CHAPTER IV

RESULTS AND DISCUSSIONS

Procedures

A 300-ml stirred batch reactor is used to evaluate arsenic removal by alumina, nickel, molybdenum and nickel-molybdenum adsorbents. Phenylarsine oxide and arsenic oxide which represent typical arsenic compounds in petroleum are used as models of organic and inorganic arsenics. There are 356 experiments in this study which are categorized into five parts.

Part A - Preliminary experiments are conducted to find the suitable quantity of adsorbent and contacting time.

Part B - The experiments are conducted to study experimental errors.

Part C - The experiments are directed to study effect of reactor on arsenic adsorption (Blank Test).

Part D - The experiments are designed to study effects of pressures and temperatures.

Part E - The experiments are conducted to study the effects of each adsorbents.

In each experiments, 100 mL of toluene containing are arsenic compound is used as a feedstock. The adsorbents that used are Al_2O_3, Ni/Al_2O_3, Mo/Al_2O_3, $Ni\text{-}Mo/Al_2O_3$ and $Mo\text{-}Ni/Al_2O_3$. During each experiment, the pressure in batch reactor is controlled by nitrogen gas. The liquid samples and adsorbents are separated and kept after each experiments to analyze for their characteristics.

Before start-up of each experiments, the system is checked for leak by gradually pressurizing with nitrogen gas. The leak test is carried out at pressure that is 100 psig higher than operating pressure. A pressure drop of 10 psig in 30 minutes is a maximum acceptable leak.

After each experiment, the mixture is separated to liquid product and spent adsorbent by filter paper (Whatman No.1). The liquid product is digested with acid solution and then extracted with water to separate arsenic from toluene phase to water phase. Arsenic in water is analyzed for its concentration by Graphite Furnace Atomic Absorption Spectroscopy. The spent adsorbent is dried in muffle furnace at 100°C for 3 hours to remove volatile substances. Then, fresh and spent adsorbents are analyzed for pore size distribution, pore volume and total surface area by Micromeritics AZAP 2000.

Toluene is chosen as a liquid carrier because it has good solubility for arsenic compounds, high boiling point (maintains in liquid state), and negligible conversion at our operating conditions. Phenylarsine oxide, an organic arsenic compound, and arsenic oxide, an inorganic arsenic compound, are chosen as arsenic model compounds because of their presence in petroleum. Initial concentration of phenylarsine oxide is selected to be 20 ppm which is the because its concentration commonly found in petroleum (Fish and Brinckman, 1983). Initial concentration of arsenic oxide is selected to be 10 ppm (its maximum solubility in toluene). Adsorbents are prepared by dry impregnation technique. The gramma alumina is prepared from aluminum hydroxide. Aluminum hydroxide is dehydrated and calcined at about 900°C in CO_2 stream. Therefore, the individual alumina particles is coated with a thin layer of aluminum oxycarbonate approximating the formula $[Al_2(OH)_5]_2CO_3.H_2O$. Details and results of each experiments are shown in Appendix A.

Results and Discussions

Effect of quantity of Adsorbent and Contacting Time

The objectives of this section are to find a suitable quantity of adsorbent and a suitable length of time required for each experiment which are used in subsequent studies. The experiments are conducted at a temperature of 30°C and a pressure of 400 psig. Alumina is used as an adsorbent.

The suitable quantity of adsorbent is evaluated by conducting experiments with variation of adsorbent weight, from 0.3 gram to 1.0 gram for phenylarsine oxide study and from 0.01 gram to 0.1 gram for arsenic oxide study, at fixed contacting time of 60 minutes. Figures 4.1 and 4.2 show the results of this study which indicate that remaining arsenic in the solution depends on quantity of adsorbent. When higher quantity of adsorbent is used in the reactor, the remaining arsenic concentration is lower. Increasing the amount of adsorbent gives more surface of adsorbent for arsenic adsorption. When 0.3 gram and 0.4 gram are used for phenylarsine oxide removal, the remaining arsenic concentration is rather high and has uncertain values. The remaining arsenic concentration approaches 0 ppb when adsorbent weight of more than 0.6 gram is used. Consequently, the weight of adsorbent chosen for further study is 0.5 gram. Similarly, adsorbent weight of 0.03 gram is found to be the suitable quantity for arsenic oxide removal study.

The suitable length of time is evaluated by conducting experiments with variation of time, from 15 minutes to 120 minutes. The weight of alumina adsorbent is chosen at 0.5 gram and 0.03 gram for phenylarsine remval and arsenic oxide removal, respectively. Figures 4.3 and 4.4 show the results of this study which indicate that remaining arsenic, both phenylarsine oxide and arsenic oxide, in the solution depends on the length of time. The remaining arsenic decreases rapidly in the initial period (0-30 minutes), and approaches a constant value at the final period (30-120 minutes). In the initial period, the concentration of arsenic in bulk of solution is high and causes the arsenic to adsorb on the adsorbent and accumulate on its surface quickly.

During the last period, the remaining arsenic concentration in solution is nearly constant and it is much less than that of the initial period. Slope of concentration curve in during the last period approaches to zero which means adsorption of arsenic on adsorbent is slow. The suitable time from this study is the time which the concentration of remaining arsenic is independent of time. So, the experimental time of 60 minutes is chosen for further study.

From the previous section, the results show that adsorption of arsenic on alumina depends strongly on concentration of arsenic in solution. If arsenic is maintained in high concentration, arsenic can be adsorbed on alumina continuously. This can be confirmed by the study of adsorptive capacity of alumina in arsenic removal. Alumina adsorbent is used for removal of 50 ppm of phenylarsine oxide for 5 times. Figure 4.5 shows the comparison of remaining phenylarsine oxide versus number of times. It shows that the remaining arsenic increases linearly with the number of times. However, the remaining arsenic in each times is less than the initial concentration (50ppm). This indicates that arsenic can be adsorbed on alumina as long as the concentration in solution is high. The results is corresponded to the above assumption.

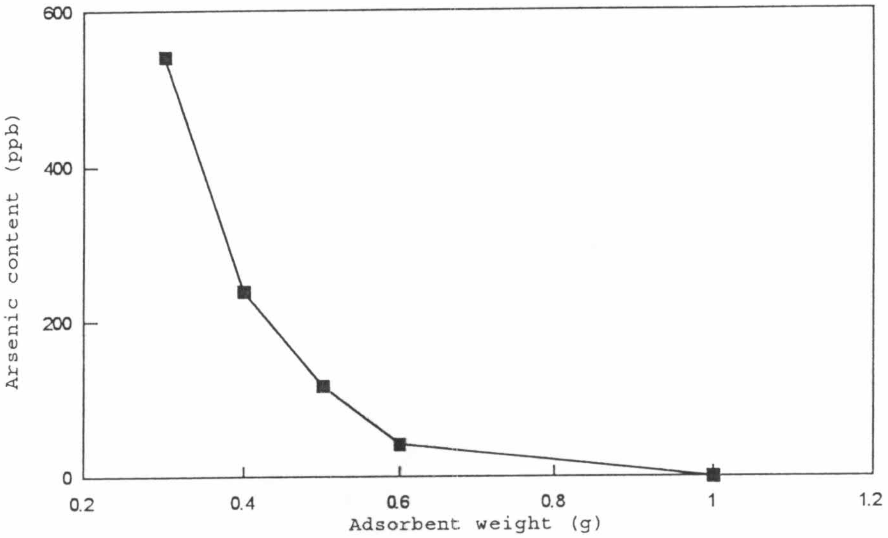

Figure 4.1 Remaining phenylarsine oxide at 30°C and 400 psig in study the effect of the amount of adsorbent.

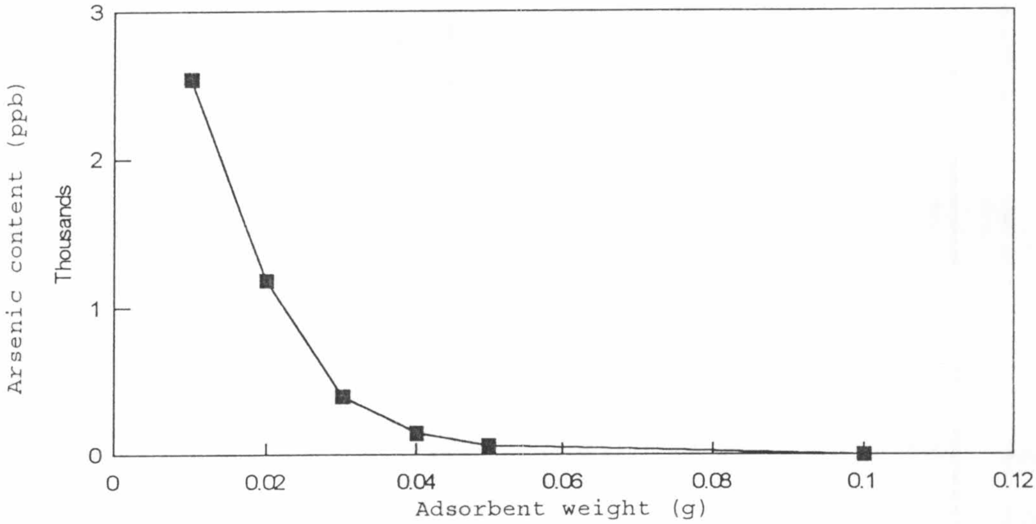

Figure 4.2 Remaining arsenic oxide at 30 °C and 400 psig in study the effect of the amount of adsorbent.

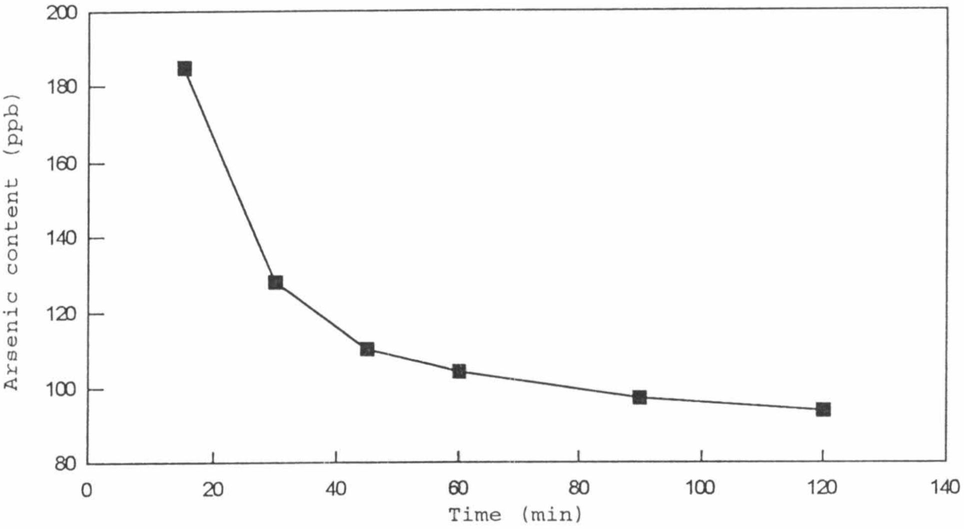

Figure 4.3 Remaining phenylarsine oxide at 30°C and 400 psig in study the effect of contacting time.

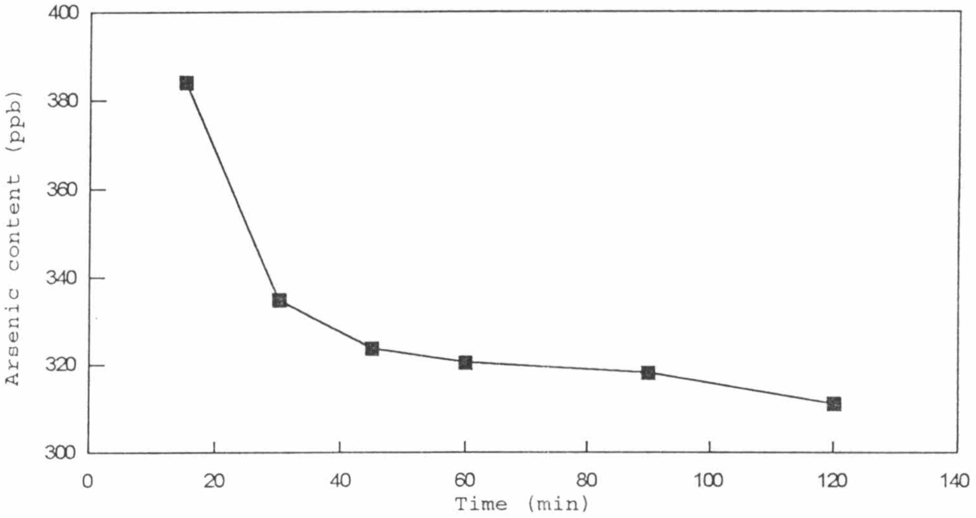

Figure 4.4 Remaining arsenic oxide at 30°C and 400 psig in study the effect of contacting time.

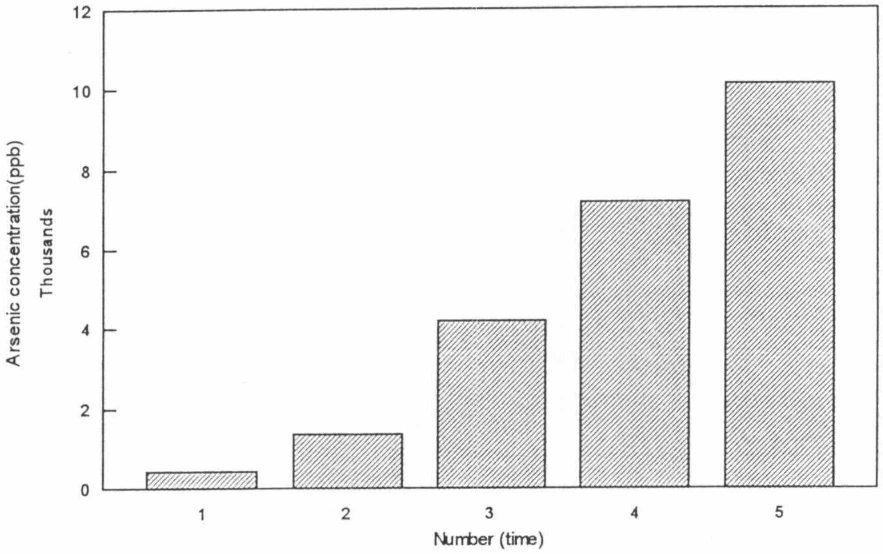

Figure 4.5 Remaining phenylarsine oxide which used alumina in each times at 30°C and 400 psig.

Effect of Reactor

The objective of this section is to find the adsorption ability of arsenic on reactor wall and to confirm that arsenic does not disappear by other parameters, except adsorption on adsorbent. There is no adsorbent used in this section. The temperatures are varied from 30°C to 75°C (30, 50 and 75°C) and pressures are varied from 200 psig to 600 psig (at an increment of 200 psig.). The remaining arsenic in product is shown in Figures 4.6 to 4.7. The results show that arsenic concentration in feed and product is almost identical. It indicates that phenylarsine oxide and arsenic oxide

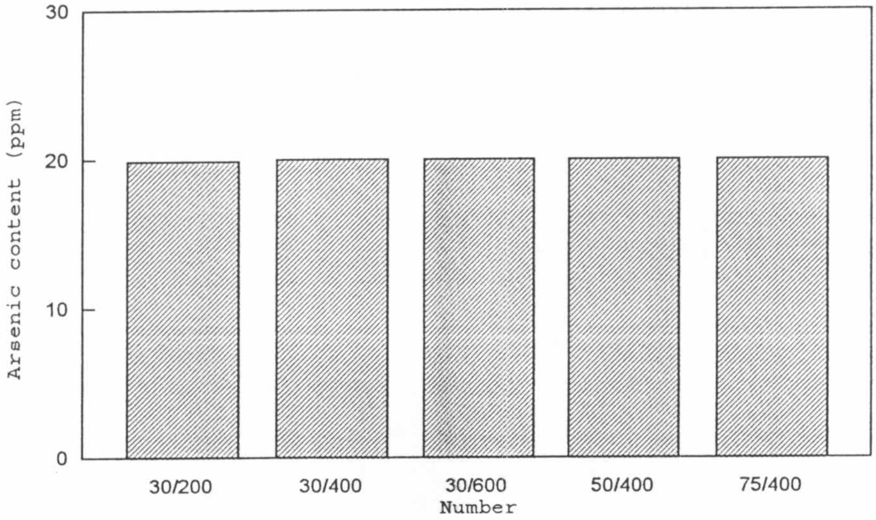

Figure 4.6 Remaining phenylarsine oxide which used alumina at 30°C and 400 psig in study the the effect of reactor.

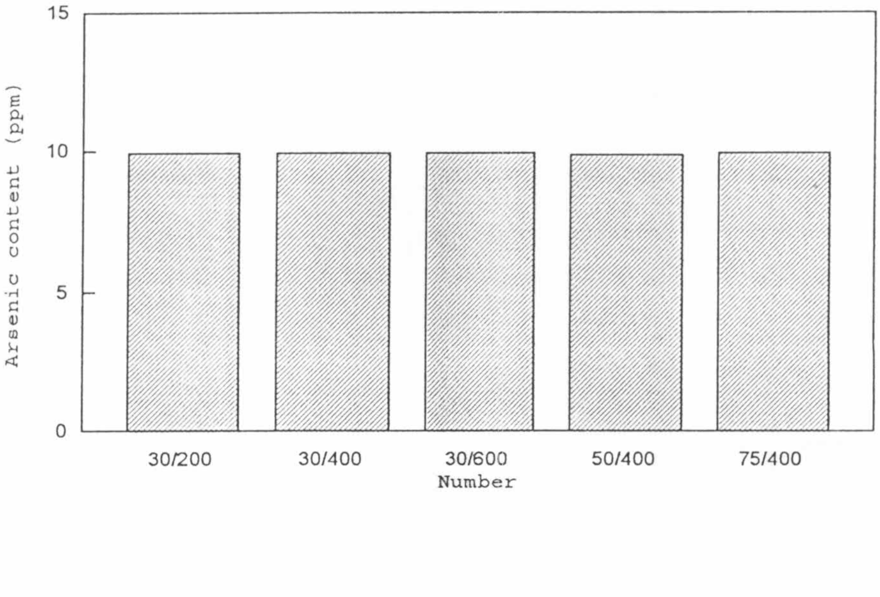

Figure 4.7 Remaining arsenic oxide at 30°C and 400 psig in study the effect of reactor.

are not adsorbed on stainless steel which is used to make the reactor and does not disappear by other parameters.

The small difference of arsenic concentration between feed and product is that expected for the error of analysis alone.

Experimental Errors

This section is conducted to verify repeatability of the experiments and to find error limits cover whole ranges of the experiments. The results are calculated for their average values and maximum and minimum errors. Six set of experiment are conduced at temperatures 30°C, 30°C and 75°C and pressure of 400 psig. Eight experiments are conducted at the same conditions in each set. The adsorbent is alumin.

Remaining arsenic at pressure and temperatures chosen for these experiments are shown in Figures 4.8 and 4.9. Average values, errors of remaining arsenic and percent arsenic removal are calculated and listed in Tables 4.1 and 4.2. The average values of remaining arsenic at temperatures of 30°C, 50°C and 75°C are 102.7 ppb, 50.15 ppb and 28.01 ppb, for phenylarsine study and 365.21 ppb, 279.43 ppb and 137.01 ppb, for arsenic oxide study. The results are reproducible in the range of 20% and 12% in the studies of phenylarsine oxide and arsenic oxide, respectively. Percent removal of arsenic is 99.4%, 99.75% and 99.86%, for phenylarsine oxide study and 96.35%, 97.21% and 98.63%, for arsenic oxide study.

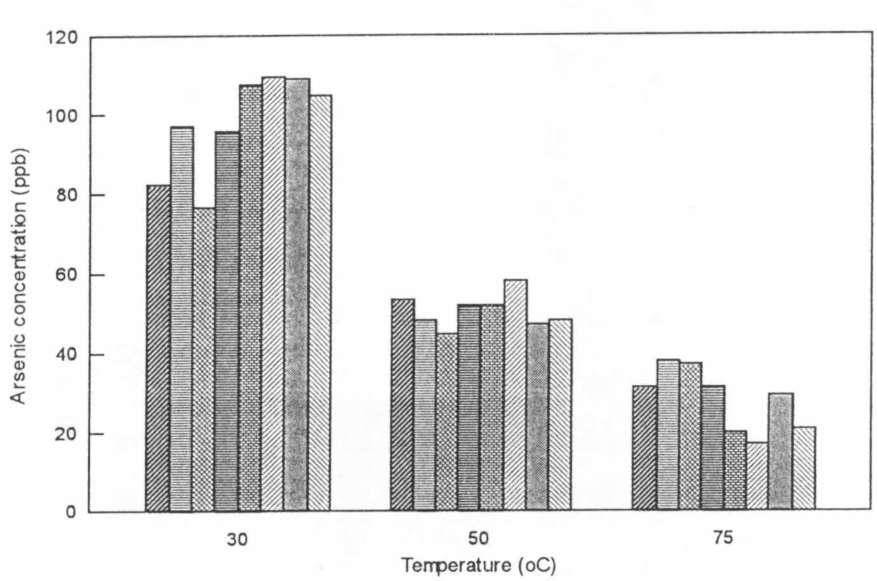

Figure 4.8 Repeatability of phenylarsine oxide removal at temperatures from 30°C to 75°C and pressure at 400 psig.

