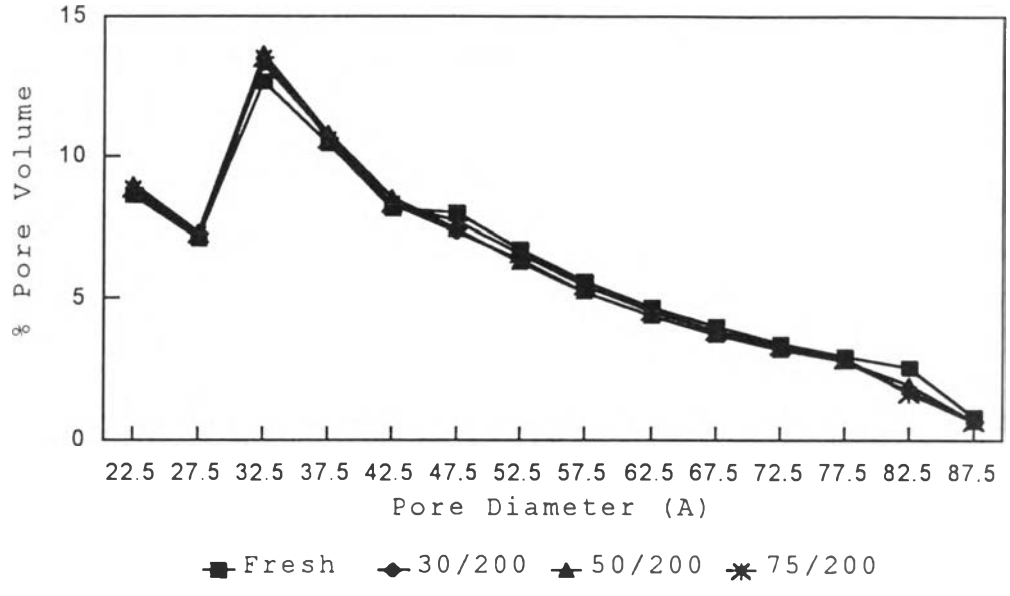

Figure 4.36 Comparison of Pore Size Distribution between Fresh and Spent 2.5Cu Adsorbent in Study of Mercuric Chloride Removal at Various Temperature and a Pressure of 200 psig

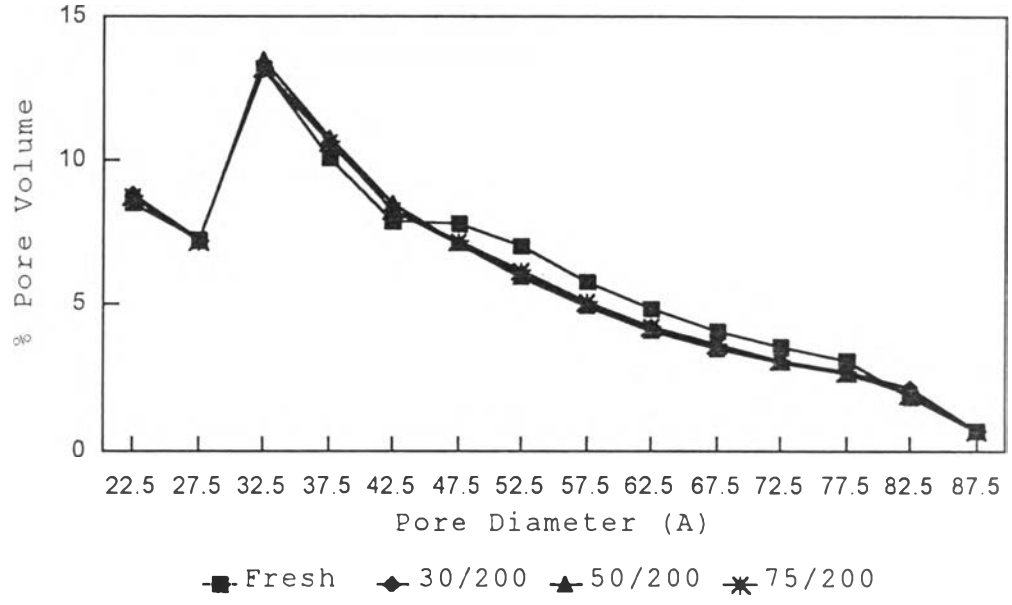

Figure 4.37 Comparison of Pore Size Distribution between Fresh and Spent 5.0Cu Adsorbent in Study of Mercuric Chloride Removal at Various Temperatures and a Pressure of 200 psig

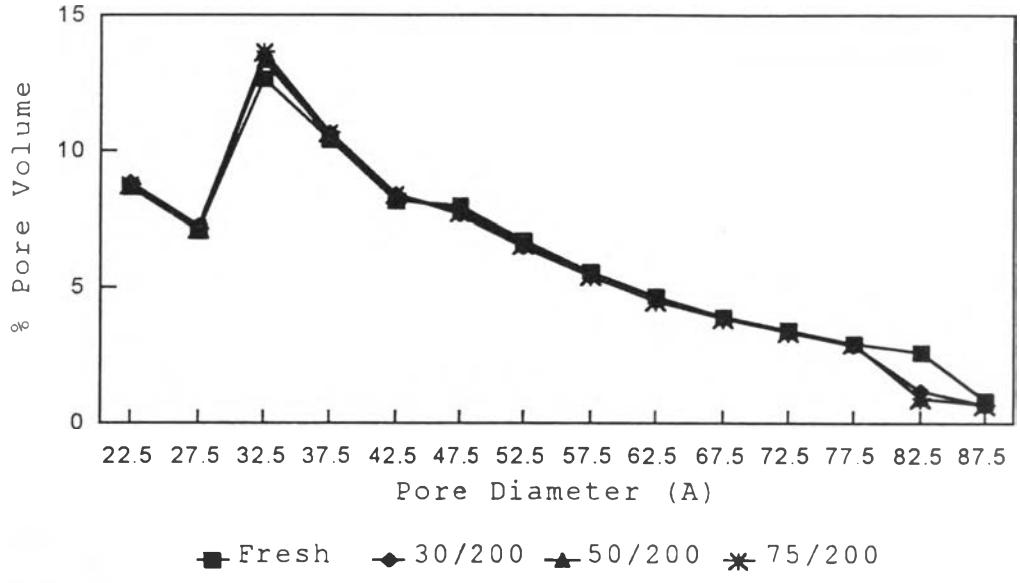

Figure 4.38 Comparison of Pore Size Distribution between Fresh and Spent 2.5Cu Adsorbent in Study of Phenylmercuric Acetate at Various Temperatures and a Pressure of 200 psig

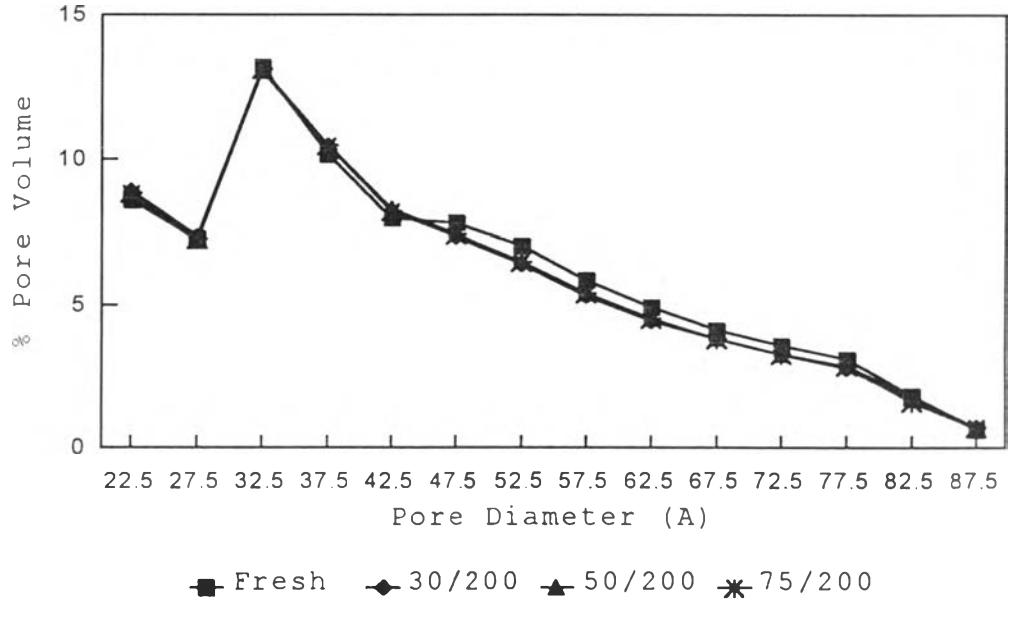

Figure 4.39 Comparison of Pore Size Distribution between Fresh and Spent 5.0Cu Adsorbent in Study Phenylmercuric Acetate at Vairous Temperatures and a Pressure of 200 psig

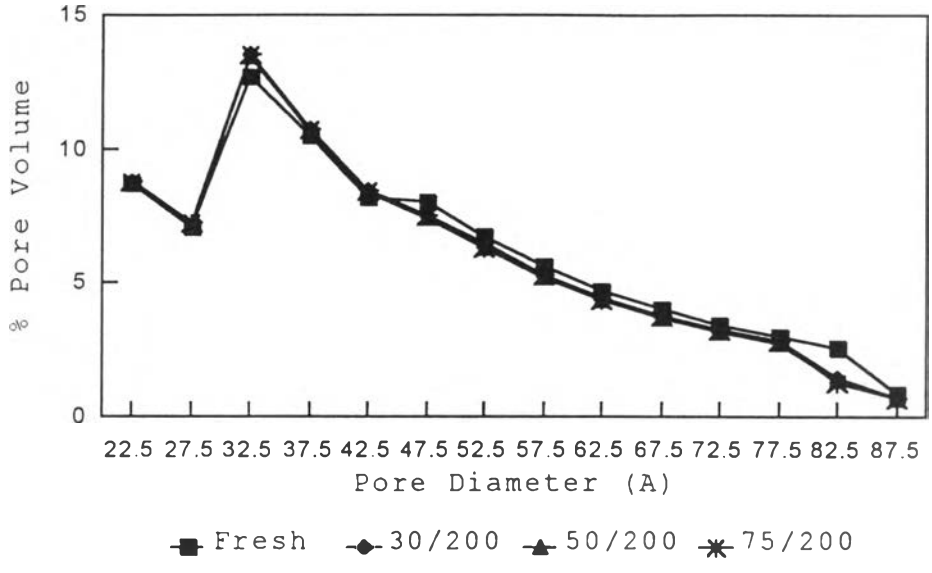

Figure 4.40 Comparison of Pore Size Distribution between Fresh and Spent 2.5cu Adsorbent in Study of Diphenylmercury at Various Temperatures and a Pressure of 200 psig

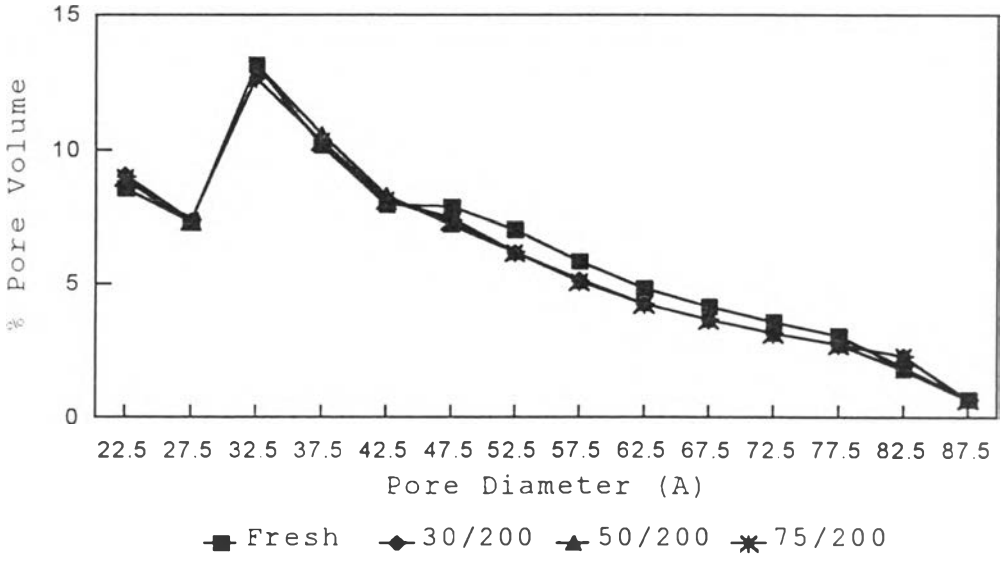

Figure 4.41 Comparison of Pore Size Distribution between Fresh and Spent 5.0Cu Adsorbent in Study of Diphenylmercury Removal at Various Temperatures and a Pressure of 200 psig

Surface area of copper adsorbents are shown in Figures 4.32 and 4.33. Figure 4.34 and 4.35 show porevolume of fresh and spent copper adsorbents in the study of mercuric chloride, phenylmercuric acetate and diphenylmercury, respectively. It is found that surface area and pore volume of spent copper adsorbent decrease with respect to fresh copper adsorbent. Since amount of adsorbed mercury on each adsorbent is not too high, difference of surface area and pore volume are also small. Pore size distribution of fresh and spent and copper adsorbents are compared in Figures 4.36 to 4.41. The difference of pore distribution of fresh and spent copper adsorbents can observed clearly, especially in 5.0Cu adsorbent. At pore size of 37.5°A and 42.5°A, pore size of spent adsorbents increase slightly while there is clear decreasing of pore size ranging from 47.5°A to 77.5°A. This variation can be also found in the study of both phenylmercuric acetate and diphenylmercury. It indicates that the adsorption of mercury compounds on copper adsorbents takes place at pore size of 37.5°A to 77.5°A. However, there is no evident difference of pore size distribution at various temperatures of 30, 50 and 75°C because amount of adsorbed mercury in each condition is rather the same.

Effect of Zinc Adsorbent

Zinc adsorbent is prepared by imprenation of alumina support with zinc nitrate solution. Percent of

zinc loading is varied at 2.5wt% and 5.0wt% which are represented by 2.5Zn and 5.0Zn adsorbent, respectively.