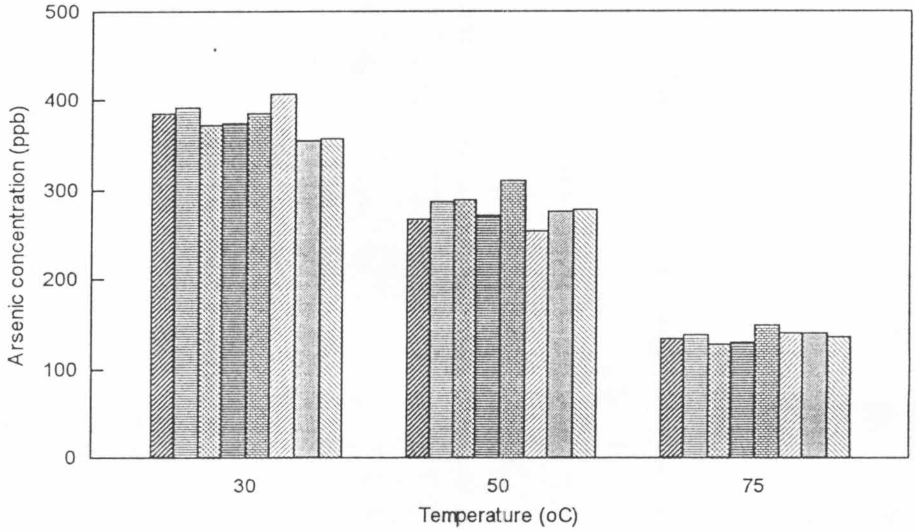

Figure 4.9 Repeatability of arsenic oxide removal at temperatures from 30°C to 75°C and pressure at 400 psig.

Deviation of percent removal phenylarsine oxide is low and can be neglected.

Table 4.1 Average and percent deviation of remaining arsenic at temperatures from 30°C to 75°C and pressure at 400 psig.

Temperature (oC)	Phenylarsine Oxide			Arsenic Oxide		
	Aver.Conc.	Deviation(%)		Aver.Conc.	Deviation(%)	
		max.	min.		max.	min.
30	102.7	16.16	20.16	365.21	7.61	8.57
50	50.15	15.25	11.07	279.43	11.44	9.17
75	28.01	19.3	14.95	137.01	3.06	7.74

Table 4.2 Average and percent deviation of percent removal of arsenic at temperatures from 30°C to 75°C and pressure at 400 psig.

Temperature (°C)	Phenylarsine Oxide		Arsenic Oxide	
	Average %removal	%Deviation	Average %removal	%Deviation
30	99.49	0.03	96.35	0.07
50	99.75	0.01	97.21	0.06
75	99.86	0.01	98.63	0.03

Effects of Pressures and Temperatures

This section is designed to study the effect of operating pressures and temperatures. This study is performed at difference conditions in order to compare the efficiency of arsenic removal. The temperatures are varied from 30°C to 75°C and pressures are varied from 200 psig to 600 psig. Five types of adsorbents which used in this study are alumina, Ni/Al2o3, Mo/Al_2O_3, $Mo-Ni/Al_2O_3$ and $Ni-Mo/Al_2O_3$. Ni/Al_2O_3 and Mo/Al_2O_3 are varied loading from 2.5% to 10% by weight based on alumina support. Percent total metal loading in $Mo-Ni/Al_2O_3$ and $Ni-Mo/Al_2O_3$ is kept on 10% by weight based on alumina support and the ratios of nickel and molybdenum are varies from 1:3 to 3:1. The amount of adsorbent is 0.5 gram and 0.03 gram in study of phenylarsine oxide and arsenic oxide, respectively.

Figures 4.10 and 4.11 show the comparison of remaining arsenic which uses alumina as the adsorbent at operating pressures and temperatures. The results indicate that the removal of arsenic, including phenylarsine oxide and arsenic oxide is shown to be independent of pressures but is sharply dependent on temperatures. The removal of arsenic increases as the temperature of the condition increases. This effect of pressure and temperature on arsenic removal by molybdenum adsorbents are corresponded to the others that shown in Figures 4.12 through 4.39.

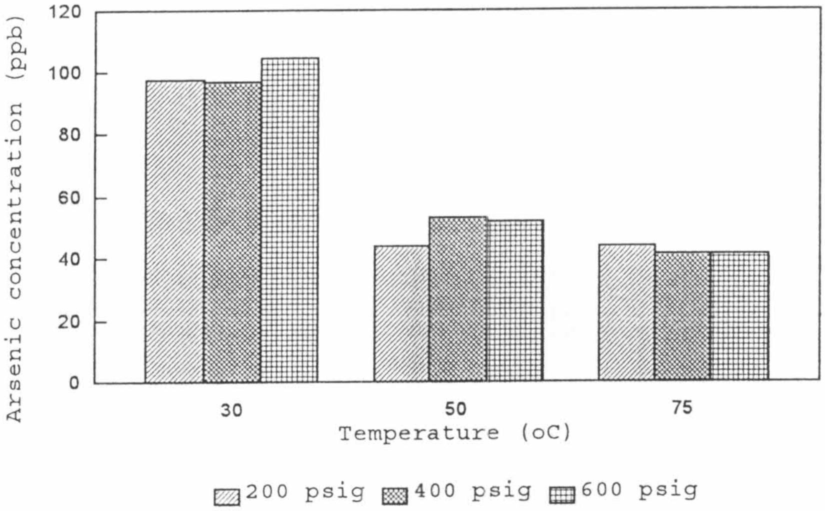

Figure 4.10 Remaining phenyarsine oxide in study the effect of pressures and temperatures on efficiency of alumina adsorbent.

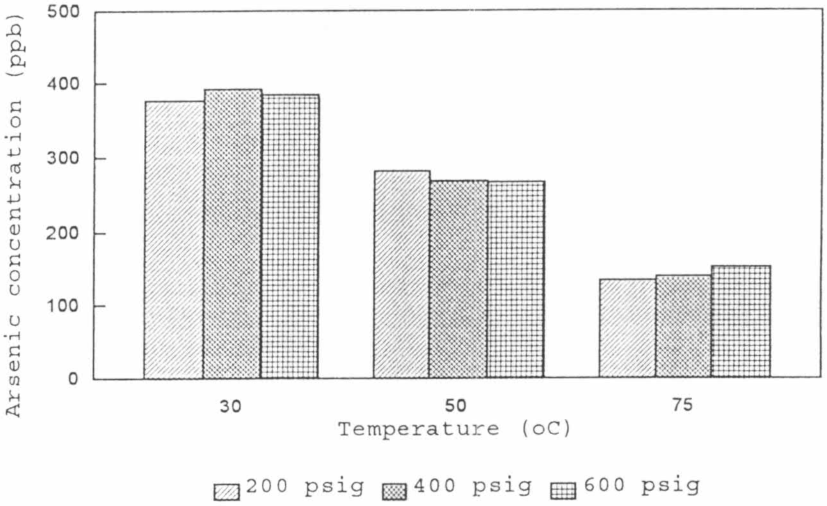

Figure 4.11 Remaining arsenic oxide in study the effect of pressures and temperatures on efficiency of alumina adsorbent.

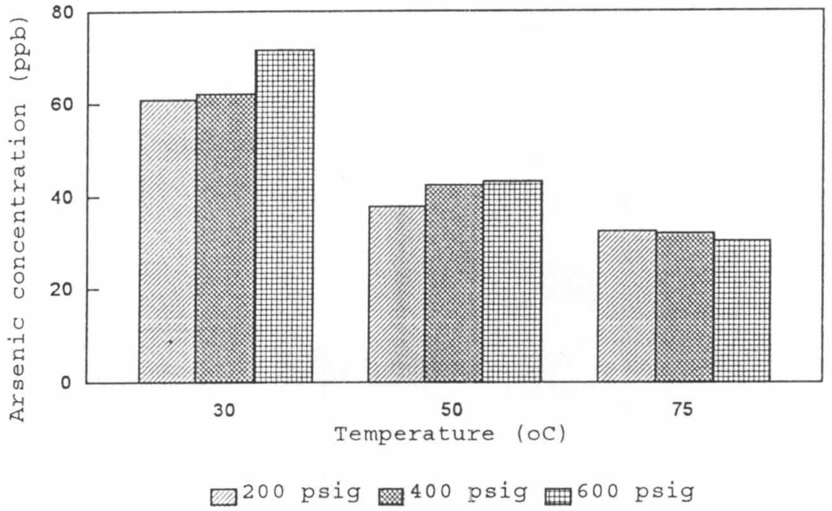

Figure 4.12 Remaining phenyarsine oxide in study the effect of pressures and temperatures on efficiency of 2.5 Ni adsorbent.

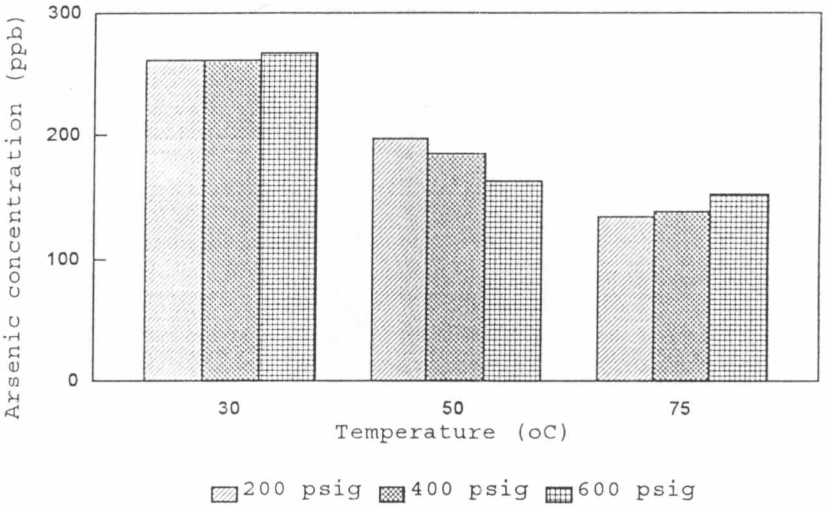

Figure 4.13 Remaining arsenic oxide in study the effect of pressures and temperatures on efficiency of 2.5 Ni adsorbent.

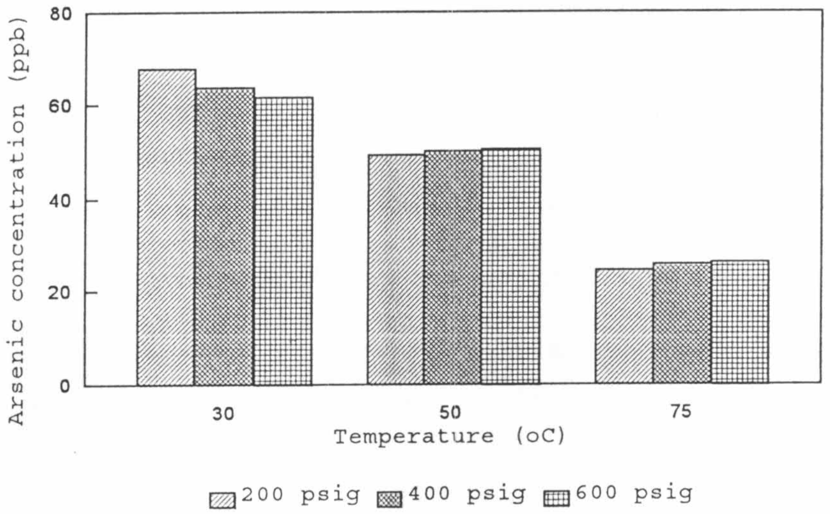

Figure 4.14 Remaining phenyarsine oxide in study the effect of pressures and temperatures on efficiency of 5 Ni adsorbent.

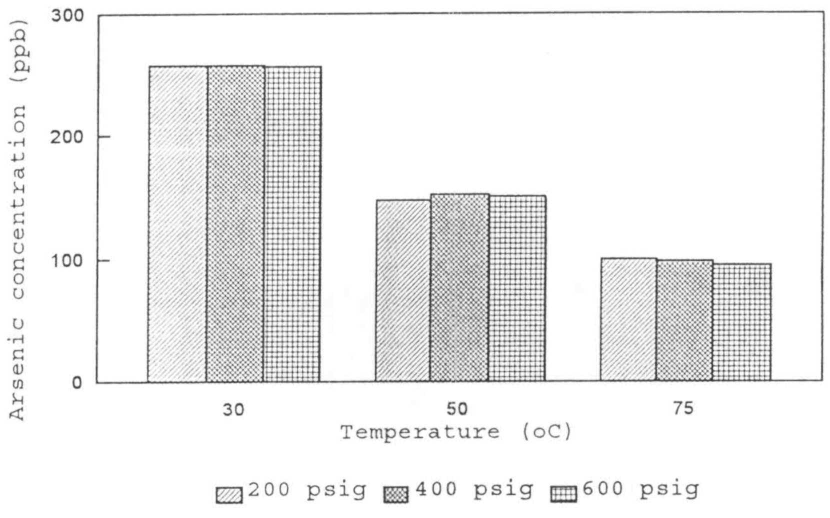

Figure 4.15 Remaining arsenic oxide in study the effect of pressures and temperatures on efficiency on 5 Ni adsorbent.

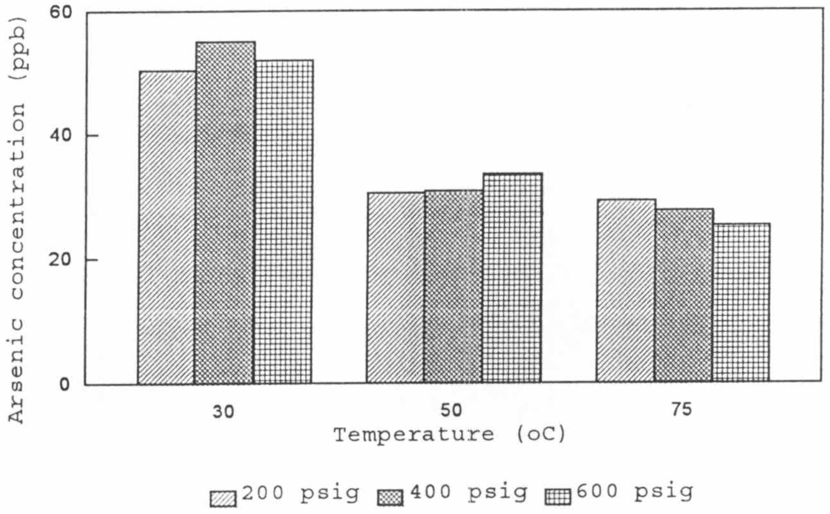

Figure 4.16 Remaining phenyarsine oxide in study the effect of pressures and temperatures on efficiency of 7.5 Ni adsorbent.

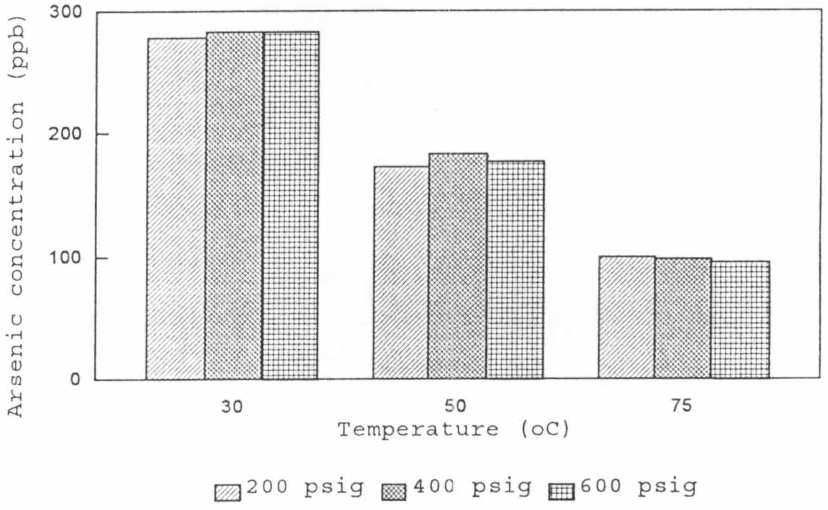

Figure 4.17 Remaining arsenic oxide in study the effect of pressures and temperatures on efficiency of 7.5 Ni adsorbent.

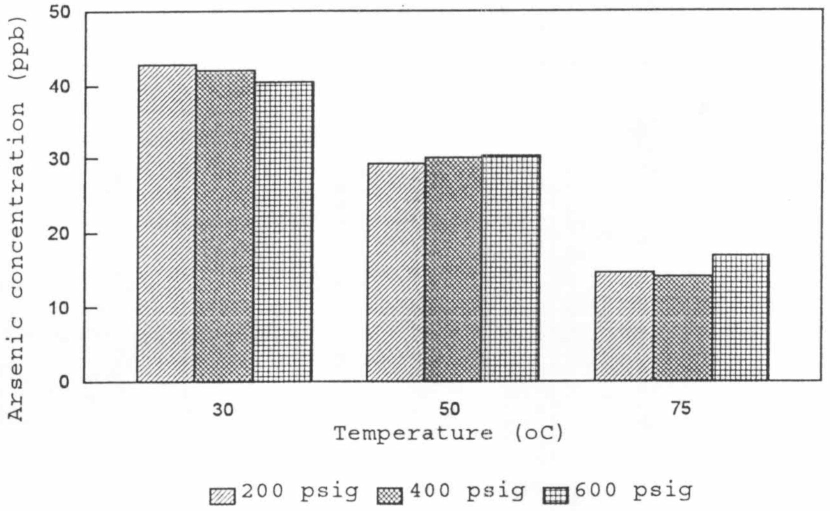

Figure 4.18 Remaining phenyarsine oxide in study the effect of pressures and temperatures on efficiency of 10 Ni adsorbent.

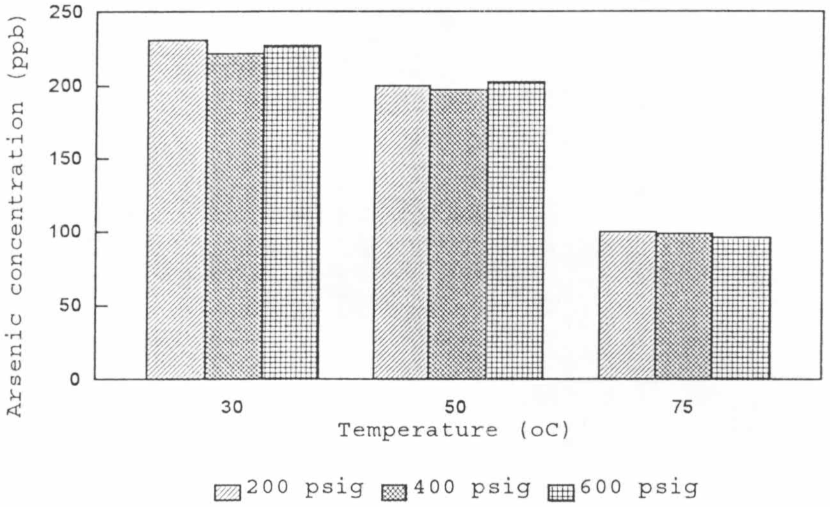

Figure 4.19 Remaining arsenic oxide in study the effect of pressures and temperatures on efficiency of 10 Ni adsorbent.

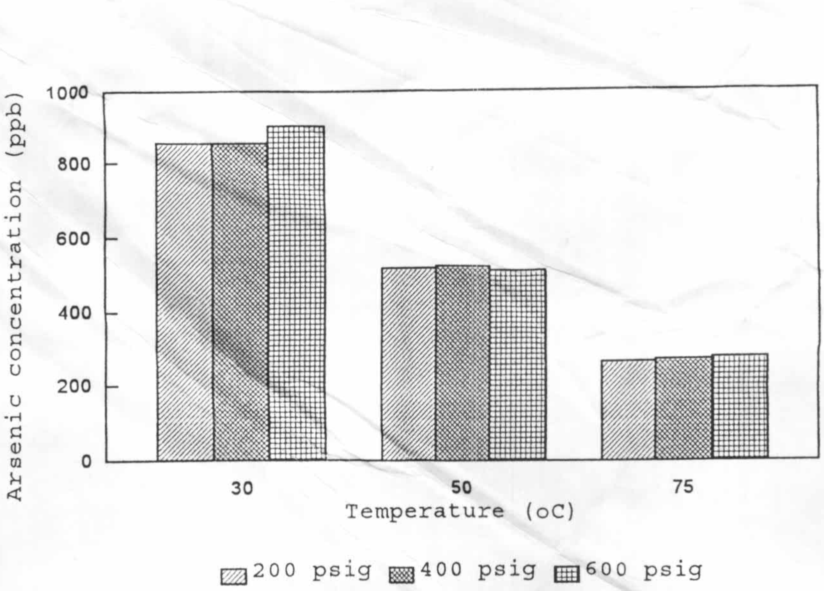

Figure 4.20 Remaining phenylarsine oxide in study the effect of pressures and temperatures on efficiency of 2.5 Mo adsorbent.