Experimental results of mercury removal by zinc adsorbent are shown in Figures 4.42 to 4.44. Figure 4.42 shows concentration of remaining mercuric chloride. It is found that when percent of zinc loading increases, efficiency of mercury removal decreases significantly. This indicates that zinc is not suitable site for mercuric chloride adsorption. In case of phenylmercuric acetate, 5.0Zn shows higher efficiency for removal of mercury than 2.5Zn (as shown in Figure 4.43). Figure 4.44 shows experimental result of diphenylmercury which is removed by 2.5Zn and 5.0Zn. When percent of zinc loading increases from 2.5% to 5.0% by weight, removal of

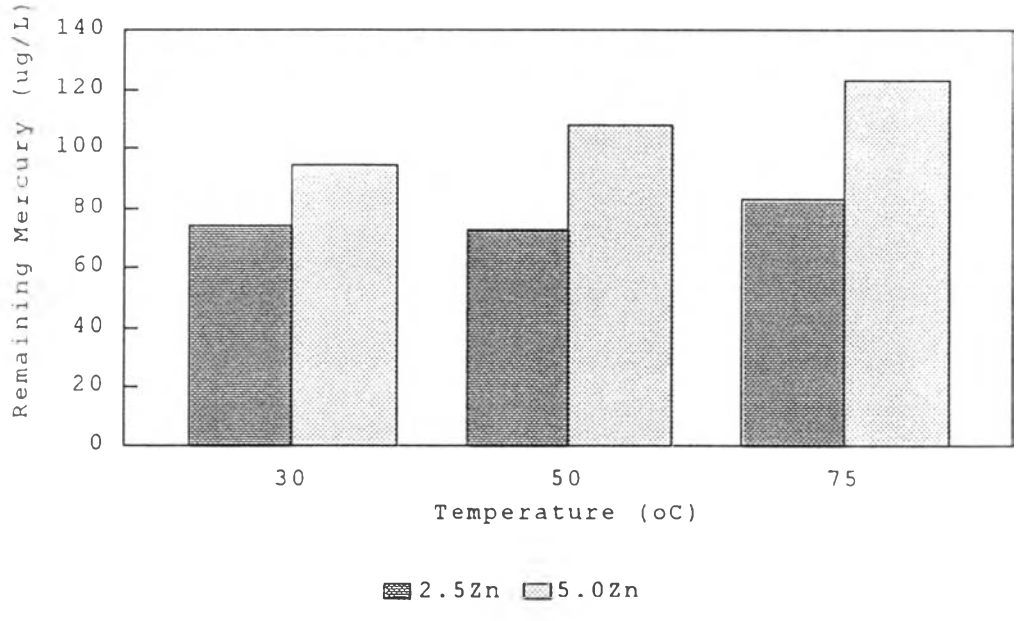

Figure 4.42 Remaining Mercury in Study of Mercuric Chloride Removal by Zinc Adsorbents at Various Temperatures and a Pressure of 200 psig

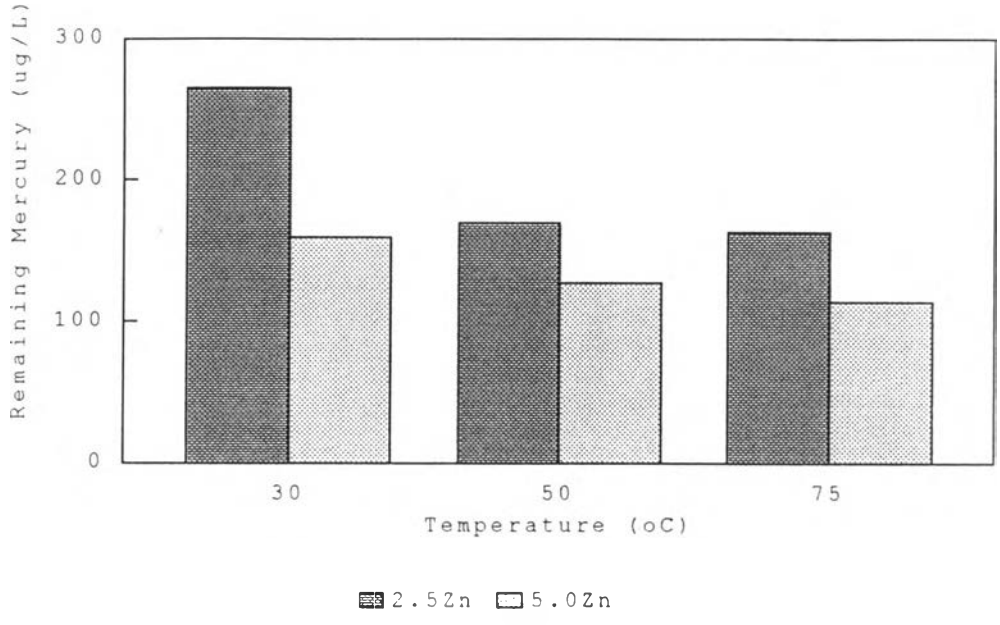

Figure 4.43 Remaining Mercury in Study of Phenylmercuric Acetate by Zinc Adsorbents at Various Temperatures and a Pressure of 200 paig

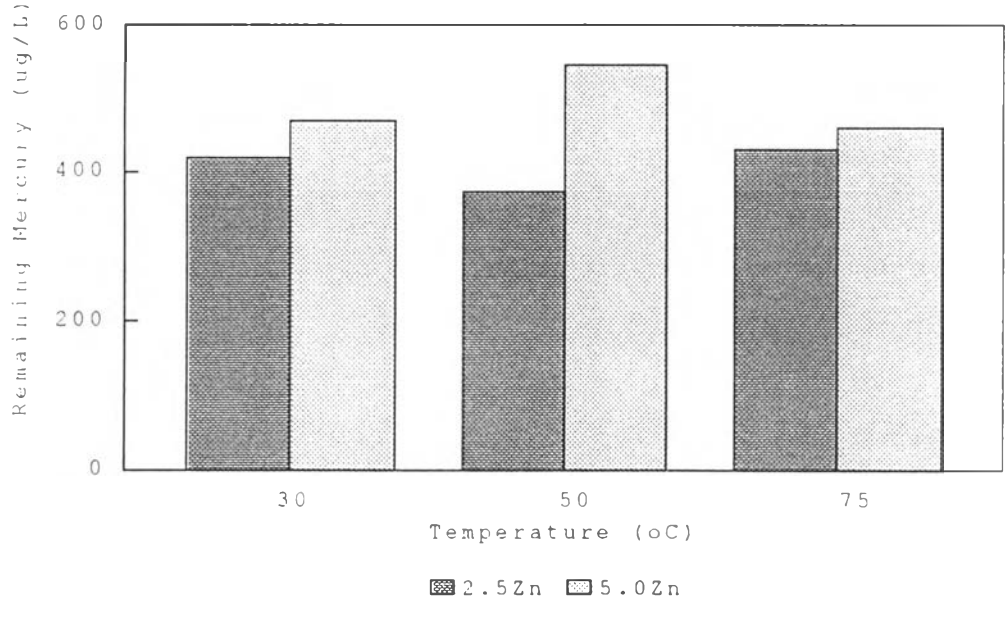

Figure 4.44 Remaining Mercury in Study of Diphenylmercury Removal by Zinc Adsorbents at Various Temperatures and a Pressure of 200 psig

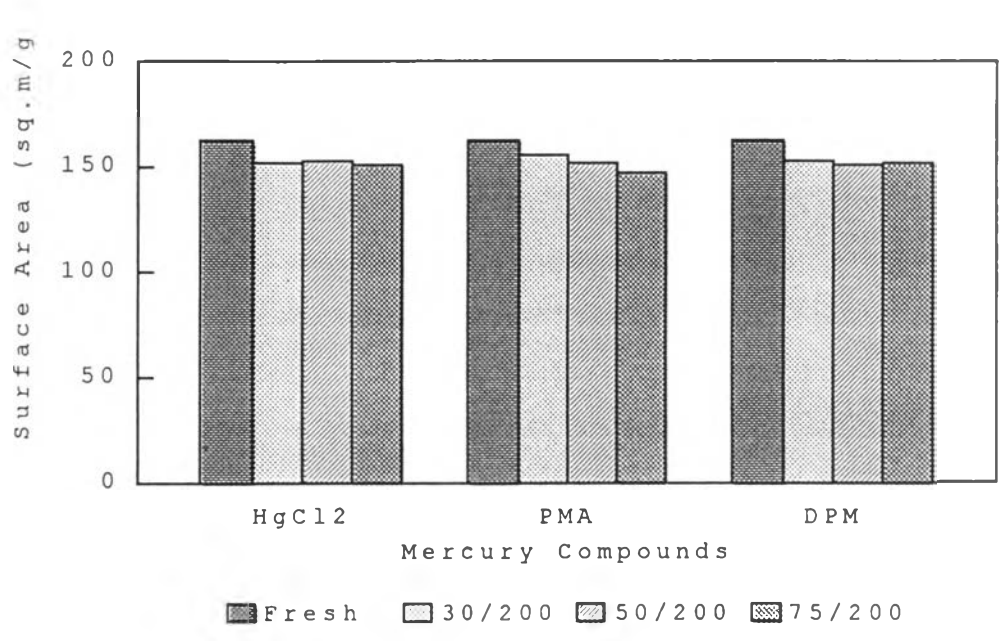

Figure 4.45 Comparison of Surface Area between Fresh and Spent 2.5Zn Adsorbent at Various Temperatures and a Pressure of 200 psig

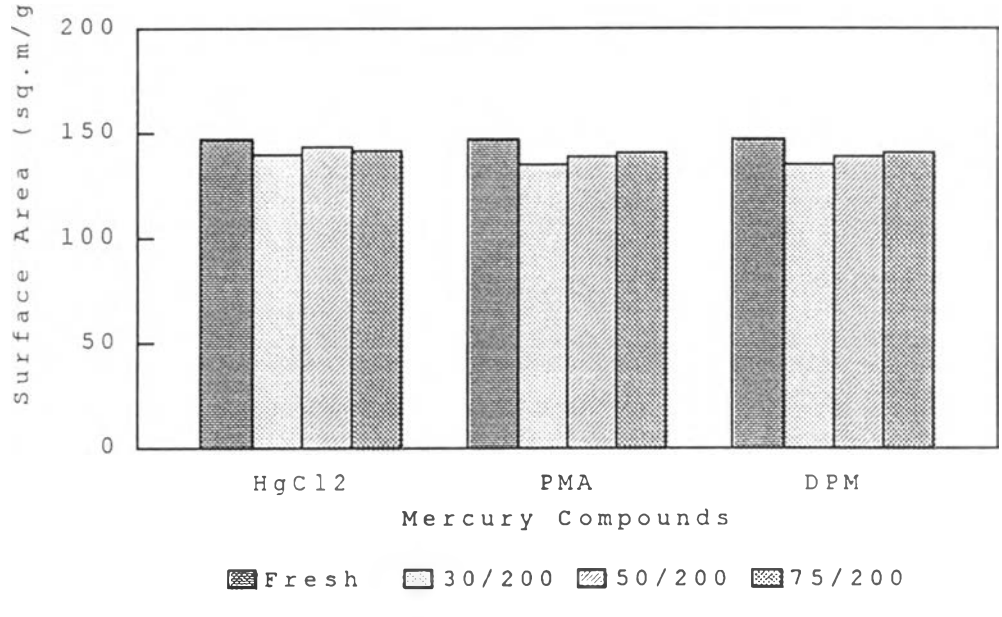

Figure 4.46 Comparison of Surface Area between Fresh and Spent 5.0Zn Adsorbent at Various Temperatures and a Pressure of 200 psig

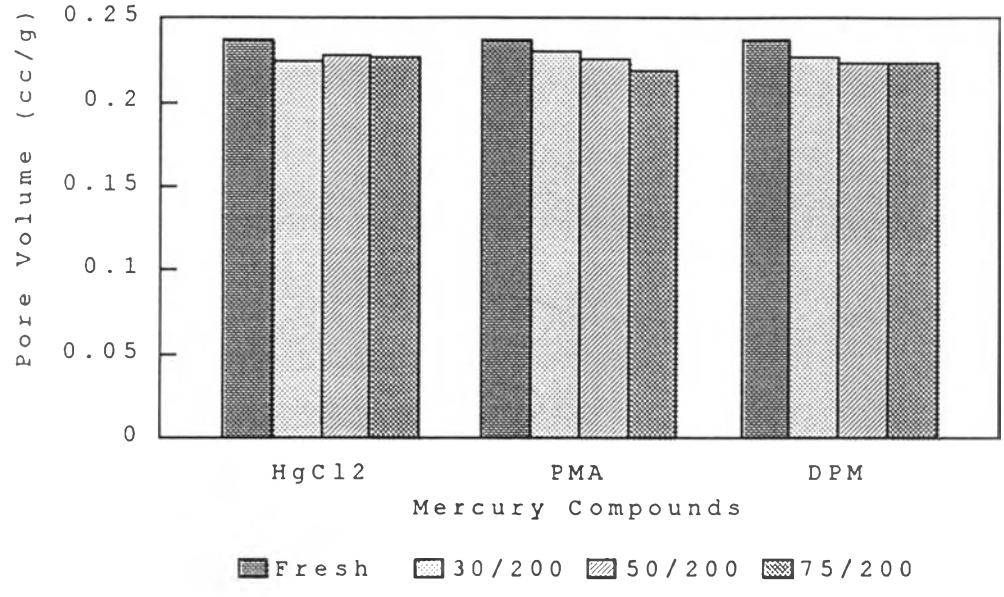

Figure 4.47 Comparison of Pore Volume between Fresh and Spent 2.5Zn Adsorbent at Various Temperatures and a Pressure of 200 psig

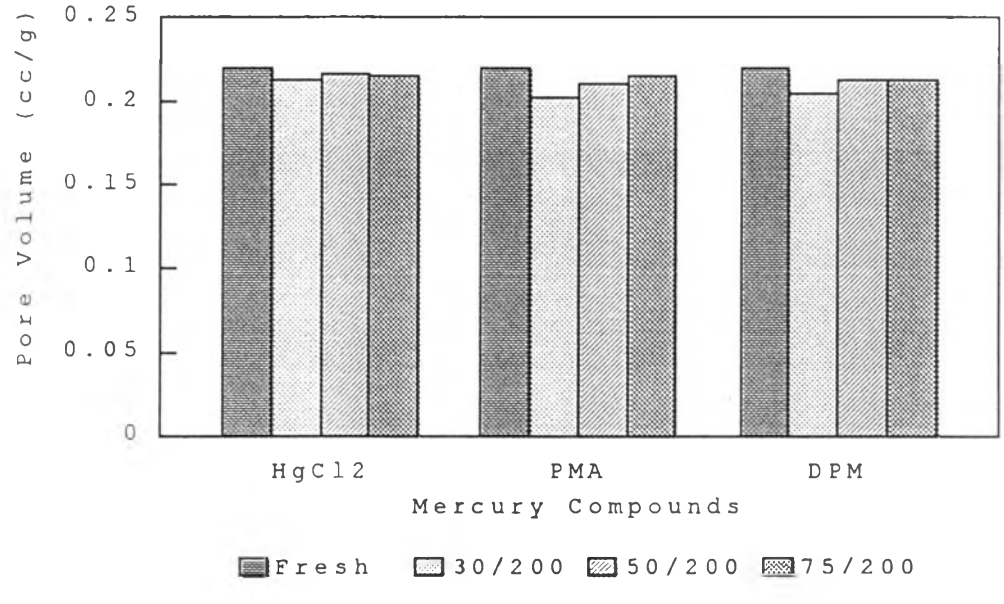

Figure 4.48 Comparison of Pore Volume between Fresh and Spent 5.0Zn Adsorbent at Various Temperatures and a Pressure of 200 psig

mercury decreases very slightly. It can conclude that removal of mercury compounds by zinc adsorbents depends on the nature of mercury compound.