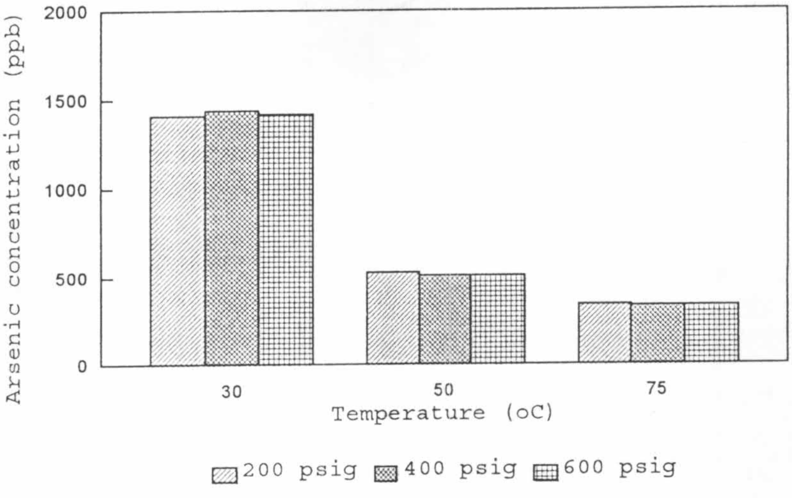

Figure 4.21 Remaining arsenic oxide in study the effect of pressures and temperatures on efficiency of 2.5 Mo adsorbent.

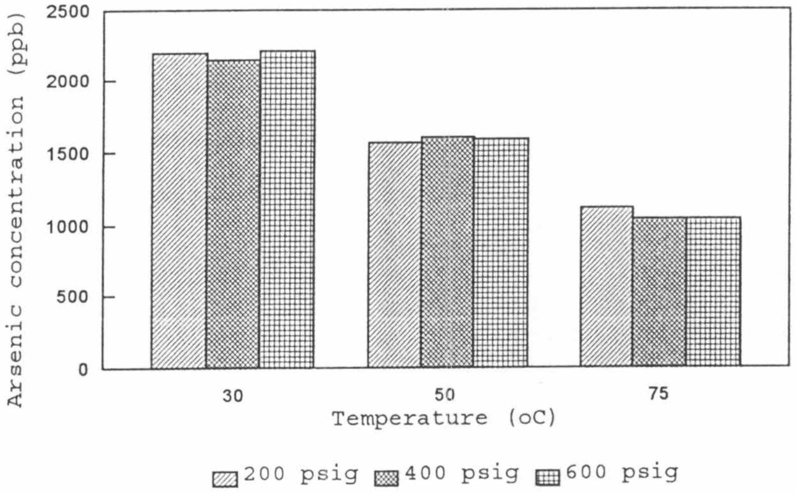

Figure 4.22 Remaining phenylarsine oxide in study the effect of pressures and temperatures on efficiency of 5 Mo adsorbents.

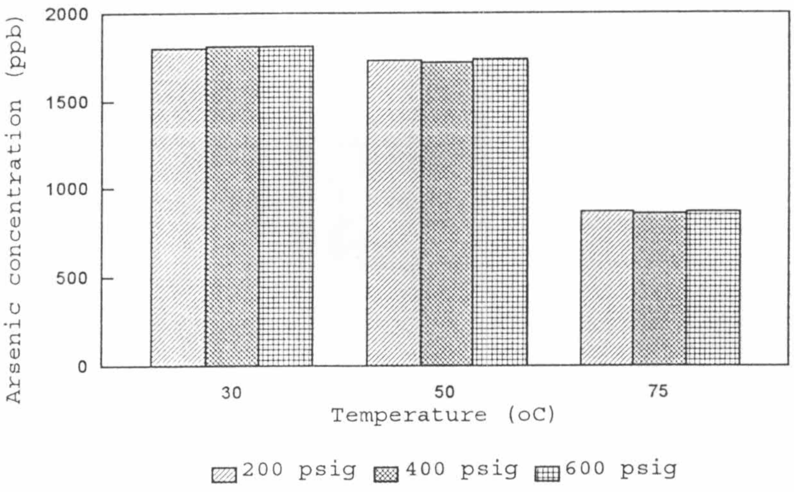

Figure 4.23 Remaining arsenic oxide in study the effect of pressures and temperatures on efficiency of 5 Mo adsorbent.

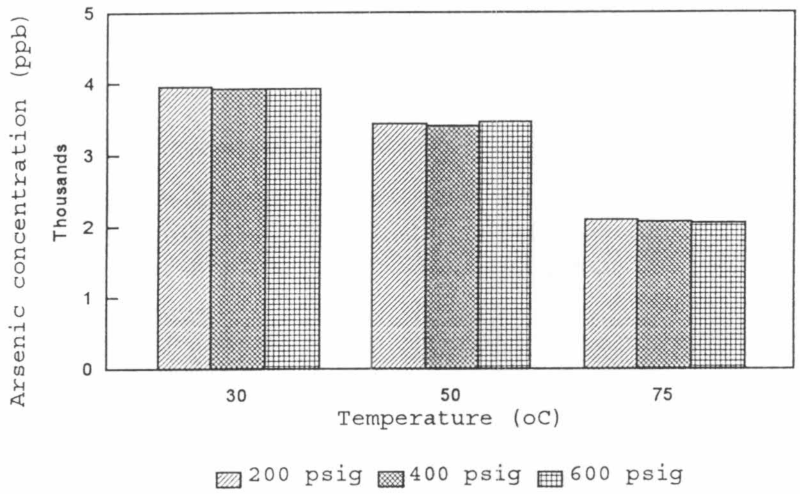

Figure 4.24 Remaining phenylarsine oxide in study the effect of pressures and temperatures on efficiency of 7.5 Mo adsorbent.

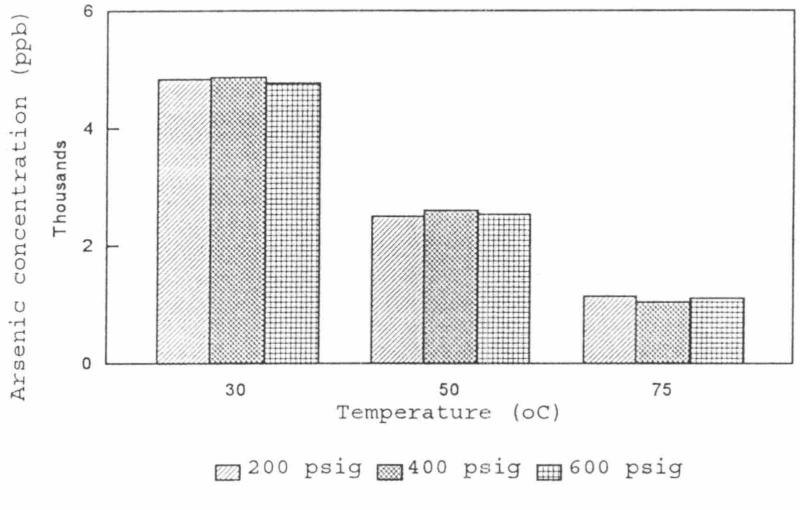

Figure 4.25 Remaining arsenic oxide in study the effect of pressures and temperatures on efficiency of 7.5 Mo adsorbent.

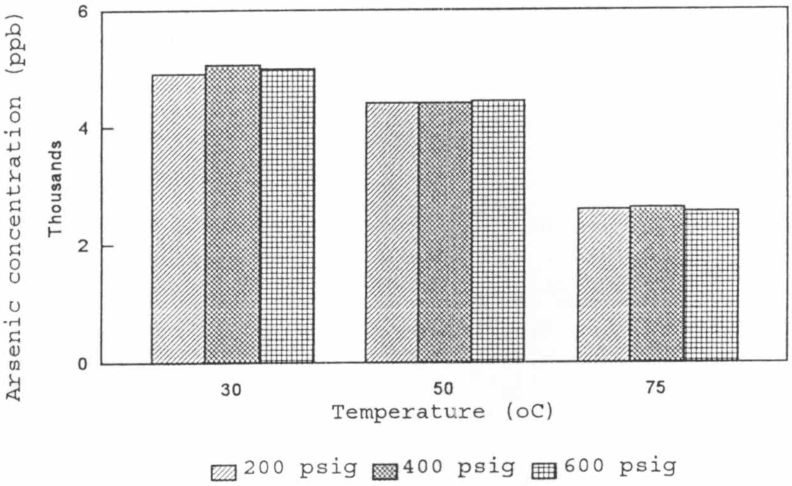

Figure 4.26 Remaining phenylarsine oxide in study the effect of pressures and temperatures on efficiency of 10 Mo adsorbents.

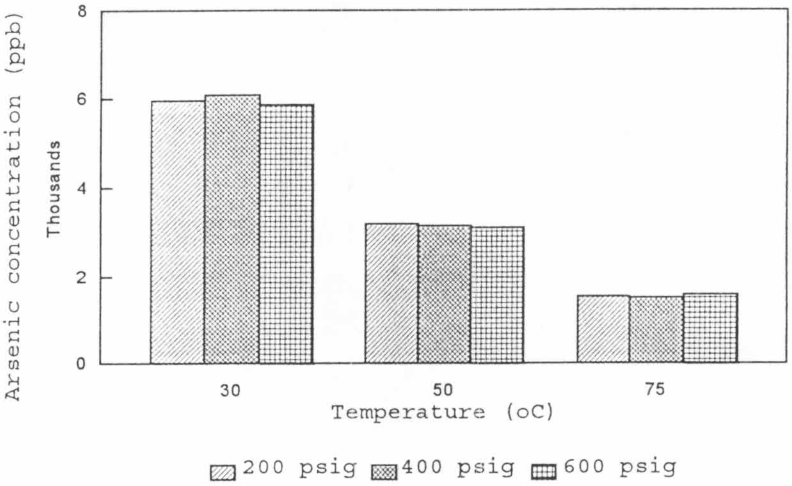

Figure 4.27 Remaining arsenic oxide in study the effect of pressures and temperatures on efficiency of 10 Mo adsorbent.

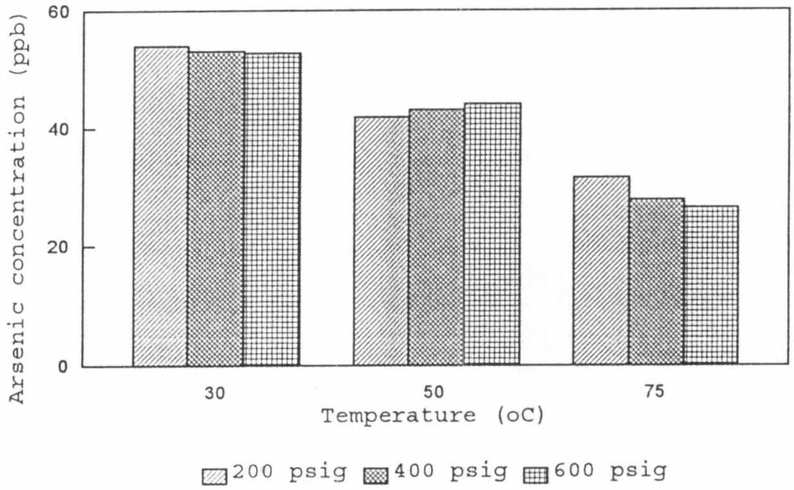

Figure 4.28 Remaining phenylarsine oxide in study the effect of pressures and temperatures on efficiency of 2.5-7.5 MoNi adsorbent.

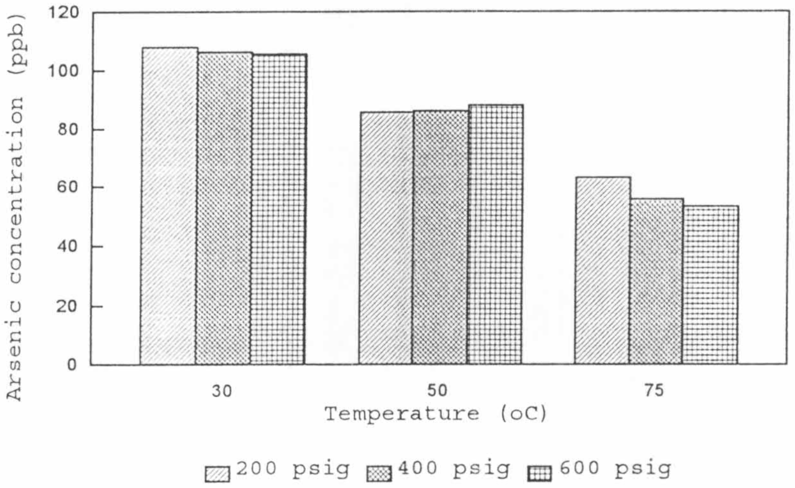

Figure 4.29 Remaining arsenic oxide in study the effect of pressures and temperatures on efficiency of 2.5-7.5 MoNi adsorbent.

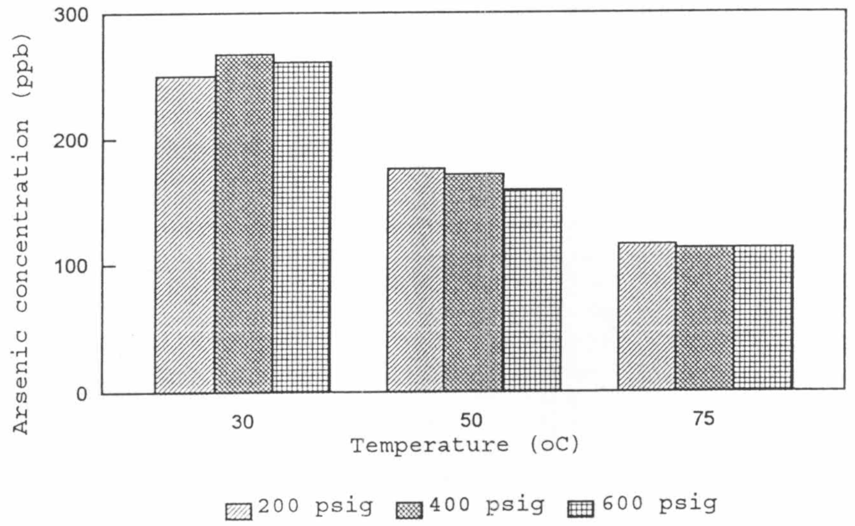

Figure 4.30 Remaining phenylarsine oxide in study the effect of pressures and temperatures on efficiency of 5-5 MoNi adsorbent.

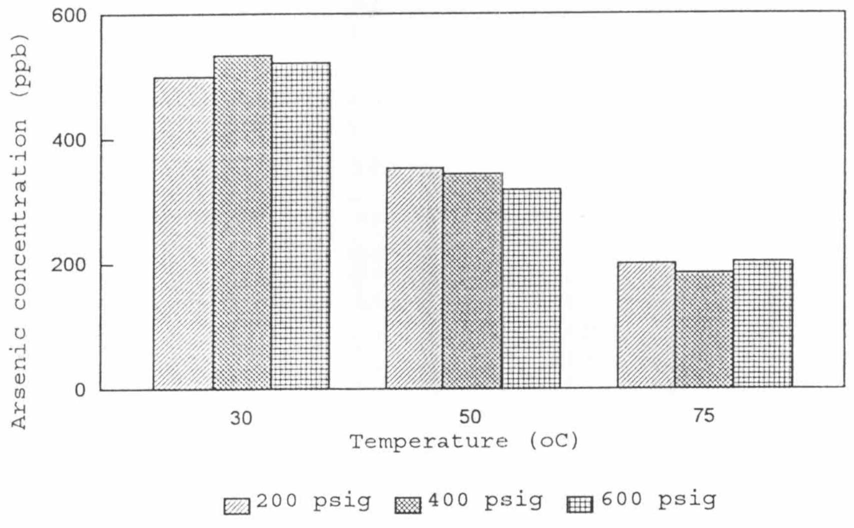

Figure 4.31 Remaining arsenic oxide in study the effect of pressures and temperatures on efficiency of 5-5 MoNi adsorbent.

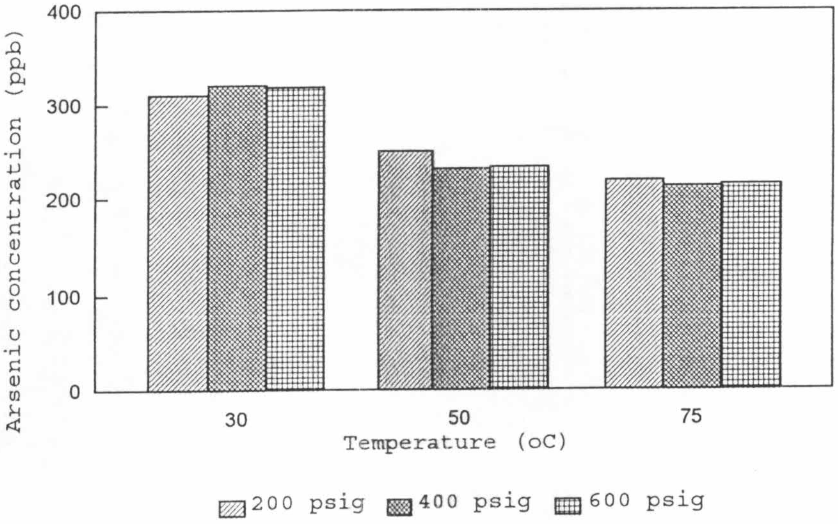

Figure 4.32 Remaining phenylarsine oxide in study the effect of pressures and temperatures on efficiency of 7.5-2.5 MoNi adsorbent.

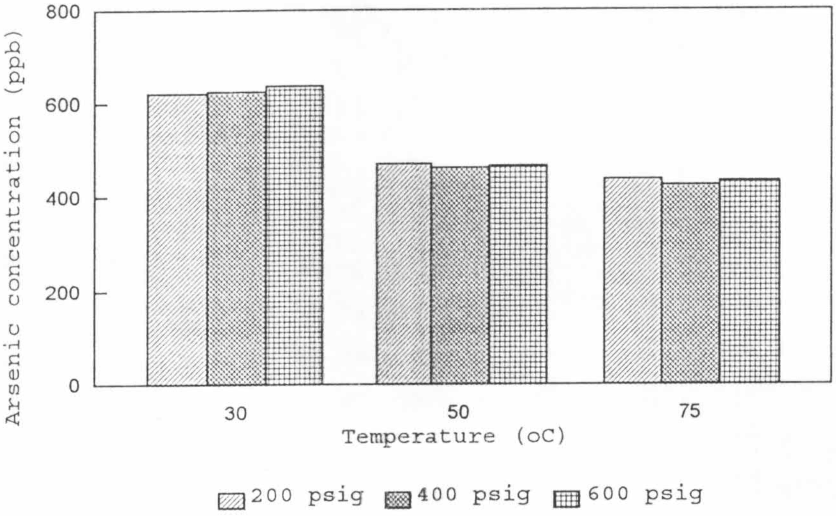

Figure 4.33 Remaining arsenic oxide in study the effect of pressures and temperatures on efficiency of 7.5-2.5 MoNi adsorbent.

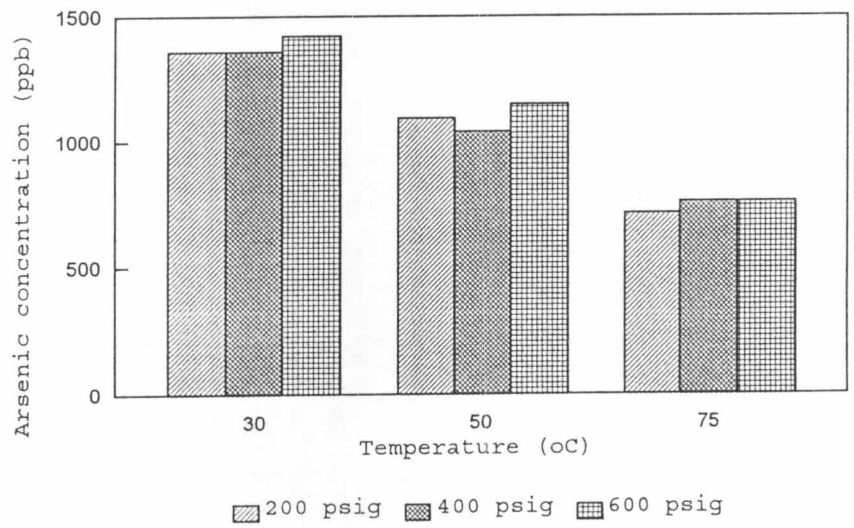

Figure 4.34 Remaining phenylarsine oxide in study the effect of pressures and temperatures on efficiency of 2.5-7.5 NiMo adsorbent.