Total surface of fresh and spent zinc adsorbents are compared and illustrated in Figures 4.45 and 4.46. The surface area of spent zinc adsorbent decreases of less than 6.0% with respect to fresh adsorbent. Difference of surface area among operating temperatures do not clearly. Pore volume of fresh and spent zinc adsorbents is shown Figures 4.47 and 4.48. The pore volume of spent 2.5%Zn and 5.0%Zn are less than that of fresh adsorbent for all of mercury compounds. This may result from mercury deposited on each adsorbent.

Pore size distribution of spent zinc adsorbent is

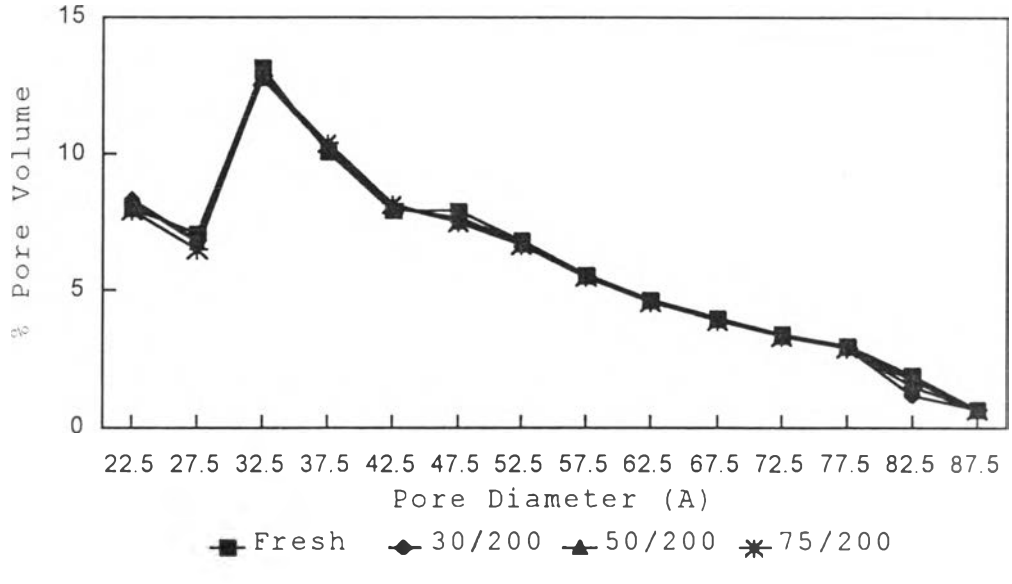

Figure 4.49 Comparison of Pore Size Distribution between Fresh and Spent 2.5Zn Adsorbent in Study of Mercuric Chloride Removal at Various Temperatures and a Pressure of 200 psig

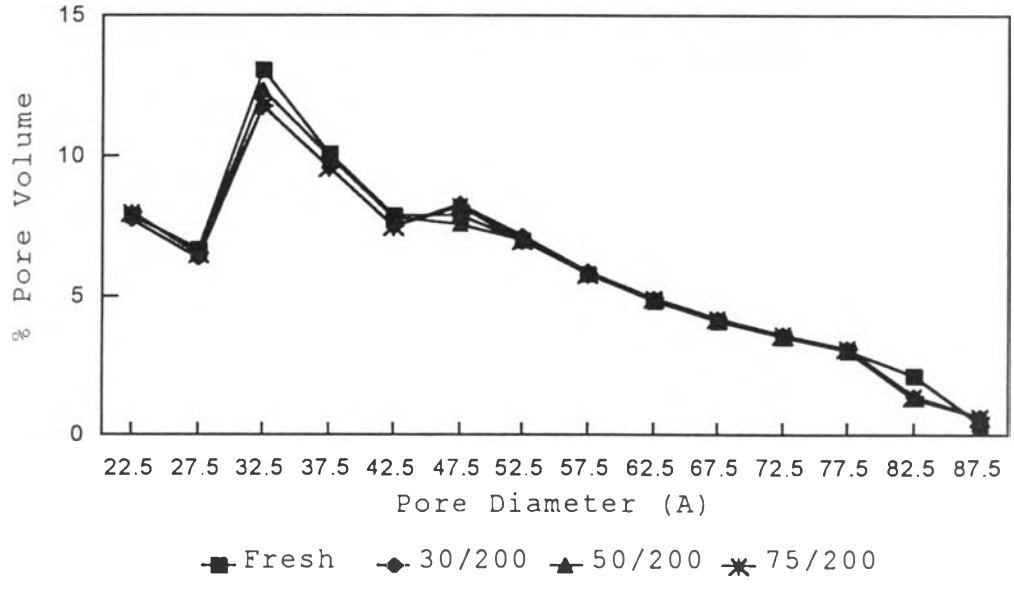

Figure 4.50 Comparison of Pore Size Distribution between Fresh and Spent 5.0Zn Adsorbent in Study of Mercuric Chloride Removal at Various Temperautres and a Pressure of 200 psig

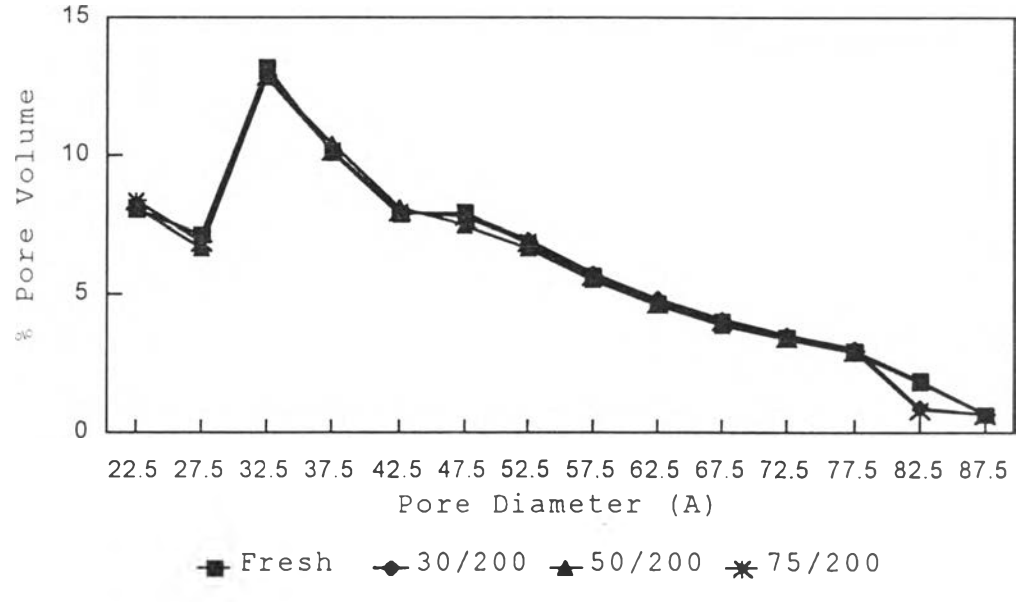

Figure 4.51 Comparison of Pore Size Distribution between Fresh and Spent 2.5Zn Adsorbent in Study of Phenylmercuric Acetate Removal at Various Temperatures and a Pressure of 200 psig

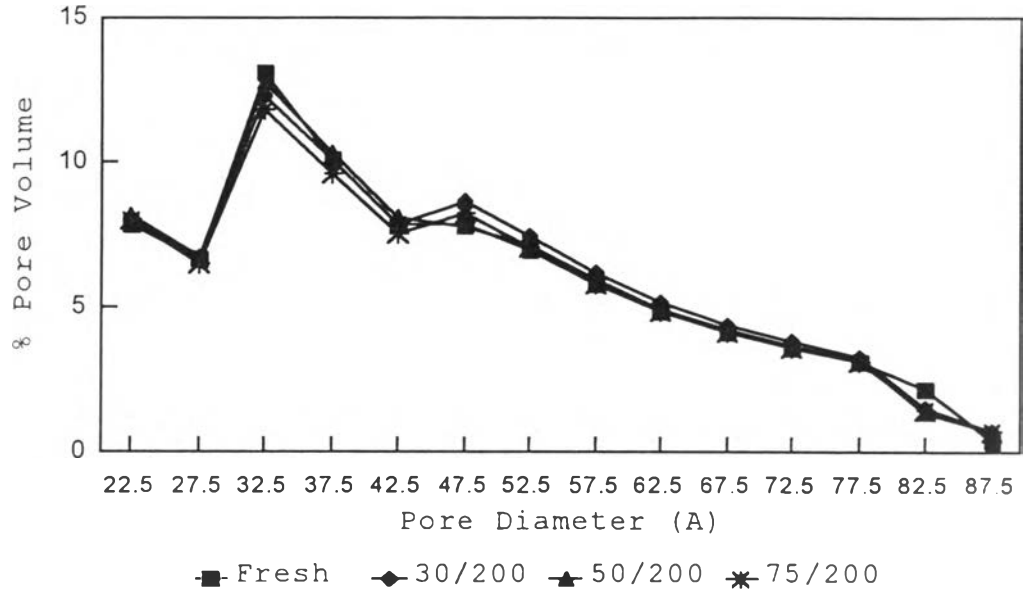

Figure 4.52 Comparison of Pore Size Distribution between Fresh and Spent 5.0Zn Adsorbent in Study of Phenylmercuric Acetate Removal at Various Temperatures and a Pressure of 200 psig

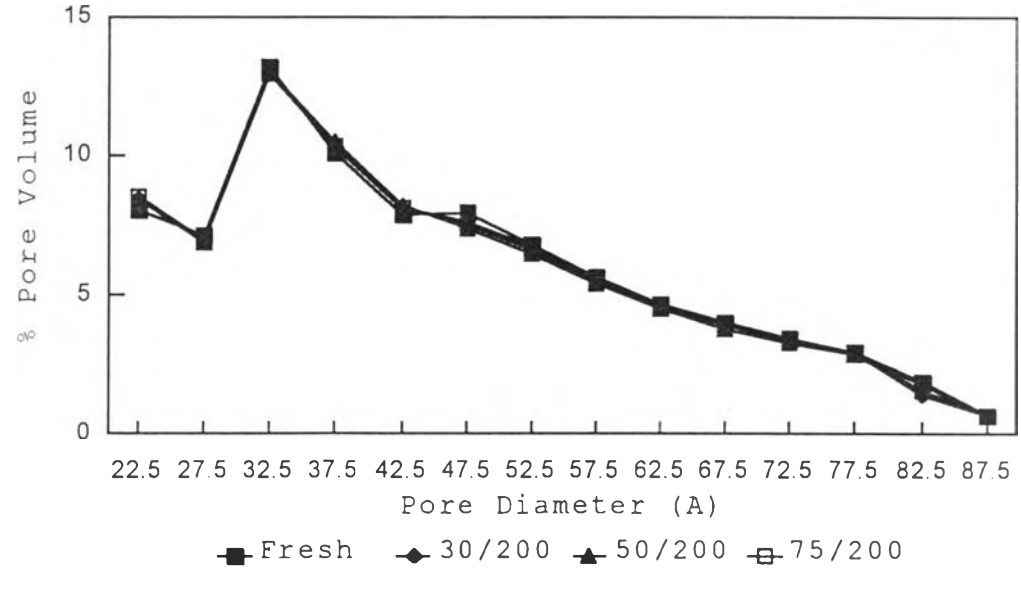

Figure 4.53 Comparison of Pore Size Distribution between Fresh and Spent 2.5Zn Adsorbent in Study of Diphenylmercury Removal at Various Temperatures and a Pressure of 200 psig

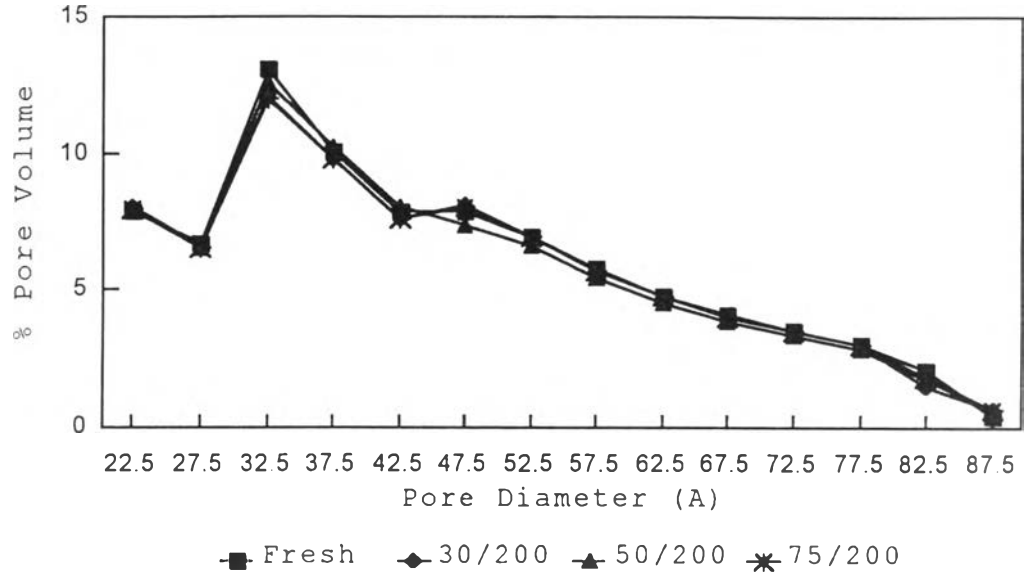

Figure 4.54 Comparison of Pore Size Distribution between Fresh and Spent 5.0Zn Adsorbent in Study of Diphenylmercury Removal at Various Temperatures and a Pressure of 200 psig

compared to fresh adsorbent and illustrated in Figures 4.49 to 4.54. In study of mercuric chloride, pore size distribution of spent adsorbent (in Figures 4.49 and 4.50) does not differ obviously from fresh adsorbent, except at pore size of 47.5°A and 82.5°A. At pore size of 47.5°A and 82.5°A, percent of pore volume is very slightly less than fresh adsorbent. This can be found in pore distribution of zinc adsorbent in study of phenylmercuric acetate and diphenylmercury as shown in Figures 4.51 to 4.54, respectively. However, there is no difference of pore distribution among operating temperatures. It indicates that mercury compounds prefer to adsorb on zinc adsorbent at pore diameter of 47.5°A and 82.5°A.

Effect of copper-zinc adsorbent

Copper-zinc adsorbent is a bimetallic adsorbent which consists of two types of metal. It is prepared by first impregnation of alumina support, then dried and reduced with pure hydrogen gas. After that, the reduced adsorbent is impregnated with approach copper nitrate solution and then reduced in hydrogen stream. Weight ratio of copper to zinc is fixed at 1:1 and total metal loading is kept at 5.0% by weight.