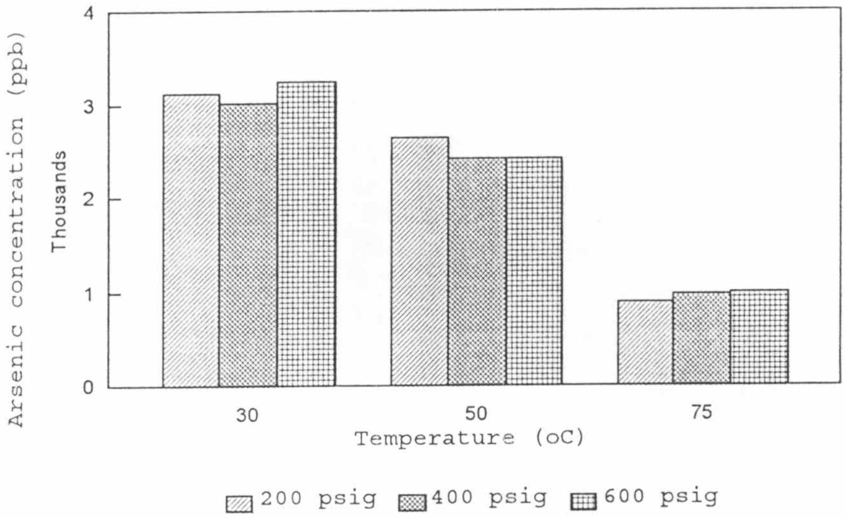

Figure 4.35 Remaining arsenic oxide in study the effect of pressures and temperatures on efficiency of 2.5-7.5 MoNi adsorbent.

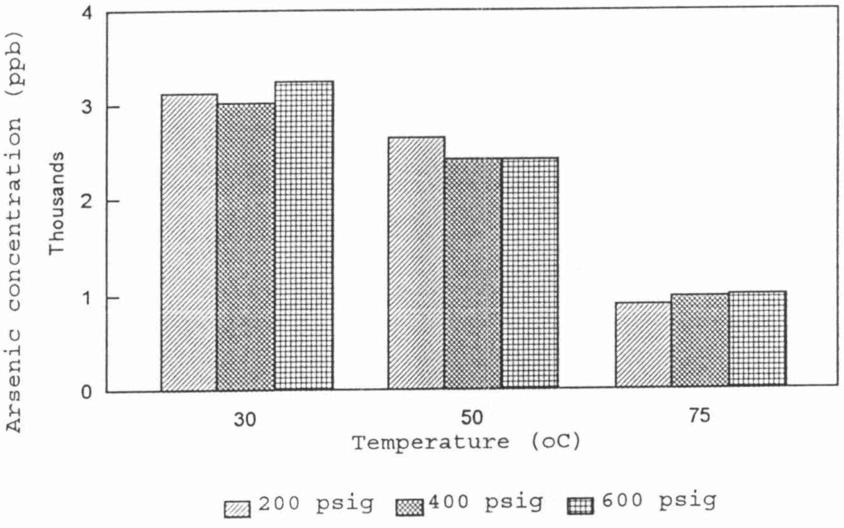

Figure 4.36 Remaining phenylarsine oxide in study the effect of pressures and temperatures on efficiency of 5-5 NiMo adsorbent.

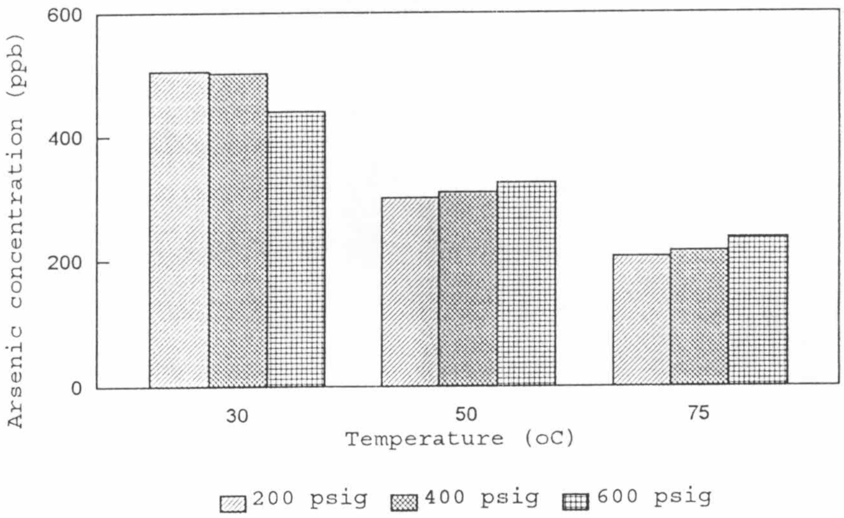

Figure 4.37 Remaining arsenic oxide in study the effect of pressures and temperatures on efficiency of 5-5 MoNi adsorbent.

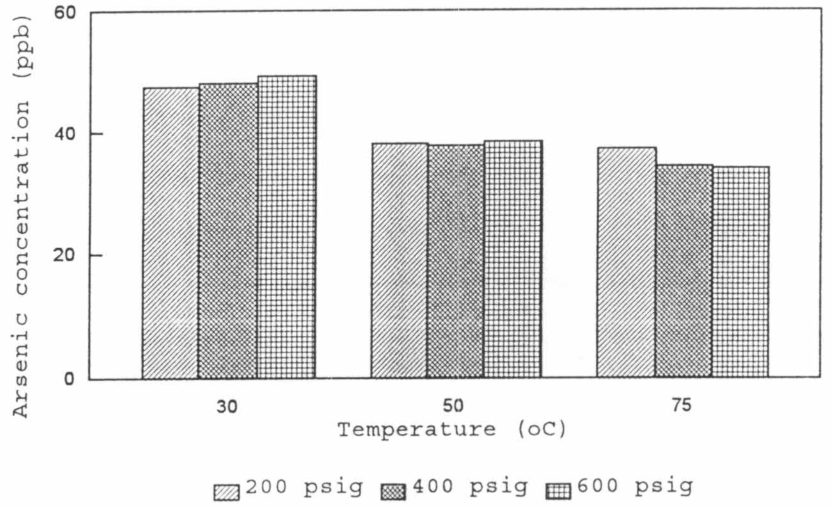

Figure 4.38 Remaining phenylarsine oxide in study the effect of pressures and temperatures on efficiency of 7.5-2.5 NiMo adsorbent.

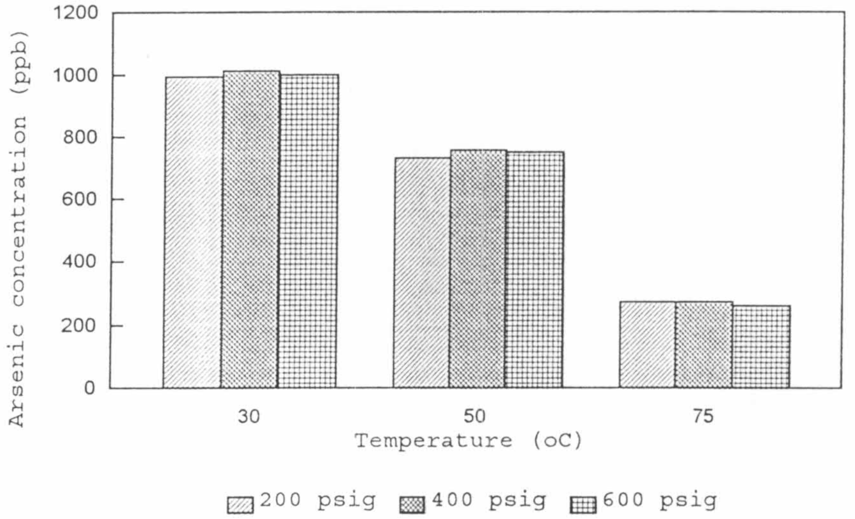

Figure 4.39 Remaining arsenic oxide in study the effect of pressures and temperatures on efficiency of 7.5-2.5 NiMo adsorbent.

In generally, the adsorption of arsenic on adsorbent depends on;

1) Factor from external adsorbent

2) Factor from internal adsorbent

Factor from external adsorbent, comes from the average molar flux from the bulk liquid to the external surface (W_{Ar}).

$$W_{Ar} = k_c(C_{Ao}-C_{As})$$

C_{Ao} and C_{As} are the concentration of reactant A in bulk of liquid and external surface of adsorbent, respectively. K_c is defined as the external mass transfer coefficient. It is considered as the ability of diffusion from bulk to external surface of adsorbent.

$$K_c = 0.6\underbrace{\left(\frac{D_{AB}^{2/3}}{\nu^{1/6}}\right)}_{\text{term1}}\underbrace{\left(\frac{U^{1/2}}{d_p^{1/2}}\right)}_{\text{term2}}$$

Term 1 is only a function of temperature for liquid system. The diffusivity always increases with increasing temperature for liquid system. However, the kinematic viscosity decreases exponentially with temperature for liquid. Term 2 is a function of the flow conditions and particle size.

Factor from internal adsorbent comes from internal mass transfer and surface adsorption controlling.

- internal mass transfer

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

D_e = effective diffusivity

D_A = bulk diffusivity

τ = tortuosity

ε_p = pellet porosity

σ = constriction factor

- surface adsorption

$$\text{Arsenic} + \text{surface} \text{ --------> } \text{Arsenic-surface}$$

$$r_a = K_d C_v C_{As}$$

r_a = surface adsorption rate

K_d = surface adsorption coefficient

C_v = vacancy site

C_{As} = arsenic concentration

Effective diffusivity and surface adsorption coefficient always increase with increasing temperature and do not depend on pressure. These experiments are not aimed to study the mechanism of arsenic adsorption. So, rate limiting step in arsenic adsorption for this study is obscured. However, the efficiency of arsenic adsorption depends on the combination of two factors described above and they depend on temperature only. This shows that the removal of arsenic depends on temperature too. The efficiency of arsenic removal increases when the temperature increases. The results are similar to Silverman (1985) who studied the removal of arsenic in shale oil over alumina. He found that the removal of arsenic was shown to be independent of pressure in the range of 250 psig to 750 psig, but sharply dependent on temperature in the range of 500°F-700°F. The similar study is conducted by Oleck (1986). He concluded that the removal of arsenic is not sensitive to the pressure ranging from 400 psig to 2200 psig. On the other hand, the temperature ranging from 300°C to 500°C have an influence on arsenic removal.

Effect of Adsorbents

A set of experiment is designed to study effect of each adsorbent on arsenic removal. The adsorption of arsenic on different adsorbents is undertaken in order to explain the nature of metal on selectivity of arsenic adsorption. This section is also aimed to study the effect of adsorbent that compares with alumina adsorbents on arsenic removal. Five types of adsorbents are examined in this work. These are alumina, Ni/Al_2O_3, Mo/Al_2O_3, $Mo-Ni/Al_2O_3$ and $Ni-Mo/Al_2O_3$ adsorbents. These adsorbents, except for alumina, are prepared by dry impregnation on alumina. The impregnated alumina is then dried and calcined by steps described previously. The metal in adsorbent is oxide form, consisting of nickel oxide (NiO) and/or molybdenum oxide (MnO_3). Ni/Al_2O_3 and Mo/Al_2O_3 is varied metal loading from 2.5% to 10% by weight based on alumina support. Percent total metal loading in $Mo-Ni/Al_2O_3$ and $Ni-Mo/Al_2O_3$ is kept on 10% by weight based on alumina and loading ratios of nickel and molybdenum are varied from 1:3 to 3:1. The amount of adsorbent used is 0.5 gram in the study of phenylarsine oxide removal and 0.03 gram in study of arsenic oxide removal. The experiments are performed at the temperatures of 30°C to 75°C and the pressures of 200 psig to 600 psig.

The effects of adsorbents on arsenic removal are categorized as follows;

-Effect of nickel and molybdenum loading in monometallic adsorbents.

-Effect of nickel and molybdenum loading in bimetallic adsorbents.

-Effect of nickel in different bimetallic adsorbents.

Before use, fresh adsorbents are analyzed for their characterization including surface area, pore volume and pore size distribution. In order to study the effect of metal loading and deposition of arsenic on adsorbents, alumina support and fresh and spent adsorbents are compared.

Effect of nickel and molybdenum loading in monometallic adsorbents

The effect of nickel and molybdenum loading is studied by comparison of experiments using nickel or molybdenum adsorbents. Nickel and molybdenum adsorbent are prepared by impregnation of nickel solution and molybdenum solution on alumina support, respectively. Before use, fresh adsorbents are analyzed for their characterization including surface area, pore volume and pore size distribution. The results are shown in Appendix (Table 2A). Figures 4.40 and 4.41 show the comparison of total surface area and pore volume between fresh alumina and fresh nickel adsorbents. It observes that total surface area and pore volume of fresh nickel adsorbent decreases when nickel loading increases. Figure 4.42 shows the comparison of pore size distribution between alumina and fresh nickel adsorbents (2.5%-10% nickel loading). It shows that pore size less than 52.5 A decrease slightly when it is compared with alumina adsorbent. The deposition of nickel, which is impregnated on alumina, is uniform throughout the entire pores of alumina which results in a slight change of surface area and pore volume of nickel adsorbents.

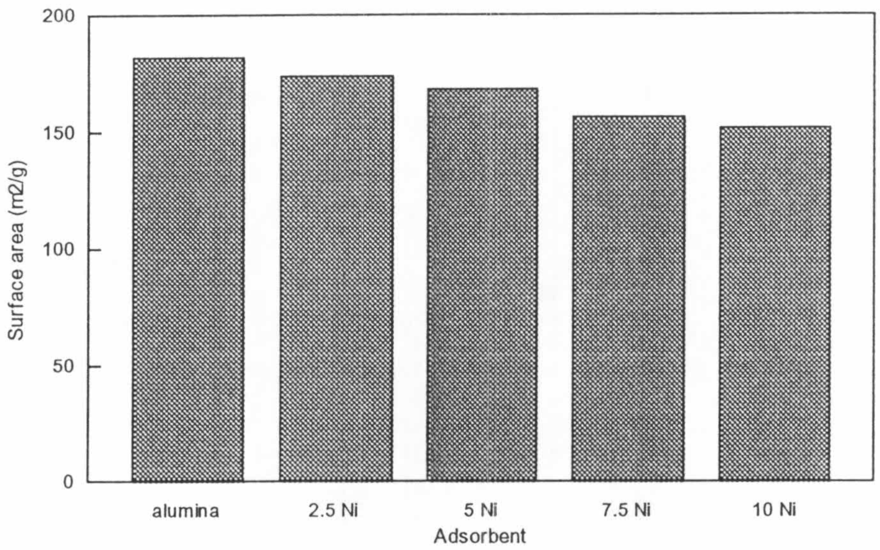

Figure 4.40 Comparison of surface area between alumina and 2.5 Ni-10 Ni adsorbents.

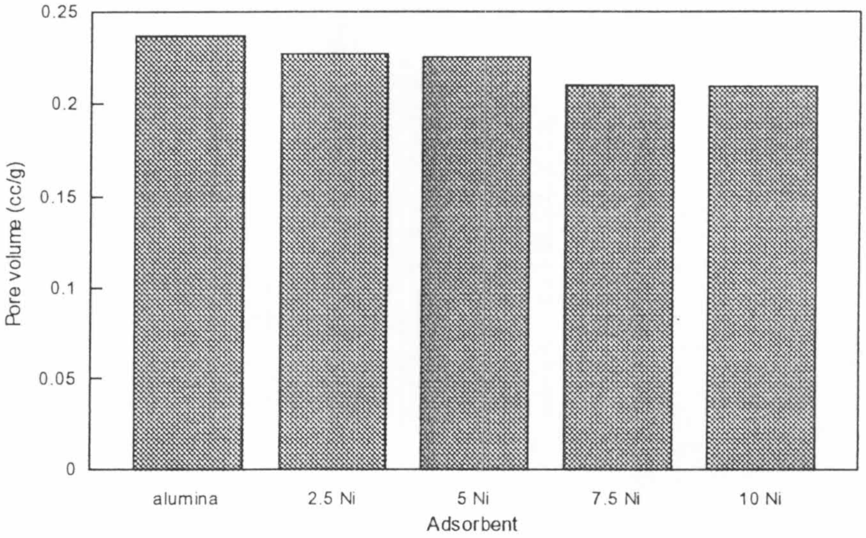

Figure 4.41 Comparison of pore volume between alumina and 2.5 Ni-10 Ni adsorbents.

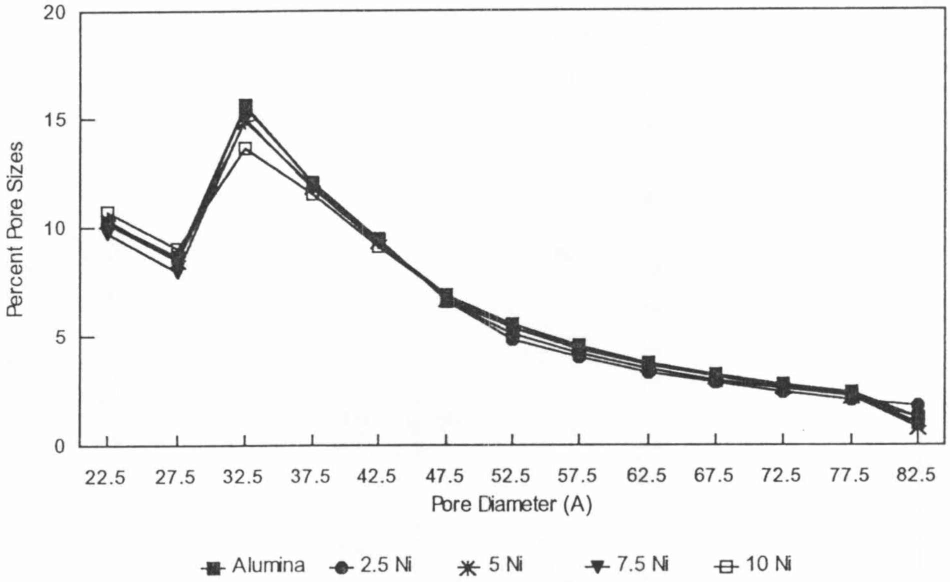

Figure 4.42 Comparison of pore sizes distribution between alumina and 2.5 Ni-10 Ni adsorbents.

The ability of adsorbents on arsenic removal is considered to compare with the quantity of remaining arsenic in each experiment. The less remaining arsenic in product is the result of high ability of adsorbent. The remaining arsenic, that is removed by alumina, is used as the reference results and is compared with the nickel adsorbents. Figures 4.43 and 4.44 show the remaining of arsenic versus the temperatures from 30°C to 75°C. The remaining arsenic, which used 2.5 Ni/Al2O3, is lower concentration than alumina used. The results are corresponding to phenylarsine oxide and arsenic oxide. It indicates that the deposition of arsenic on nickel surface is more effective than alumina surface. The efficiency of adsorption will be linked to a formation of arsenic with active metal. From the results, the adsorption of arsenic on nickel adsorbent is more effective than alumina adsorbent. Some papers dealing with the adsorption of arsenic on nickel catalyst are in accordance with a formation of arsenic. Child et al. (1986) studied the removal of arsenic in shale oil. They concluded that the effectiveness of nickel adsorbent presumably arises from the formation of nickel arsenide compounds such as $NiAs_2$. Another work was studied by Ng (1990). He concluded that arsenic is adsorbed on surface and bonded to three nickel sites ($NiAs_3$). Theses previous studied agree to the inspection of spent nickel adsorbent. The spent nickel adsorbent is measured the stoichiometry of nickel-arsenic compound by X-ray Diffraction (XRD). Figure 4.45 shows that arsenic is interacted with nickel and is formed to nickel arsenide ($NiAs_2$).

Short experiments are conducted to study the desorption of arsenic on alumina and nickel adsorbent. The objective of this section is to confirm that the adsorption of arsenic on alumina and nickel adsorbents is irreversible adsorption. The experiments are conducted by sampling spent alumina, 2.5 nickel and 2.5 molybdenum adsorbent after that they are used for removal of phenylarsine oxide at temperature of 30°C and pressure at 400 psig. The spent adsorbent are to stir in 100 mL of pure toluene at a temperature of 30°C and at atmospheric pressure. The results show that little arsenic concentration can be found (less than 30 ppb). It indicates that the adsorption of arsenic on alumina,

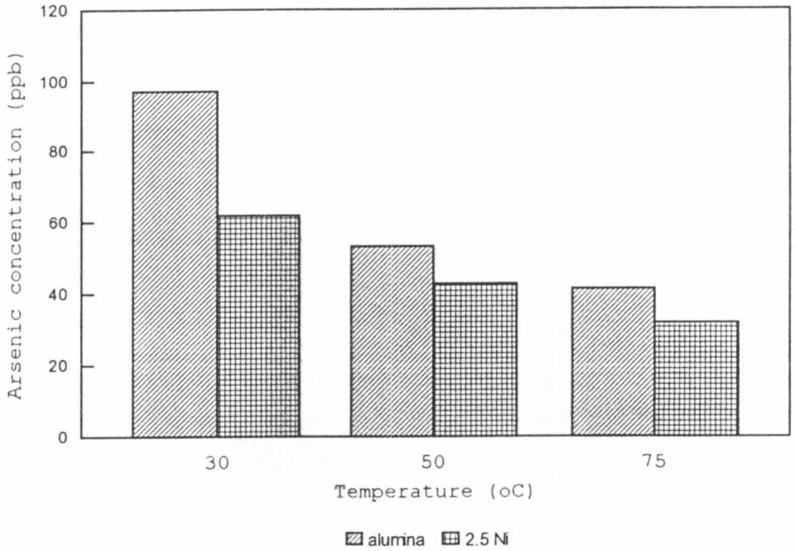

Figure 4.43 Comparison of phenylarsine oxide remaining between alumina and 2.5 Ni adsorbent at temperatures ranging from 30°C to 75°C and pressure at 400 psig.

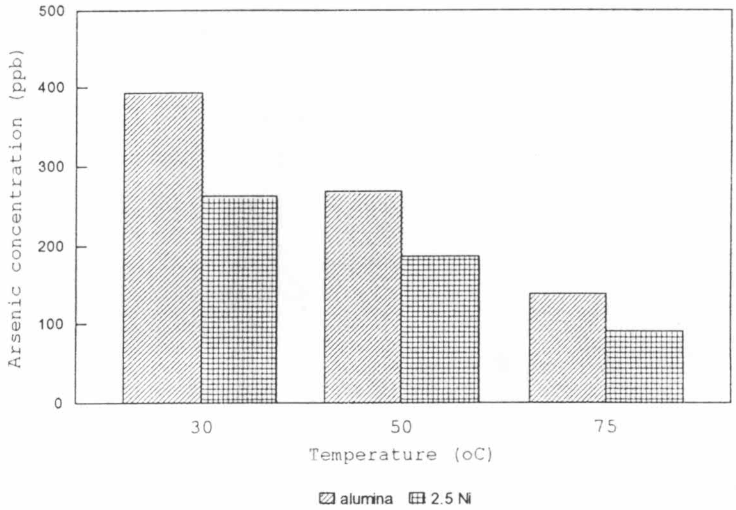

Figure 4.44 Comparison of arsenic oxide remaining between alumina and 2.5 Ni adsorbent at temperatures ranging from 30°C to 75°C and pressure at 400 psig.

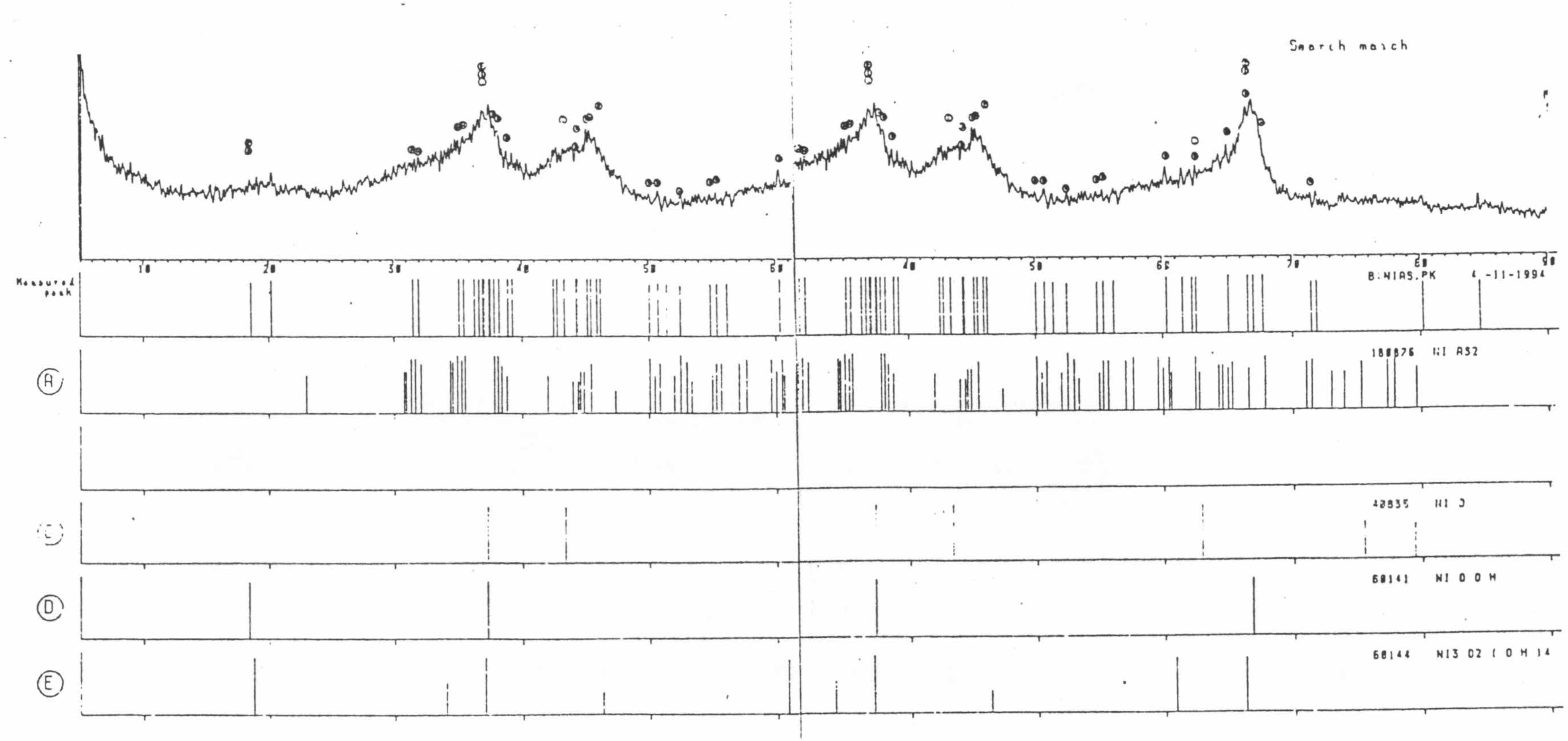

Figure 4.45 XRD pattern of spent nickel adsorbent.

nickel and molybdenum adsorbents are irreversible adsorption.

The effect of nickel loading is studied by comparison of experiments using nickel loading from 2.5% to 10% by weight. The removal of arsenic by 2.5 Ni/Al_2O_3 to 10 Ni/Al_2O_3 is shown in Figures 4.46 and 4.47. They show the remaining arsenic versus the temperatures ranging from 30°C to 75°C. It can see that the remaining arsenic undergos small change when nickel loading increases. The efficiency of more nickel containing adsorbent is a little greater than that of less nickel containing. This is true for phenylarsine oxide removal but is not noticeable variation in arsenic oxide removal. It can account for the fact that 2.5% nickel loading in nickel adsorbent is sufficient to remove arsenic. Increasing nickel loading more than 2.5% loading is not effecting on arsenic removal. Increasing nickel loading makes the thickness of nickel surface on alumina support increased together. It indicates that arsenic can be bonded with the first layer of nickel surface only. None of arsenic can be bonded with the deeper layer of nickel phase.

After each experiment, spent adsorbents are analyzed for their characterization including surface area, pore volume and pore sizes distribution. The results are shown in Appendix (Table 2A). Figure 4.48 shows the comparison of surface area between fresh and spent alumina which used at temperature from 30°C to 75°C and pressure at 400 psig. The surface area of spent aluminas decrease less than 10%. The different conditions do not lead to significant differences in surface area. This shows that the adsorption of arsenic has a little effect on surface area. These results are corresponded to pore volume of spent alumina that shown in Figure 4.49. Figure 4.50 shows pore size distribution between fresh and spent alumina adsorbent. Pore size distribution shows that some pore sizes from 22.5 A to 82.5 A are disappearance. Furthermore, pore sizes from 27.5 A to 42.5 A are lost significantly. This reason can be attributed to the fact that arsenic is adsorbed all pore sizes and is preferentially adsorbed at pore sizes from 27.5 A to 42.5 A. It can be confirmed by Figure 4.51 that is shown a comparison of the pore size distribution between fresh and spent alumina when it is treated with 50 ppm of phenylarsine oxide for 5 times. The changing of pore size distribution means that arsenic is adsorbed on the entire pores of alumina. The maximum changing of pores occurs at pore sizes ranging from 27.5 A to 42.5 A. It indicates that most of arsenic is preferentially adsorbed at pore sizes ranging from 27.5 A to 42.5 A.

Figure 4.48 shows the comparison of surface area between fresh and spent nickel adsorbent at temperatures from 30°C to 75°C and pressure at 400 psig. Surface area of spent nickel adsorbents decreases less than 8% when it is compared with fresh nickel adsorbent. The different conditions do not lead to significant differences in surface area. The results correspond to pore volume of spent nickel adsorbents that shown in Figure 4.49. In case of nickel adsorbents (2.5%-7.5%), the plot in Figures 4.52 through 4.55 show that pore size distribution changes slightly, comparison of experiments before and after runs. This reason could be attributed to the fact that the adsorption of arsenic is distributed all the pore sizes. In case of 10 Ni adsorbent, large pore sizes (37.5 A-82.5 A) are significant loss while small pore sizes increase significantly. This case can explain to the reduction of large pore sizes to small pore sizes, so small pore sizes increase.

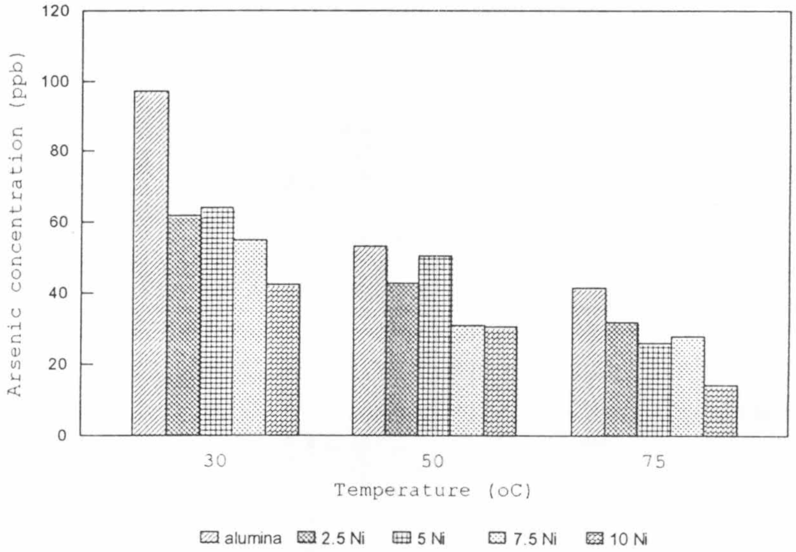

Figure 4.46 Comparison of phenylarsine oxide remaining between alumina and 2.5 Ni-10 Ni adsorbents at temperatures ranging from 30°C to 75°C and pressure at 400 psig.

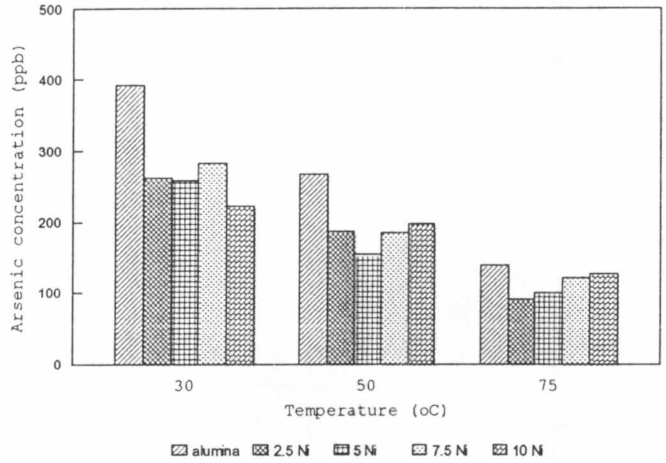

Figure 4.47 Comparison of arsenic oxide remaining between alumina and 2.5 Ni-10 Ni adsorbents at temperatures ranging from 30°C to 75°C and pressure at 400 psig.

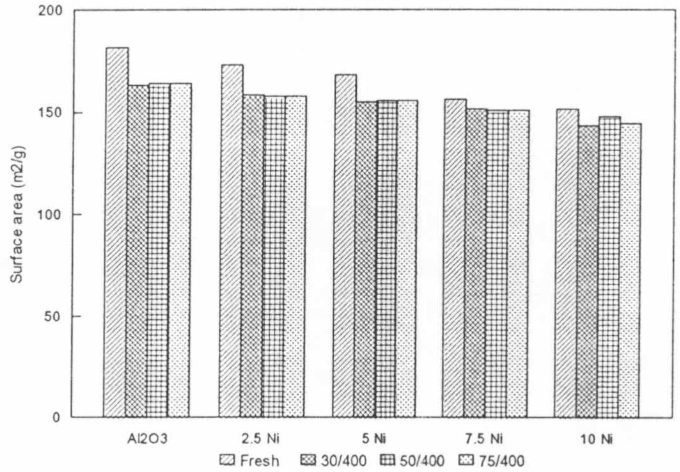

Figure 4.48 Comparison of surface area between fresh and spent alumina and 2.5 Ni-10 Ni adsorbents.

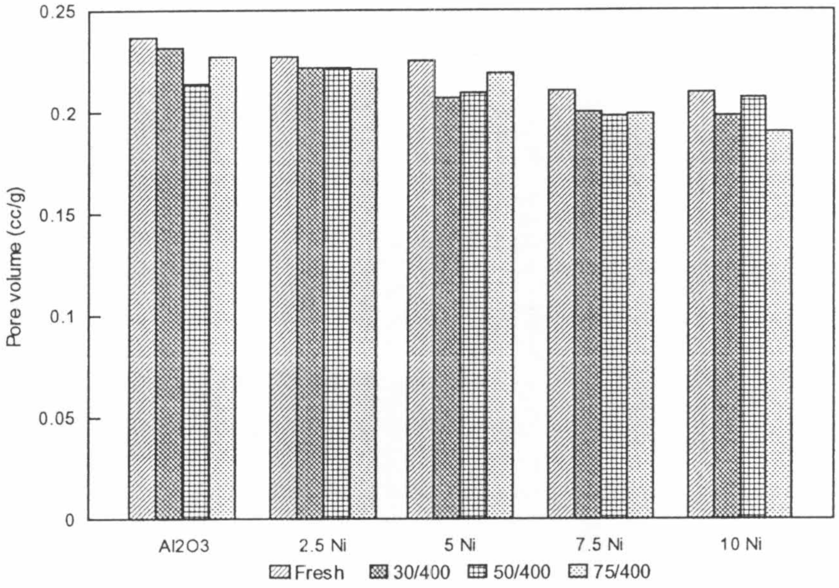

Figure 4.49 Comparison of pore volume between fresh and spent alumina and 2.5 Ni-10 Ni adsorbents.

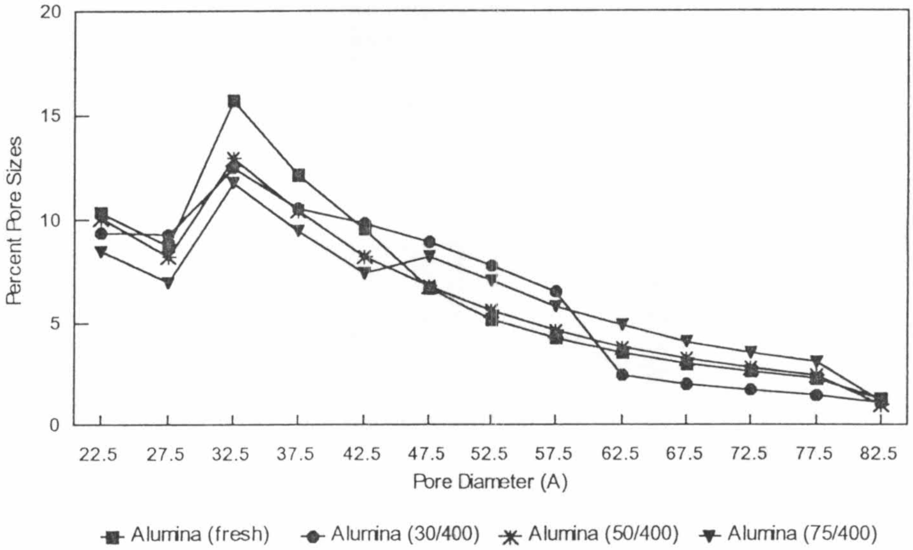

Figure 4.50 Comparison of pore sizes distribution between fresh and spent alumina adsorbents.

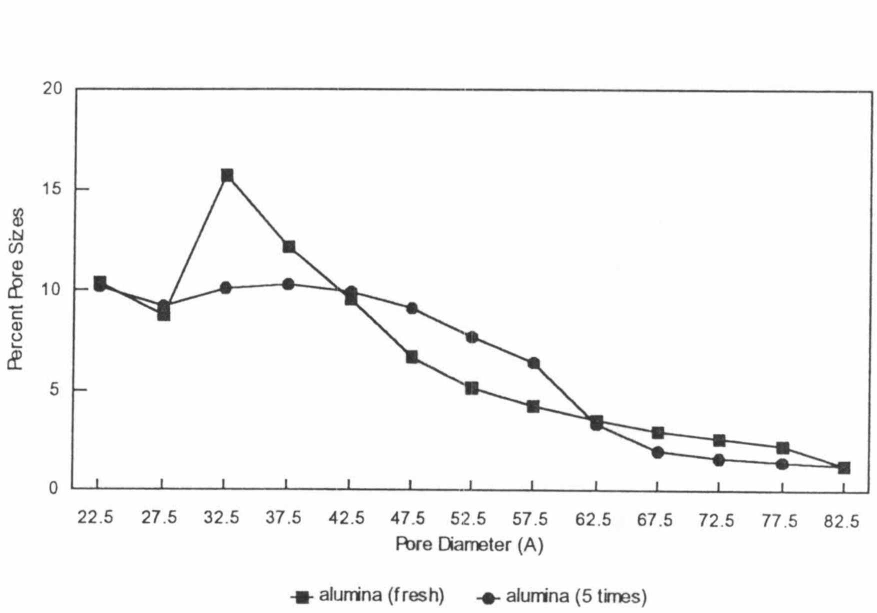

Figure 4.51 Comparison of pore sizes distribution between fresh and spent alumina adsorbents.

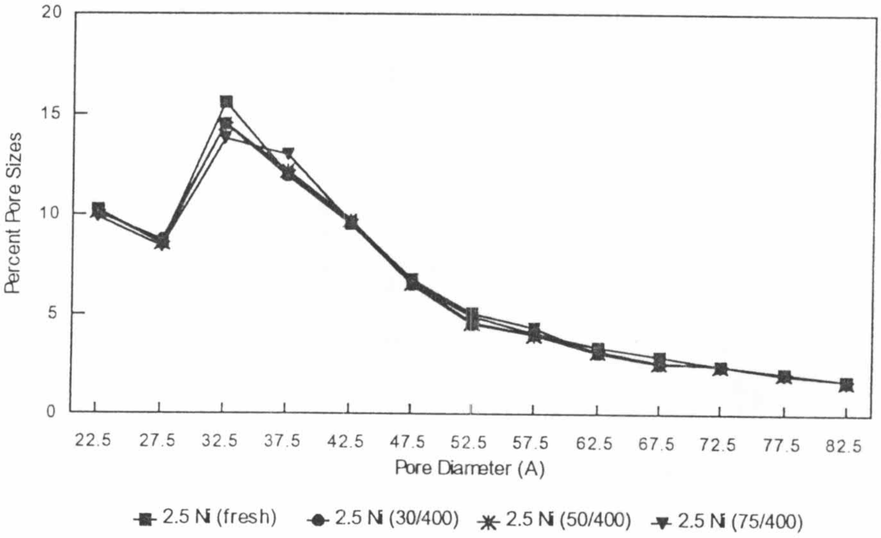

Figure 4.52 Comparison of pore sizes distribution between fresh and spent 2.5 Ni adsorbents.

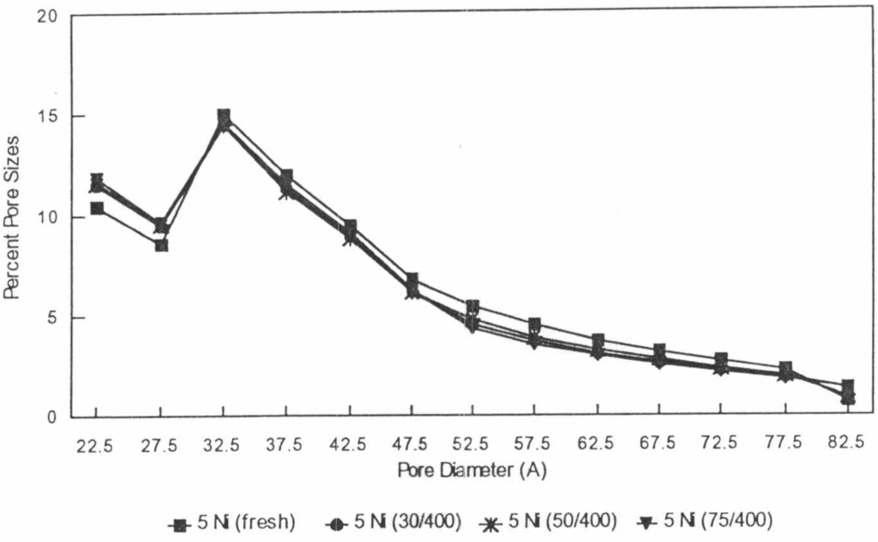

Figure 4.53 Comparison of pore sizes distribution between fresh and spent 5 Ni adsorbents.