The study on mercury removal by CuZn adsorbent is conducted at a pressure of 200 psig and temperatures varied from 30°C to 75°C . Experimental results are shown in Figure 4.55. The results show that CuZn adsorbent can remove mercury compounds effectively. The concentration of mercury in liquid product decreases significantly with

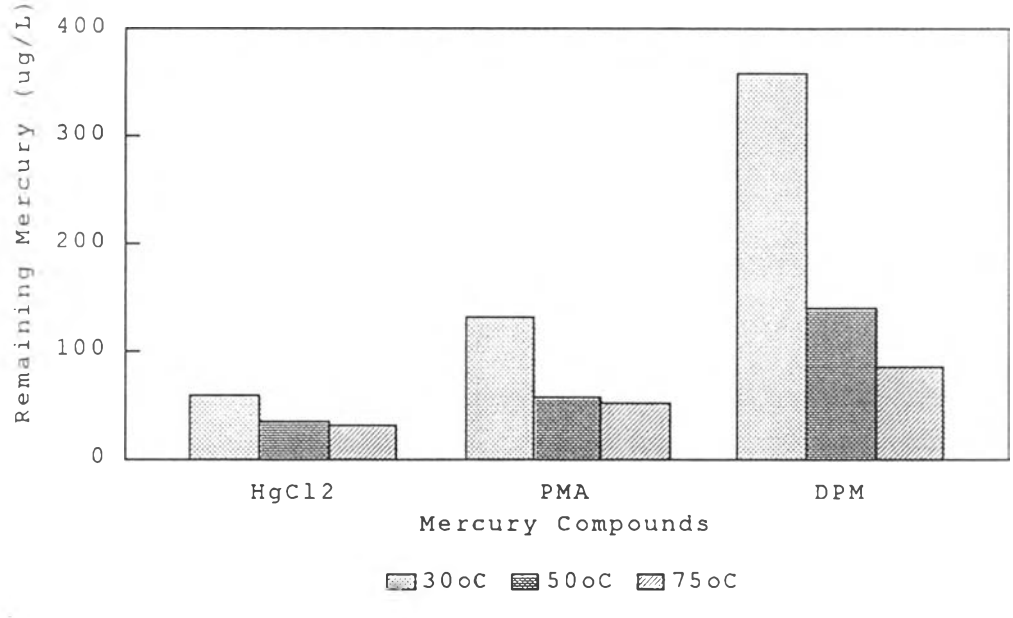

Figure 4.55 Remaining Mercury in Study of CuZn Adsorbent at Various Temperatures and a Pressure of 200 psig

temperature increasing. This can be obtained for all mercury compounds. From this result, it indicates that copper and zinc in bimetallic adsorbent are the active species for mercury removal both inorganic and organic compound.

Total surface area of fresh and spent CuZn adsorbent are shown in Figure 4.56. The surface area of spent CuZn adsorbent decreases of less than 10%, with respect to fresh adsorbent. The decreasing of pore volume is also found as shown in Figure 4.57. Pore size distribution of fresh and spent CuZn adsorbent are shown in Figures 4.58 to 4.60. The variation of pore distribution is practically similar to the distribution of copper adsorbent. In study of mercuric chloride, it is noticed that pore diameter ranging from 22.5°A to 37.5°A, slightly increases while percent of pore volume decreases significantly in pore size from 47.5°A to 77.5°A. At pore diameter of 42.5°A, 82.5°A and 87.5°A, there is no difference of pore distribution. In case of phenylmercuric acetate, the decreasing of pore volume from 47.5°A to 77.5°A is also found. Pore size of 22.5°A and 27.5°A increases but there is no variation in pore diameter of 32.5°A to 42.5°A and 82.5°A to 87.5°A. The pore size distribution of spent CuZn adsorbent in study of diphenylmercury differs slightly from fresh CuZn adsorbent. However, decreasing of pore size ranging from 47.5°A to 72.5°A can be observed. From these results, the adsorption of mercury compounds on CuZn adsorbent takes

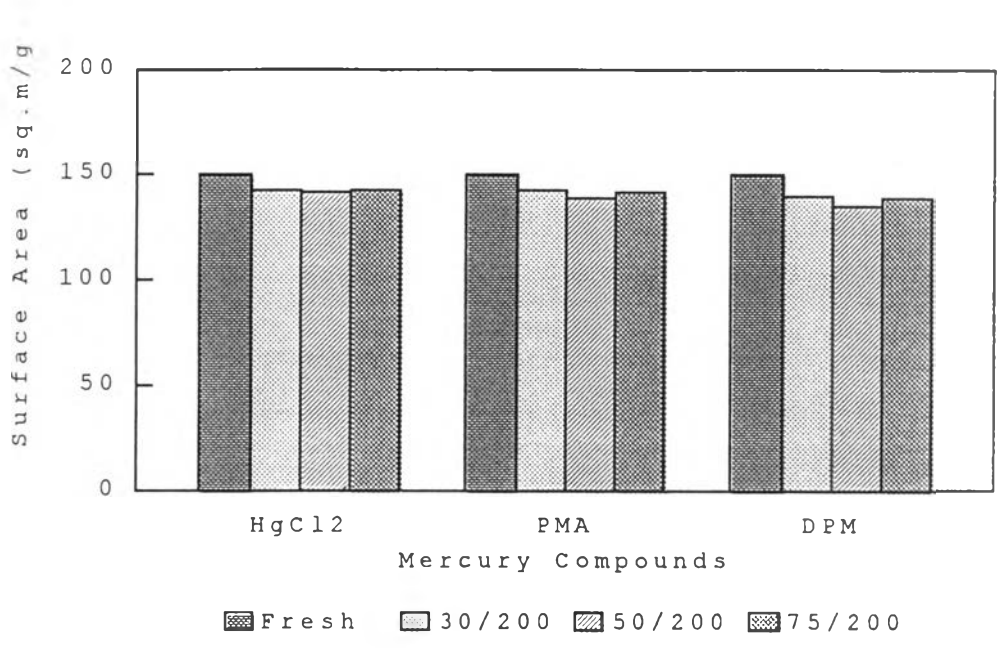

Figure 4.56 Comparison of Surface between Fresh and Spent CuZn Adsorbent at Various Temperatures and a Pressure of 200 psig

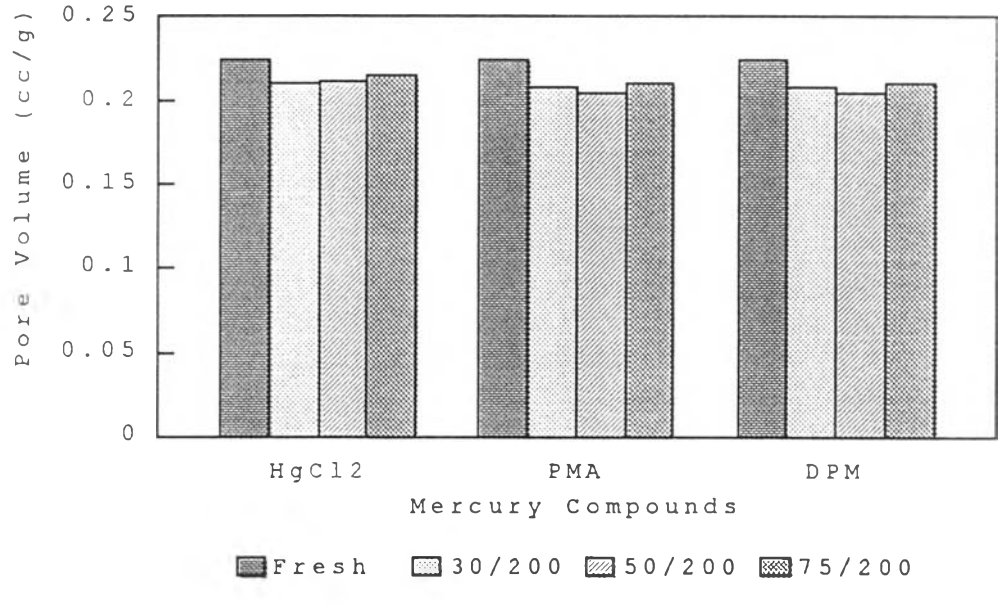

Figure 4.57 Comparison of Pore Volume between Fresh and Spent CuZn Adsorbent at Various Temperatures and a Pressure of 200 psig