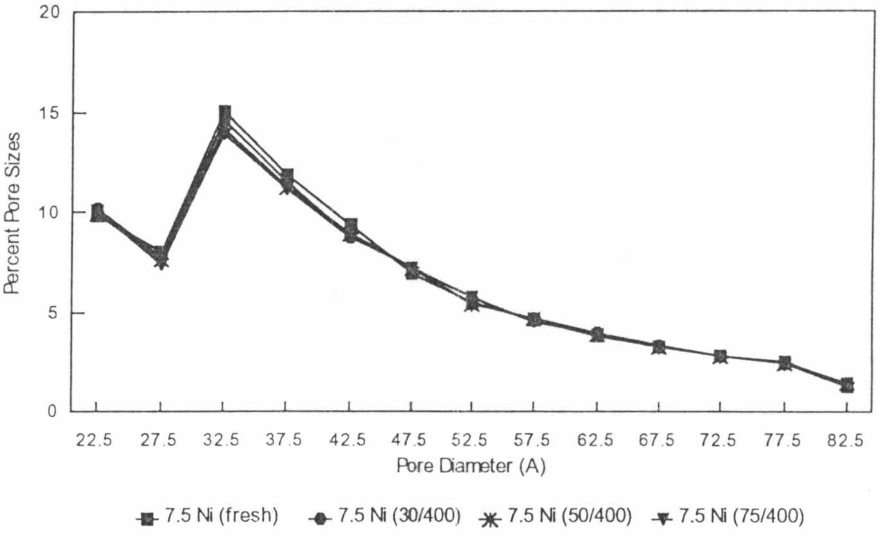

Figure 4.54 Comparison of pore sizes distribution between fresh and spent 7.5 Ni adsorbents.

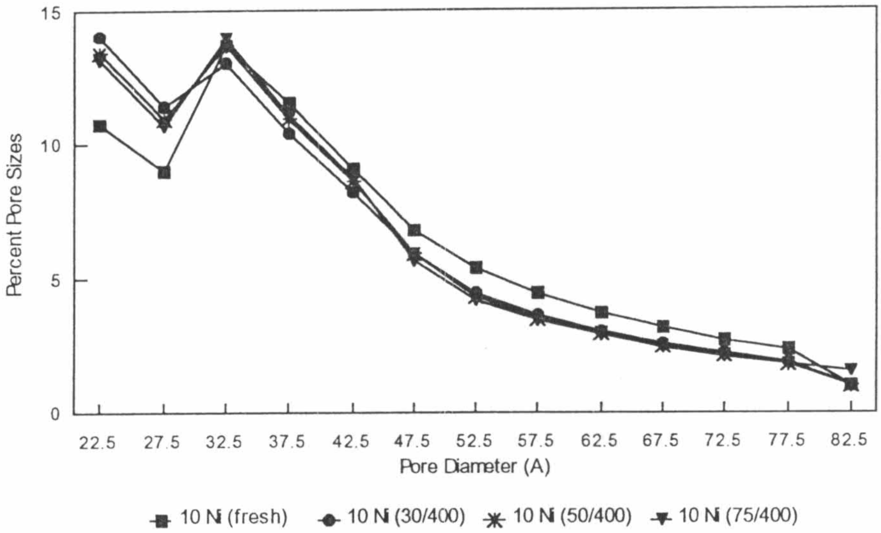

Figure 4.55 Comparison of pore sizes distribution between fresh and spent 10 Ni adsorbents.

Figures 4.56 and 4.57 show the comparison of total surface area and pore volume between alumina and molybdenum adsorbents. It indicates that total surface area and pore volume of molybdenum adsorbent decreases when molybdenum loading increases. Pore sizes distribution of molybdenum adsorbents when they are compared to alumina support in Figure 4.58 change slightly. This indicates that the preparation steps of molybdenum adsorbent are not effecting on pore sizes distribution of alumina support. The deposition of molybdenum, which is impregnated on alumina, is uniform throughout entire the pores of alumina support which results in a slight change of surface area and pore volume.

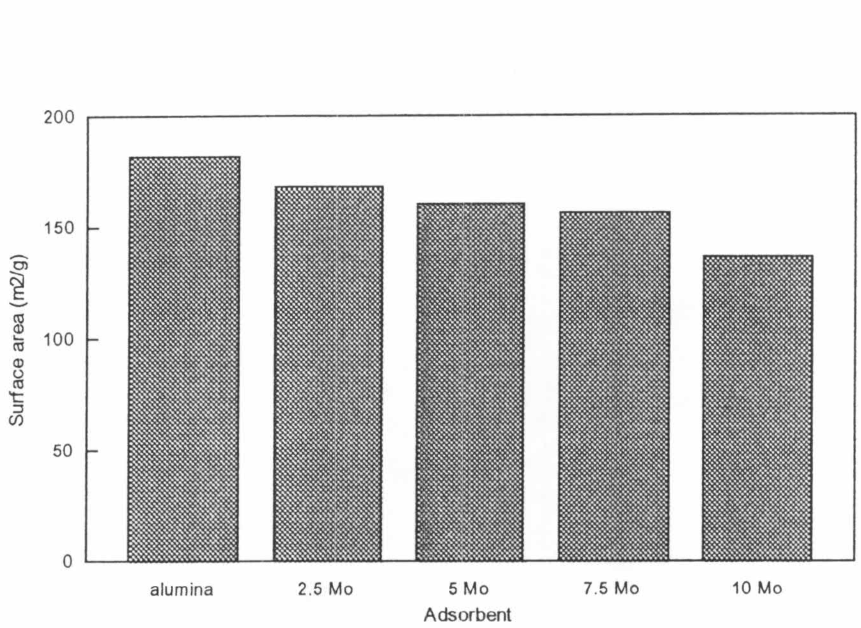

Figure 4.56 Comparison of surface area between alumina and 2.5 Mo-10 Mo adsrbents.

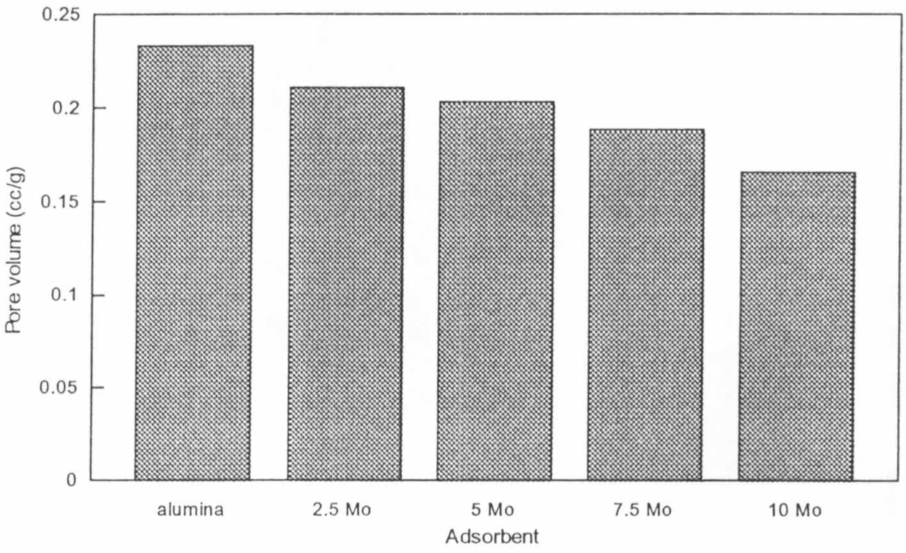

Figure 4.57 Comparison of pore volume between alumina and 2.5 Mo-10 Mo adsorbents.

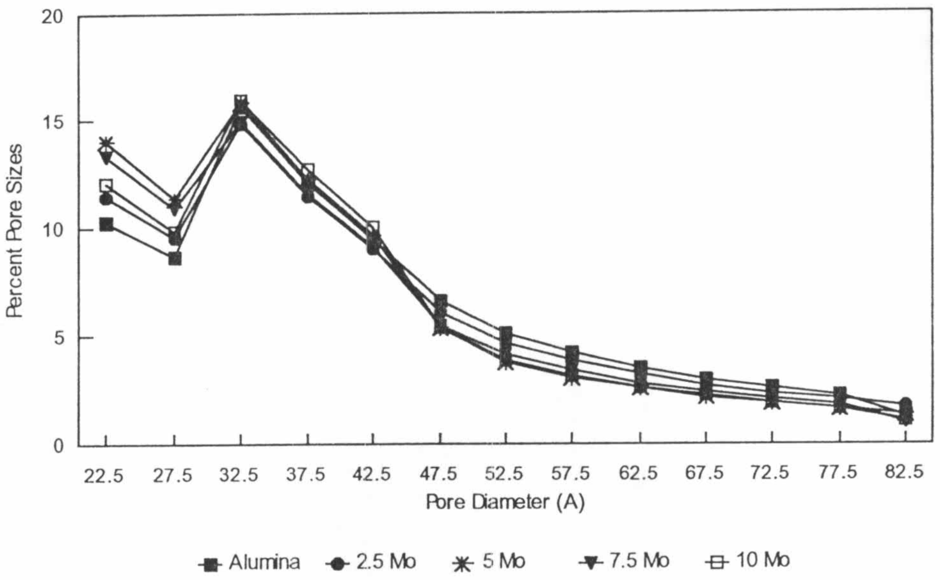

Figure 4.58 Comparison of pore sizes distribution between alumina and 2.5 Mo-10 Mo adsorbents.

Figures 4.59 and 4.60 show that the remaining arsenic that used 2.5 Mo/Al_2O_3 is higher concentration than alumina. The results are corresponding to phenylarsine oxide and arsenic oxide. It indicates that arsenic is not interacted and adsorbed on molybdenum surface. The decreasing arsenic in product may be come from the adsorption of arsenic on alumina surface.

The spent adsorbent is measured the stoichiometry of molybdenum-arsenic compound that is shown in Figure 4.61. There is an evidence in X-ray Diffraction(XRD) pattern to show that the formation between molybdenum and arsenic is not appearance. Figures 4.62 and 4.63 show the comparison of remaining arsenic for the adsorbent containing different molybdenum content (2.5% to 10%). They can be seen that the remaining arsenic in two forms have remarkable boost, when increasing molybdenum content. The results show that the efficiency of molybdenum adsorbents decrease in the order 10% Mo/Al_2O_3 > 7.5% Mo/Al_2O_3 > 5% Mo/Al_2O_3 > 2.5% Mo/Al_2O_3.

These results can be explained by the reactivity of molybdenum. As stated previously, the results suggest that arsenic is not adsorbed on molybdenum phase but is adsorbed on alumina phase. When increasing molybdenum loading, most surfaces of alumina are nearly shielded with molybdenum phase. A little alumina surface can be interacted with arsenic, so the remaining of arsenic is large. Figure 4.64 shows the comparison of surface area between fresh and spent molybdenum adsorbents at temperatures from 30°C to 75°C and pressure at 400 psig. Surface area of spent molybdenum adsorbents decrease slightly less than 4% when it is compared with fresh molybdenum adsorbent. The different conditions do not lead to significant differences in surface area. The results correspond to pore volume that shown in Figure 4.65. In case of molybdenum adsorbents (2.5%-10% loading), the plot in Figures 4.66 through 4.69 show that the smaller pores (27.5 A-47.5 A) structure in spent adsorbent are changed to a greater degree than the larger pores. Pore size distribution in small pores is decreased significantly from fresh to spent adsorbents. This means that arsenic is likely to diffuse deeper into the small pores and the adsorption of arsenic is occurred in small pores. The interaction force between arsenic and molybdenum adsorbents, as described above, do

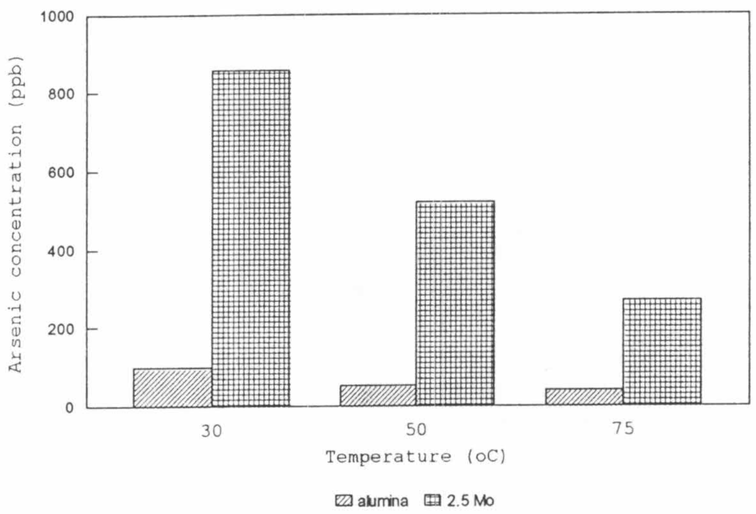

Figure 4.59 Comparison of remaining phenylarsine oxide in study the efficiency of alumina and 2.5 Mo adsorbent at temperatures ranging from 30°C to 75°C and pressure at 400 psig.

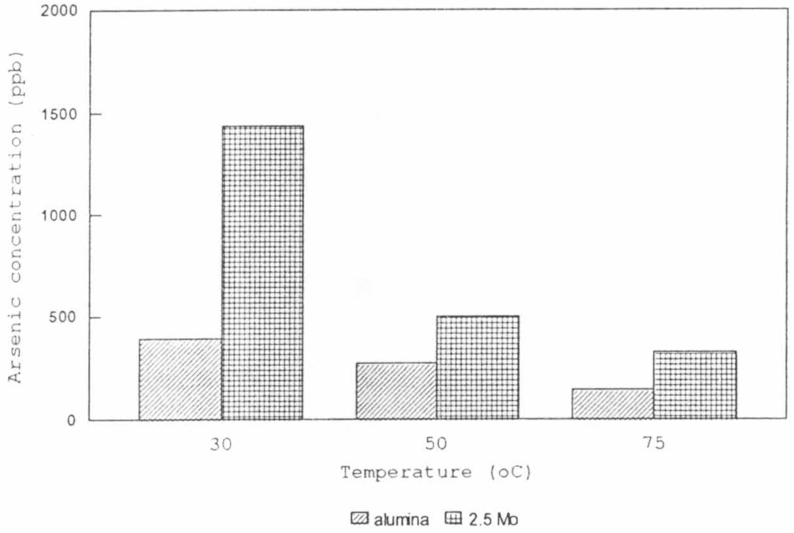

Figure 4.60 Comparison of remaining arsenic oxide in study the efficiency of alumina and 2.5 Mo adsorbent at temperatures ranging from 30°C to 75°C and pressure at 400 psig.

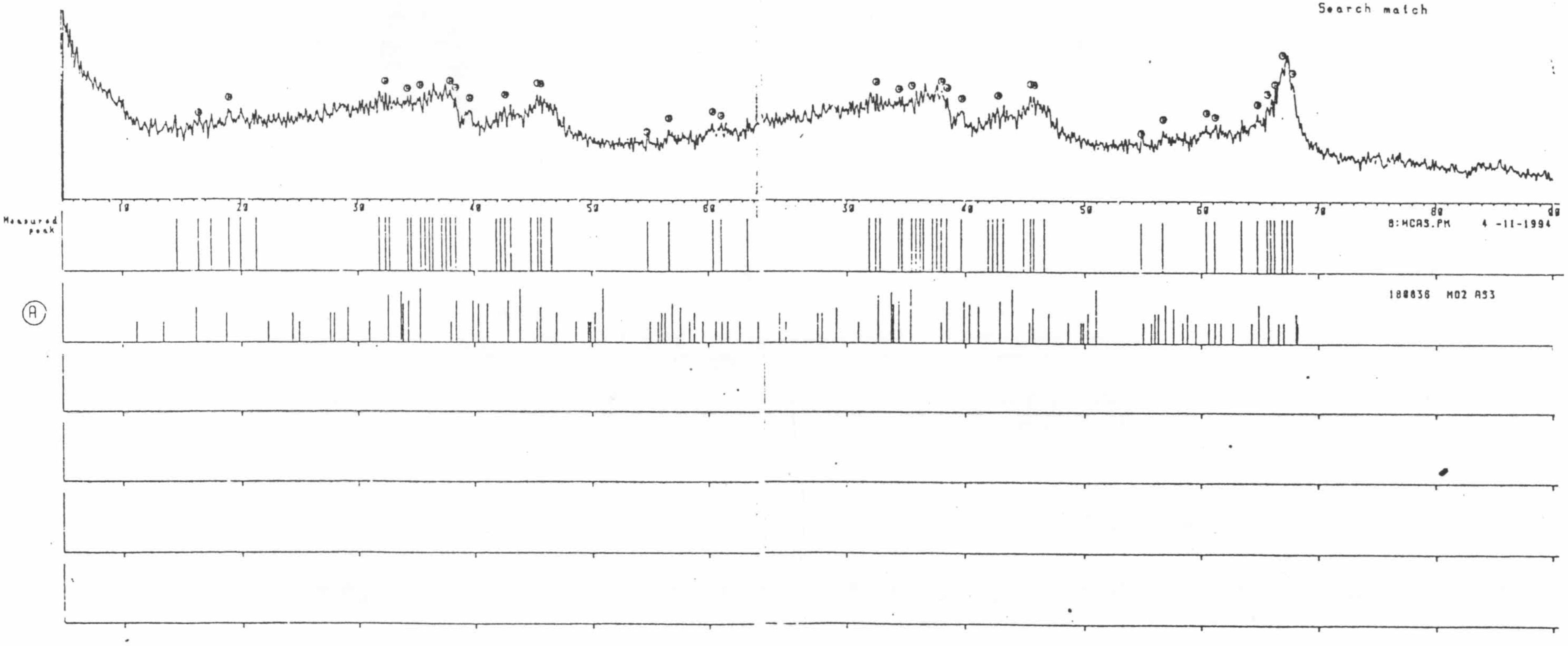

Figure 4.61 XRD pattern of spent molybdenum adsorbent.

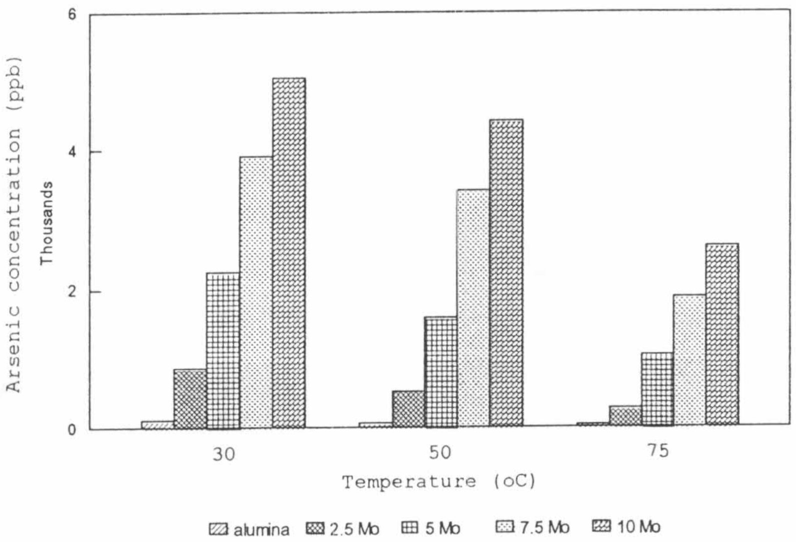

Figure 4.62 Comparison of remaining phenylarsine oxide in study the efficiency of alumina and 2.5Mo-10Mo adsorbent at temperatures ranging from 30°C to 75°C and pressure at 400 psig.

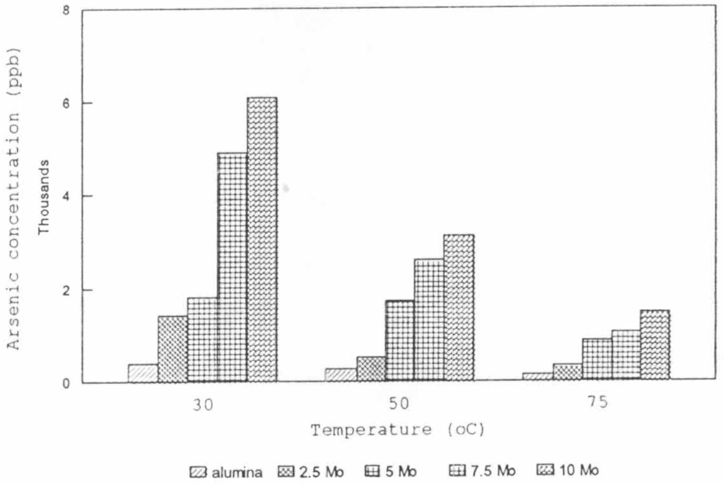

Figure 4.63 Comparison of remaining arsenic oxide in study the efficiency of alumina and 2.5 Mo-10 Mo adsorbent at temperatures ranging from 30°C to 75°C and pressure at 400 psig.

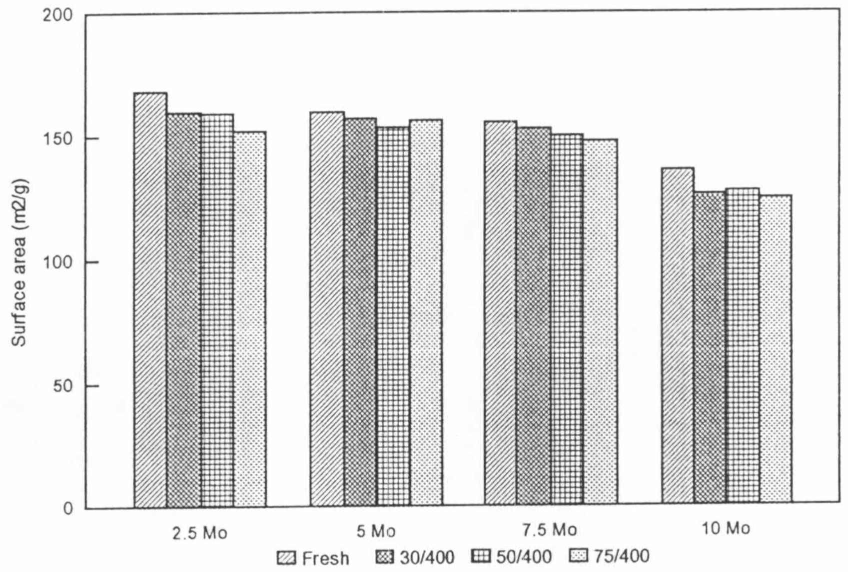

Figure 4.64 Comparison of surface area between fresh and spent 2.5Mo-10Mo adsorbents.

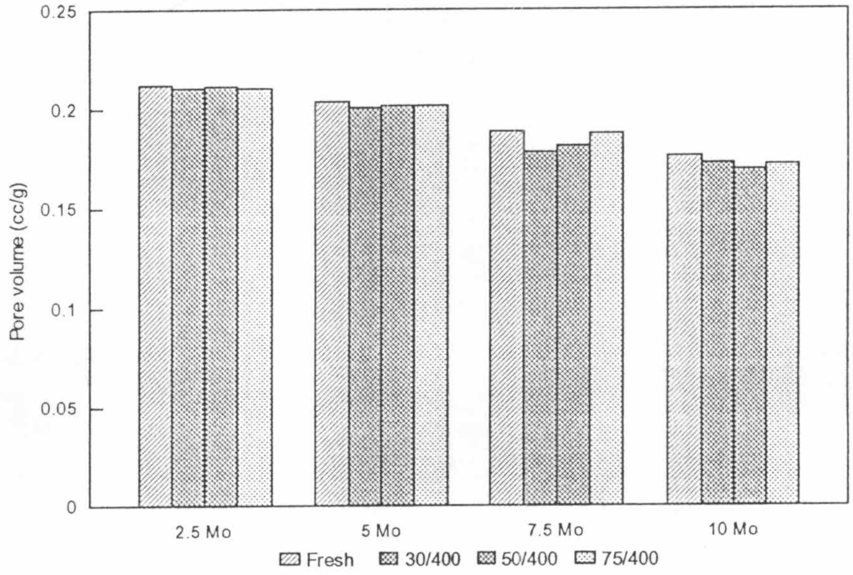

Figure 4.65 Comparison of pore volume between fresh and spent 2.5Mo-10Mo adsorbents.

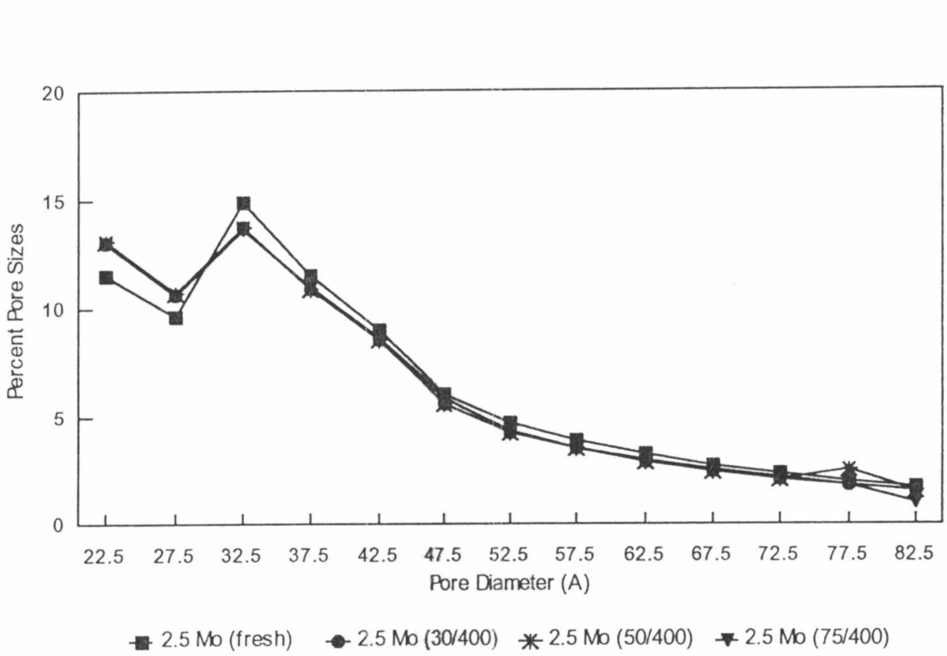

Figure 4.66 Comparison of pore sizes distribution between fresh and spent 2.5 Mo adsorbents.

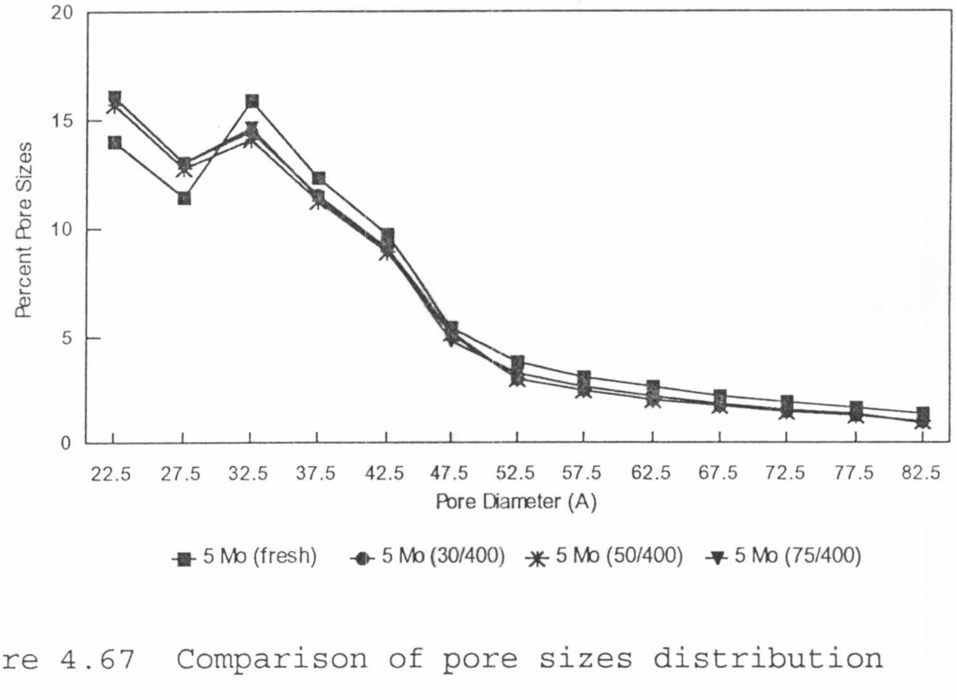

Figure 4.67 Comparison of pore sizes distribution between fresh and spent 5 Mo adsorbents.

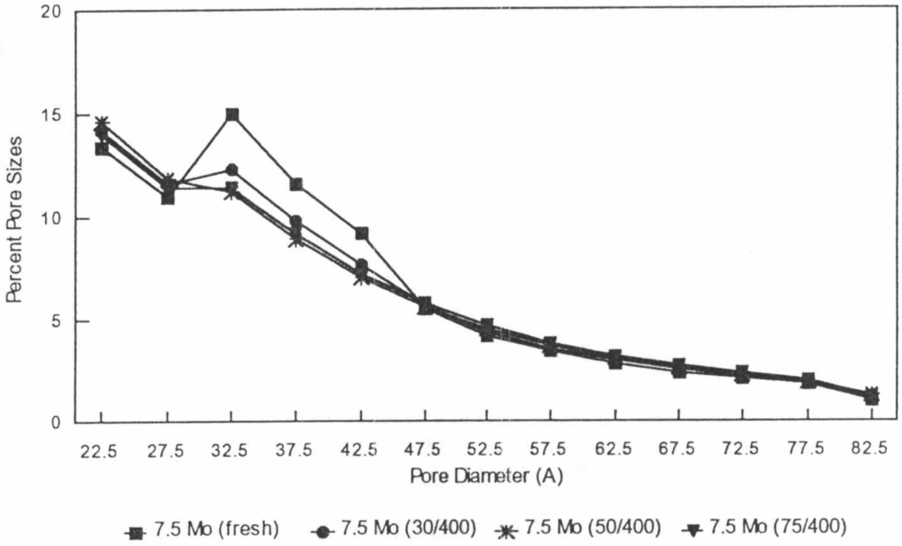

Figure 4.68 Comparison of pore sizes distribution between fresh and spent 7.5 Mo adsorbents.

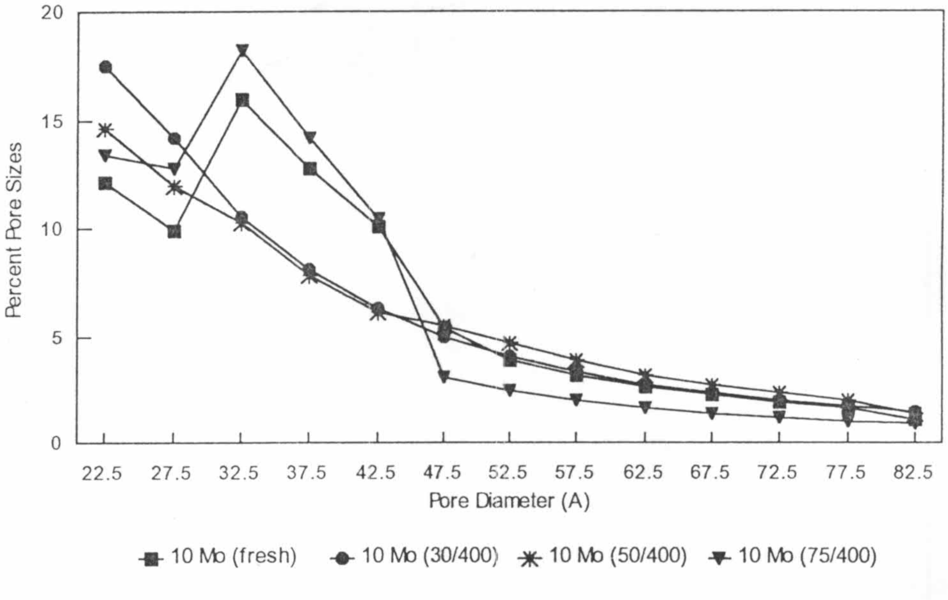

Figure 4.69 Comparison of pore sizes distribution between fresh and spent 10 Mo adsorbents.

not happen. It indicates that the adsorption of arsenic in molybdenum adsorbent occurs on alumina surface only.

Effect of Nickel and Molybdenum in Bimetallic Adsorbents

From above mentioned, we can conclude that arsenic can be interacted and can be adsorbed on nickel and alumina phases. On the other hand, arsenic can not be interacted with molybdenum. So, this section will be focused on the effect of bimetallic compound if both nickel and molybdenum are presenting together. This section designed to study the effect of each bimetallic adsorbent on arsenic removal. Adsorbents which used are 2.5-7.5 NiMo/Al_2O_3 to 7.5-2.5 NiMo/Al_2O_3 and 2.5-7.5 MoNi/Al_2O_3 to 7.5-2.5 MoNi/Al_2O_3. The different adsorbents between NiMo/Al_2O_3 and MoNi/Al_2O_3 come from adsorbent preparation steps. NiMo/Al_2O_3 is first impregnated by nickel solution and by molybdenum solution in the latter. On the other hand, MoNi/Al_2O_3 is first impregnated by molybdenum solution and nickel solution in the latter. The total loading metal is kept at 10 %wt based on alumina support. The adsorbents are referred as y-x MoMi/Al_2O_3 and x-y NiMo/Al_2O_3 in which x and y stand for molybdenum and nickel loading, respectively.

Before use, fresh adsorbents are analyzed for their characterization including surface area, pore volume and pore size distribution. The results are shown in Appendix (Table 2A). Figures 4.70 through 4.73 show the comparison of total surface area between fresh alumina and fresh MoNi/Al_2O_3 and fresh NiMo/Al_2O_3

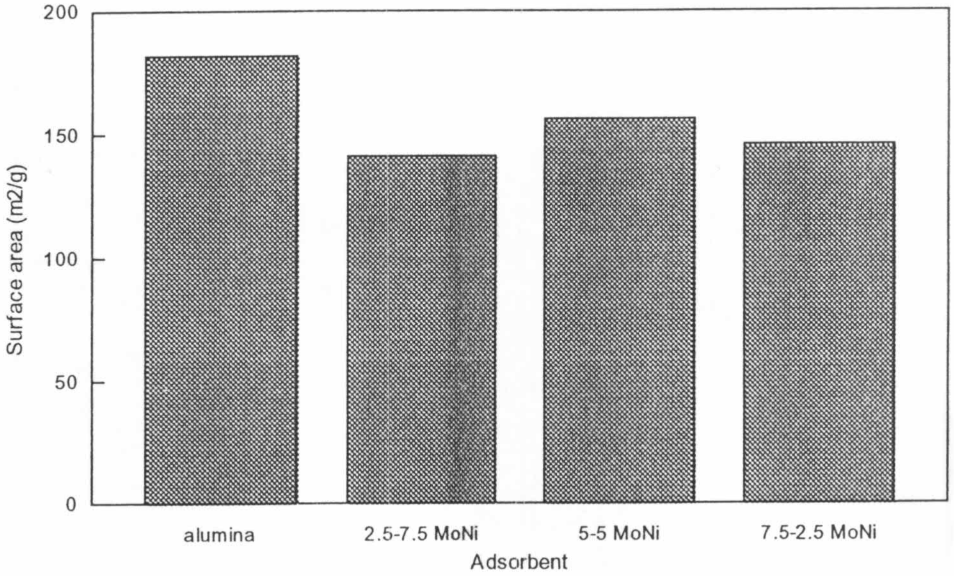

Figure 4.70 Comparison of surface area between alumina and 2.5-7.5 MoNi - 7.5-2.5 MoNi adsorbents.

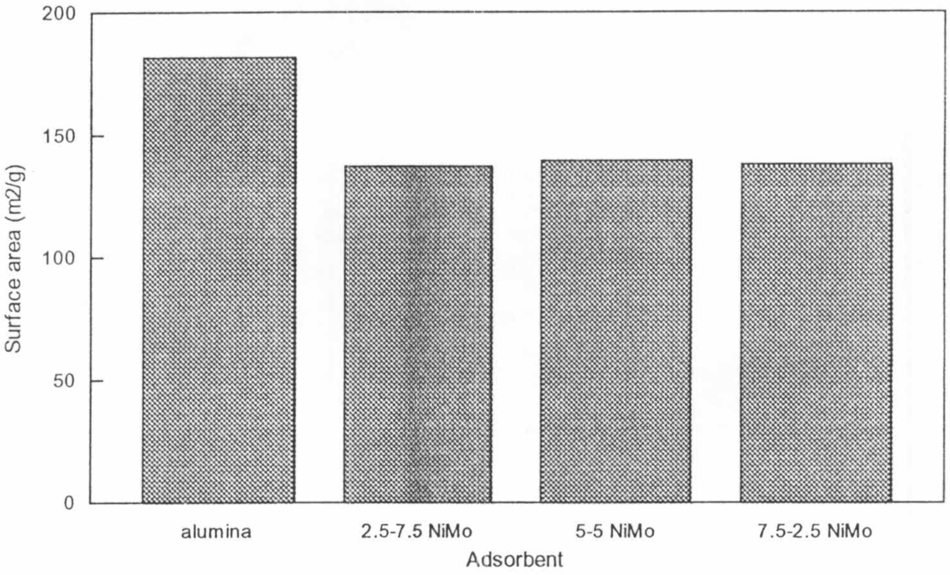

Figure 4.71 Comparison of surface area between alumina and 2.5-7.5 NiMo - 7.5-2.5 NiMo adsorbents.

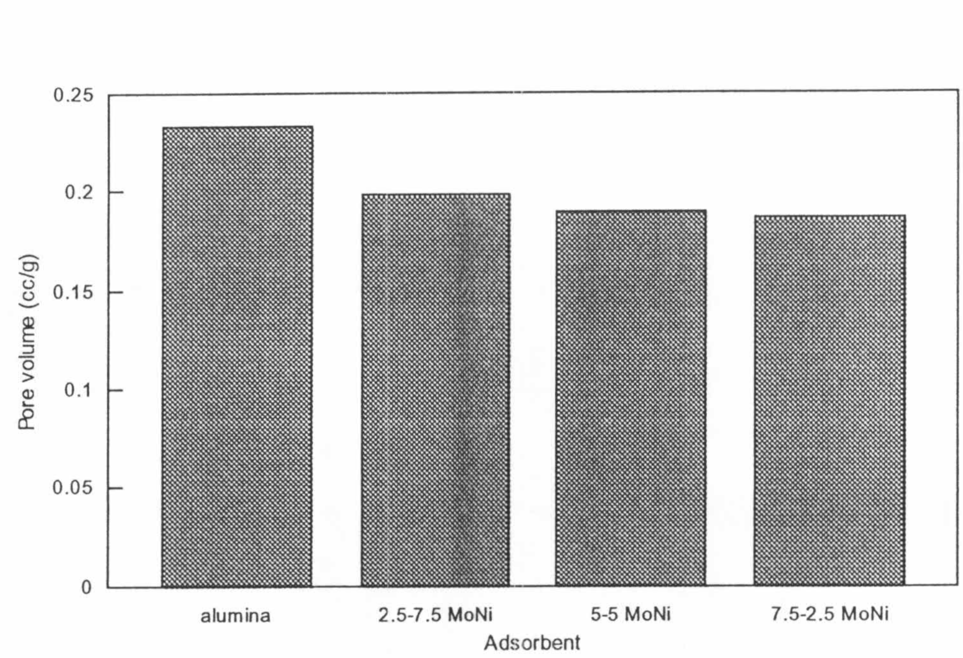

Figure 4.72 Comparison of pore volume between alumina and 2.5-7.5 MoNi - 7.5-2.5 MoNi adsorbents.

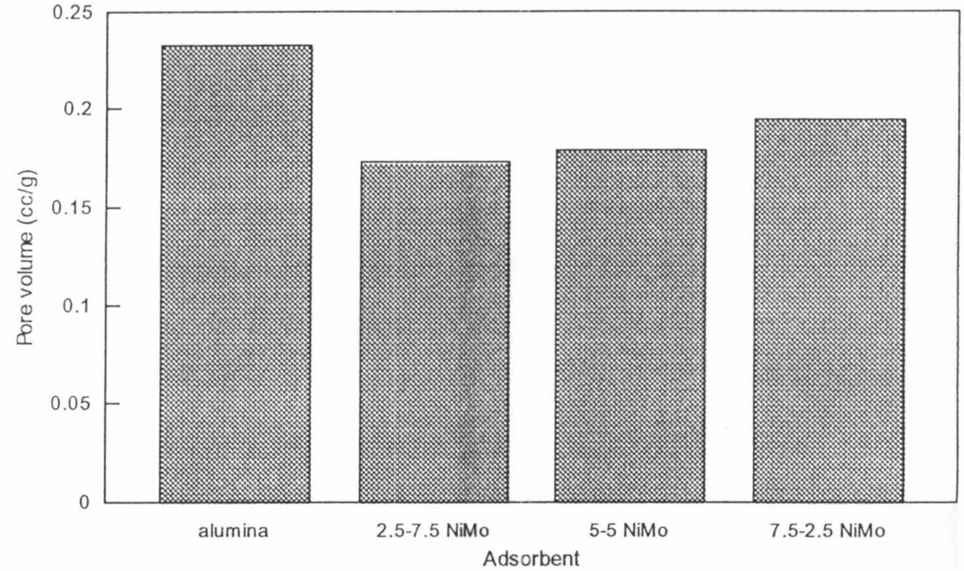

Figure 4.73 Comparison of pore volume between alumina and 2.5-7.5 NiMo - 7.5-2.5 NiMo adsorbents.