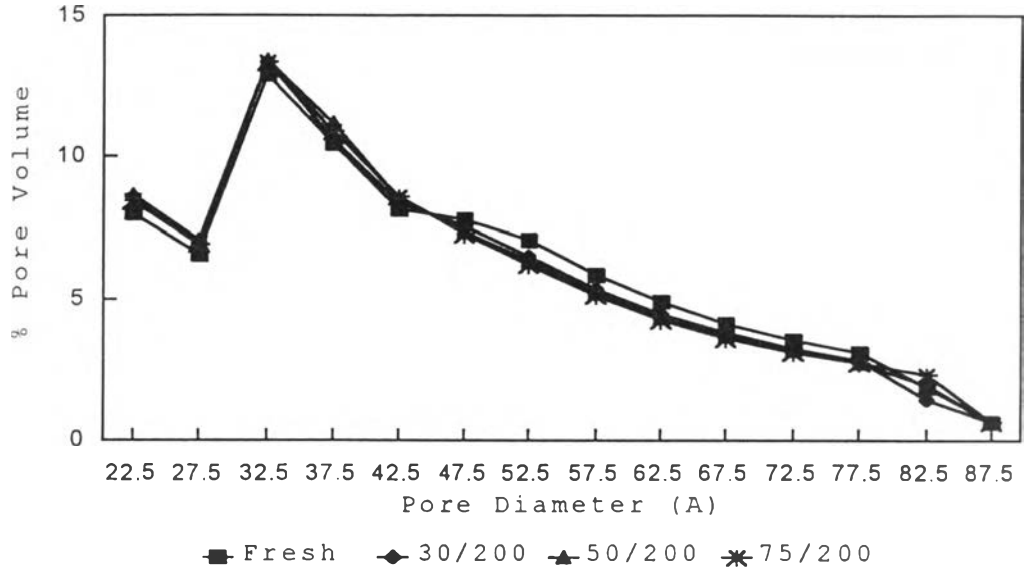

Figure 4.58 Comparison of Pore Size Distribution between Fresh and Spent CuZn Adsorbent in Study of Mercuric Chloride Removal at Various Temperatures and a Pressure of 200 psig

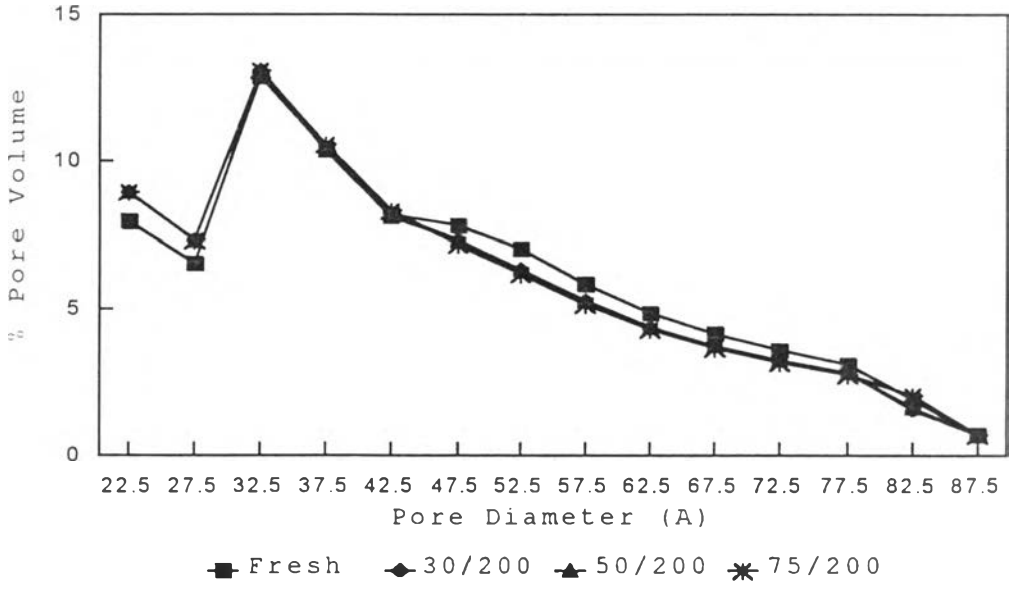

Figure 4.59 Comparison of Pore Size Distribution between Fresh and Spent CuZn Adsorbent in Study of Phenylmercuric Acetate Removal at Various Temperatures and a Pressure of 200 psig

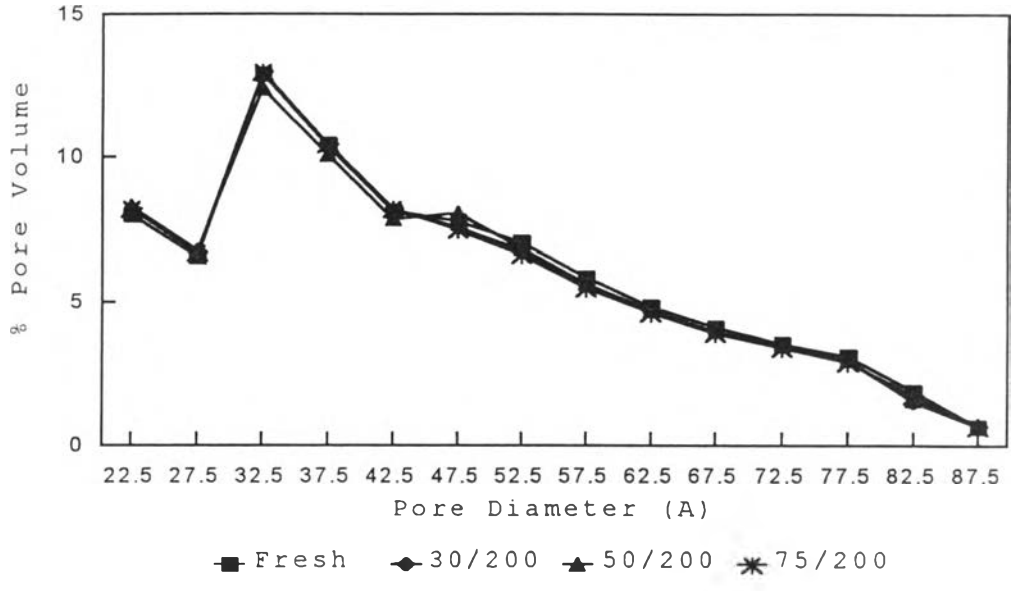

Figure 4.60 Comparison of Pore Size Distribution between Fresh and Spent CuZn Adsorbent in Study of Diphenylmercury Removal at Various Temperatures and a Pressure of 200 psig

place more effectively at pore diameter from 47.5°A to 77.5°A and lesser at pore size of 22.5°A to 37.5°A. Itcan be found that variation of pore size distribution of spent copper-zinc adsorbent is rather the same as that of the copper adsorbent. This indicates that the most surface of copper-zinc adsorbent is covered by loaded copper.