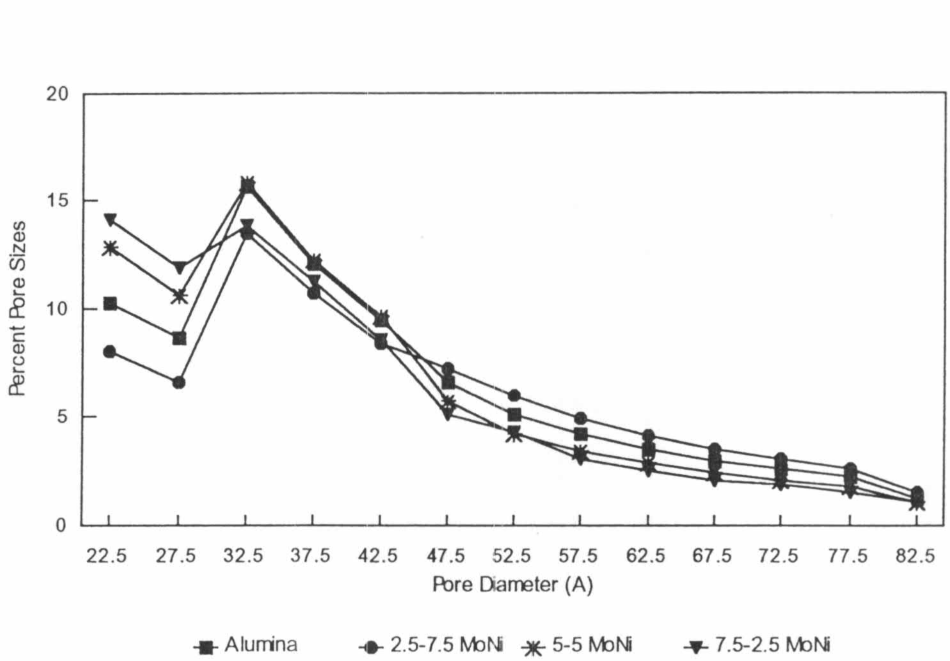

Figure 4.74 Comparison of pore sizes distribution between alumina and MoNi adsorbents.

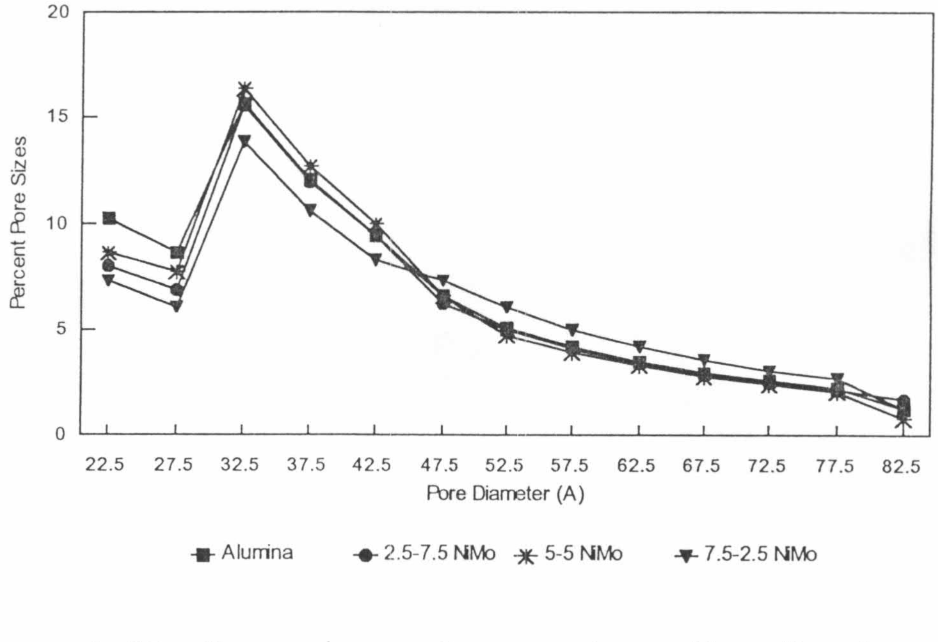

Figure 4.75 Comparison of pore sizes distribution between alumina and NiMo adsorbents.

adsorbents. It observes that total surface area of fresh MoNi/Al_2O_3 and fresh NiMo/Al_2O_3 adsorbents decrease when it is compared with alumina support. Pore size distribution of fresh nickel-molybdenum adsorbents when are compared with fresh alumina in Figures 4.74 and 4.75 changes significantly. This indicates that the preparation steps of MoNi/Al_2O_3 and fresh NiMo/Al_2O_3 adsorbents affect slightly on pores of alumina.

The ability of adsorbents on arsenic removal is considered to compare with the quantity of remaining arsenic in each experiment. The less remaining arsenic in product is the reason of high ability of adsorbent for arsenic removal. Figures 4.76 and 4.77 show a comparison of remaining arsenic which used MoNi/Al_2O_3 adsorbents at pressure 400 psig and temperatures ranging from 30°C to 75°C. The results show that the efficiency of MoNi/Al_2O_3 adsorbents increase in the order 2.5-7.5 MoNi/Al_2O_3 > 5-5 MoNi/Al_2O_3 > 7.5-2.5 MoNi/Al_2O_3 . MoNi/Al_2O_3 adsorbents are more effective on arsenic removal when nickel loading increases. On the other hand, MoNi/Al_2O_3 adsorbents are less effective on arsenic removal when molybdenum loading increase. Figures 4.78 and 4.79 show a comparison of remaining arsenic which used NiMo/Al_2O_3 adsorbents at pressure 400 psig and temperatures ranging from 30°C to 75°C. The results show that he efficiency of NiMo/Al_2O_3 adsorbents increase in the order 7.5-2.5 NiMo/Al_2O_3 > 5-5 NiMo/Al_2O_3 > 2.5-7.5 NiMo/Al_2O_3 . NiMo/Al_2O_3 adsorbents are more effective on arsenic removal when nickel loading increases. On the other hand, MoNi/Al_2O_3 adsorbents are less effective on arsenic removal when molybdenum loading increases.

This can be explained by using the concept of interaction between arsenic and active metal. From the previous section, arsenic is adsorbed and interacted with nickel or alumina surface, in contrast, arsenic is not interacted on molybdenum surface. The nickel phase is increased when nickel loading increases. This causes more nickel surface for arsenic to adsorb. Meanwhile, molybdenum is increased when molybdenum loading increases. This causes more molybdenum surface and decreases the alumina and nickel surface. Arsenic is not interacted or adsorbed on molybdenum surface, hence, the remaining arsenic is high. Figures 4.80 and 4.81 show the comparison of surface area between fresh and spent MoNi/Al_2O_3 and NiMo/Al_2O_3 adsorbent at temperature from 30°C to 75°C and pressure at 400 psig. The surface area of spent nickel-molybdenum adsorbents decrease slightly less than 6%. The different conditions evidently do not lead to significant differences in surface area. The results correspond to pore volume that shown in Figures 4.82 and 4.83. The structure changes found in spent adsorbents through arsenic adsorption are somewhat different in each case. Figures 4.84 through 4.86 show the change of pore size distribution between fresh and spent MoNi/Al_2O_3. There are significant differences in pore size distribution between them. Pores size distribution in spent 2.5-7.5 MoNi/ Al_2O_3 shows that all pore sizes are decreased in the same way. Nickel phase is considered to the major surface in 2.5-7.5MoNi/Al_2O_3 so the adsorption of arsenic on nickel surface is distributed along the every pore sizes. On the other hand, 5-5 MoNi/Al_2O_3 shows that large pores from 32.5 A to 77.5 A are lost, however, small pores (less than 27.5 A) are apparently increasing. This indicates that adsorption of arsenic reduces pore sizes larger than 32.5 A. This may cause the amount of small pore size to increase. The same case is found in 7.5-2.5 MoNi/Al_2O_3. and can be account for the increasing of molybdenum loading. In MoNi/Al_2O_3, the molybdenum loading more than 5% will disturb the adsorption of arsenic on nickel phase, so the pores size distribution is difference when it is compared with 2.5-7.5 MoNi/Al_2O_3.

Figures 4.87 through 4.89 show the change of pore size distribution between fresh and spent NiMo/Al_2O_3. There are significant difference in pore size distribution between them. Pore size distribution in spent NiMo/Al_2O_3 adsorbent shows that all pores are decreased throughout the entire pore sizes. When molybdenum loading increases, some pores size between 27.5 A to 42.5 A are losing. This can be found in 5-5 NiMo/Al_2O_3 and 2.7-7.5 NiMo/Al_2O_3. The evidence can be account for the increasing of molybdenum loading. In NiMo/Al_2O_3, alumina support is first covered with nickel and the latter is covered with molybdenum. This indicates that most outer surface of alumina is sheltered with molybdenum surface. So, the molybdenum surface in NiMO/Al_2O_3 adsorbent is the importance factor in arsenic removal. The molybdenum phase will disturb the adsorption of arsenic on adsorbent. Some of arsenic will

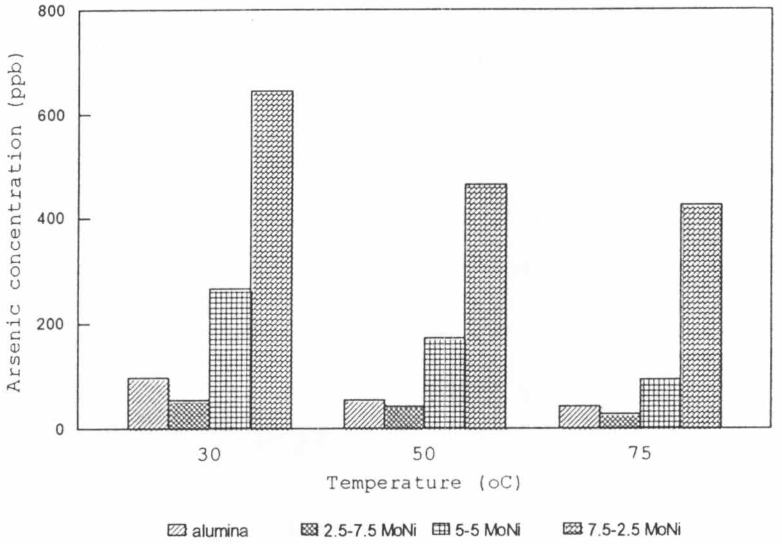

Figure 4.76 Comparison of remaining phenylarsine oxide in study the efficiency of alumina and MoNi adsorbents at temperatures from 30°C to 75°C and pressure at 400 psig.

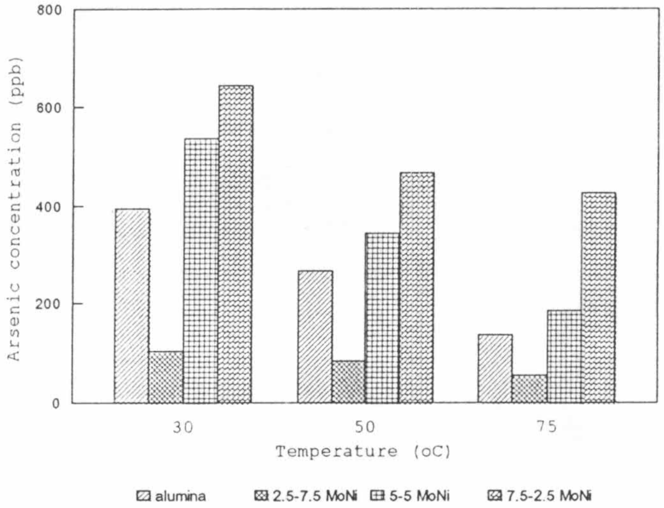

Figure 4.77 Comparison of remaining arsenic oxide in study the efficiency of alumina and MoNi adsorbents at temperatures from 30°C to 75°C and pressure at 400 psig.

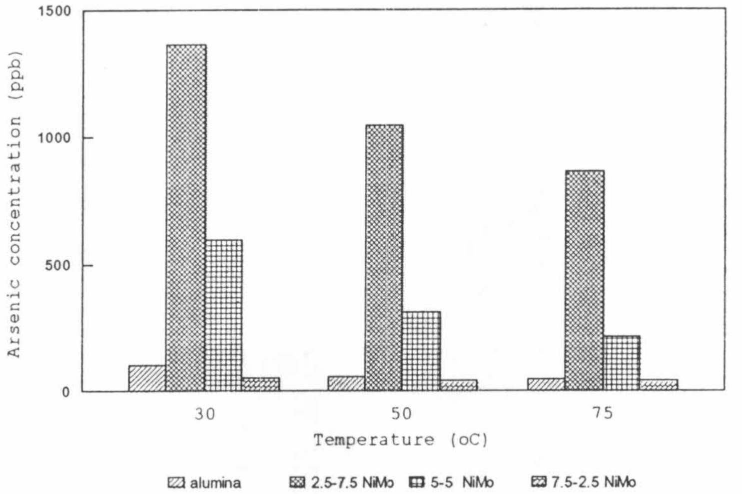

Figure 4.78 Comparison of remaining phenylarsine oxide in study the efficiency of alumina and NiMo adsorbents at temperatures from 30°C to 75°C and pressure at 400 psig.

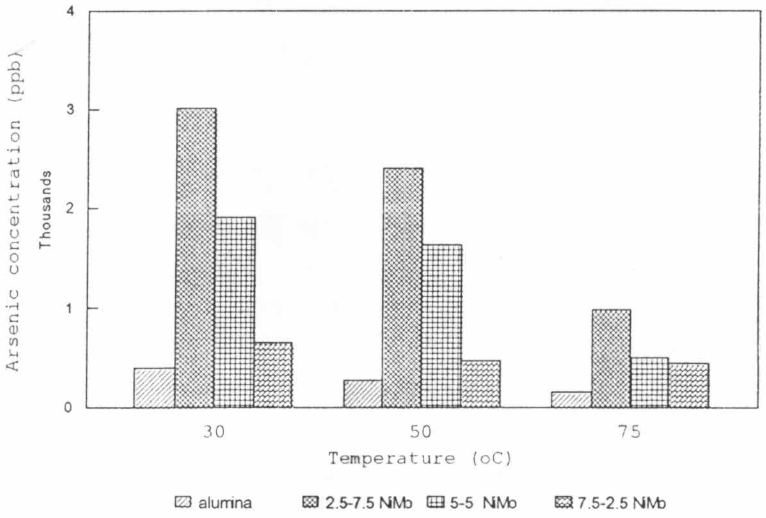

Figure 4.79 Comparison of remaining arsenic oxide in study the efficiency of alumina and NiMo adsorbents at temperatures from 30°C to 75°C and pressure at 400 psig.

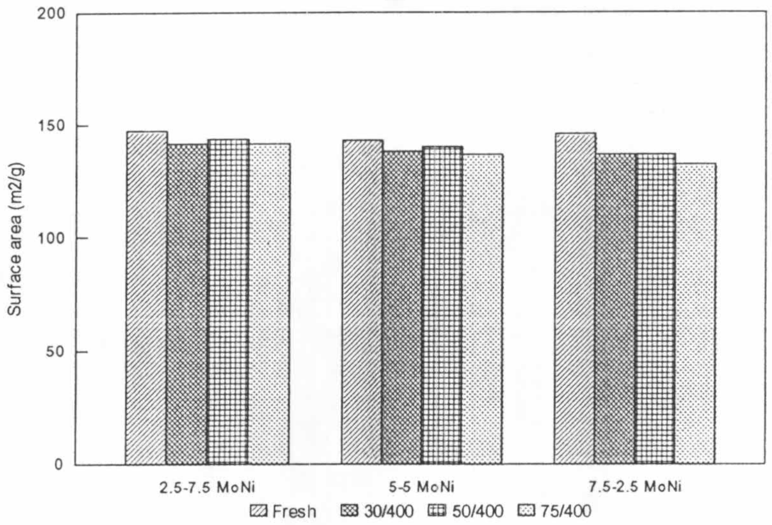

Figure 4.80 Comparison of surface area between fresh and spent MoNi adsorbents.

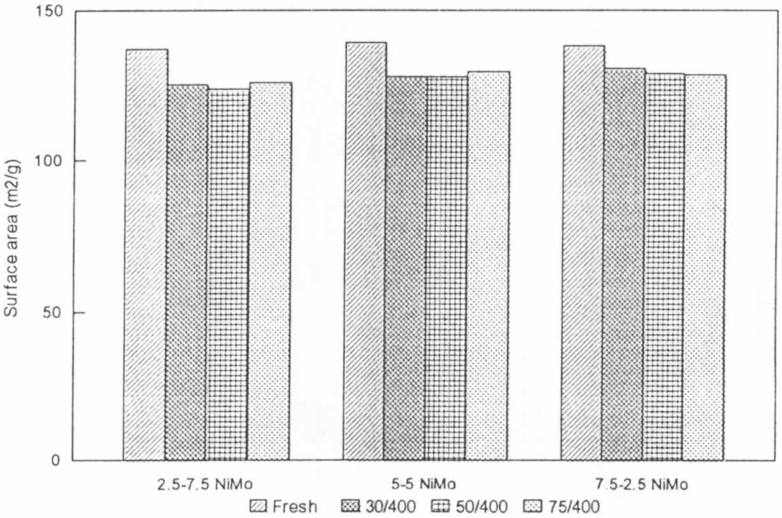

Figure 4.81 Comparison of surface area between fresh and spent NiMo adsorbents.

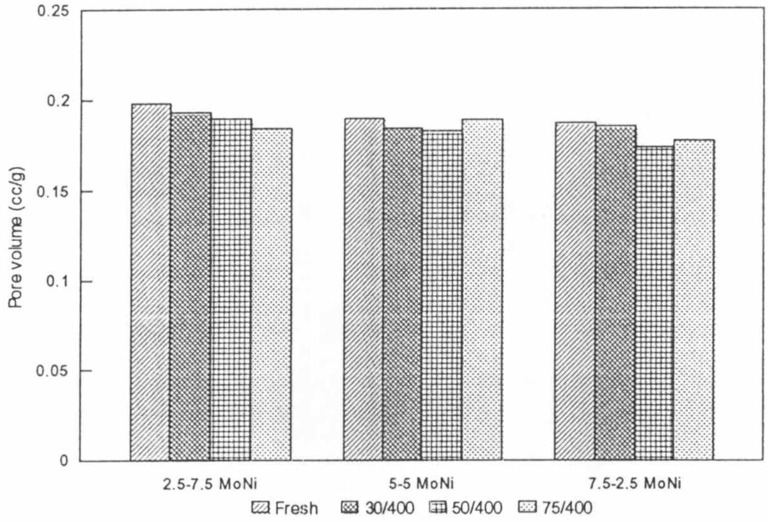

Figure 4.82 Comparison of pore volume between fresh and spent MoNi adsorbents.

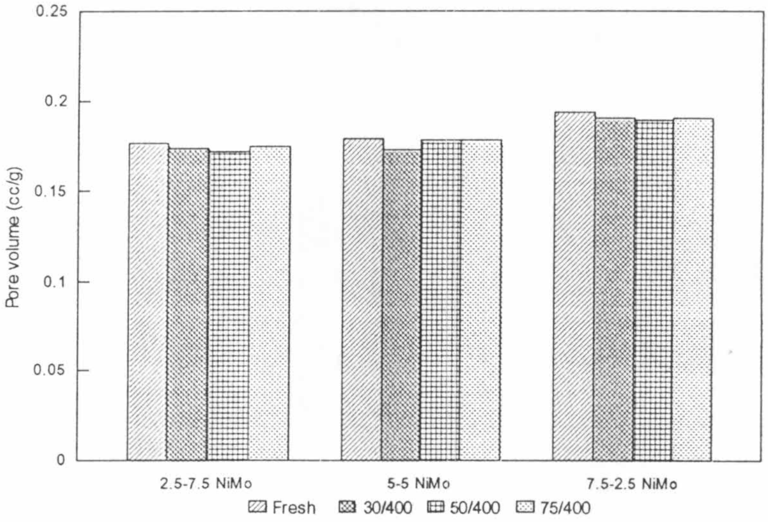

Figure 4.83 Comparison of pore volume between fresh and spent NiMo adsorbents.

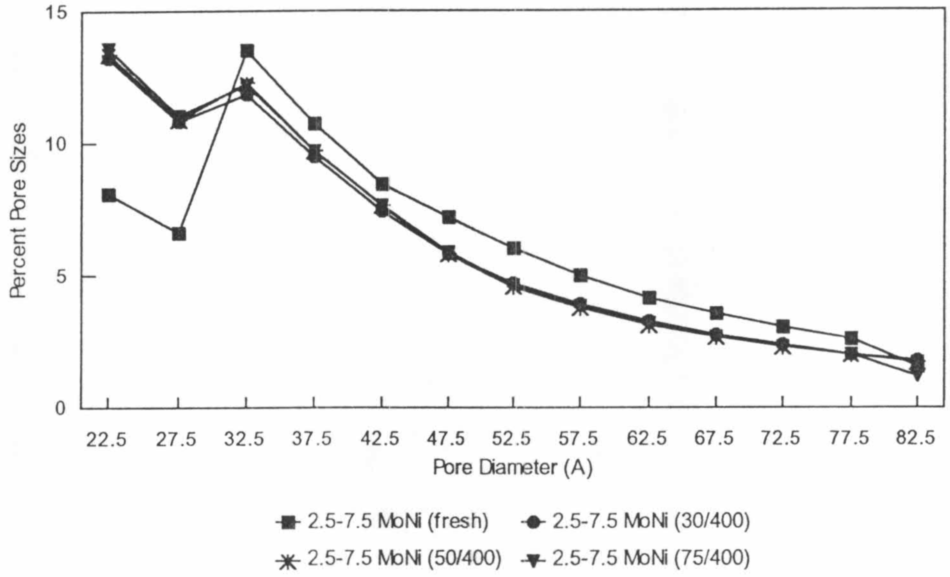

Figure 4.84 Comparison of pore sizes distribution between fresh and spent 2.5-7.5 MoNi

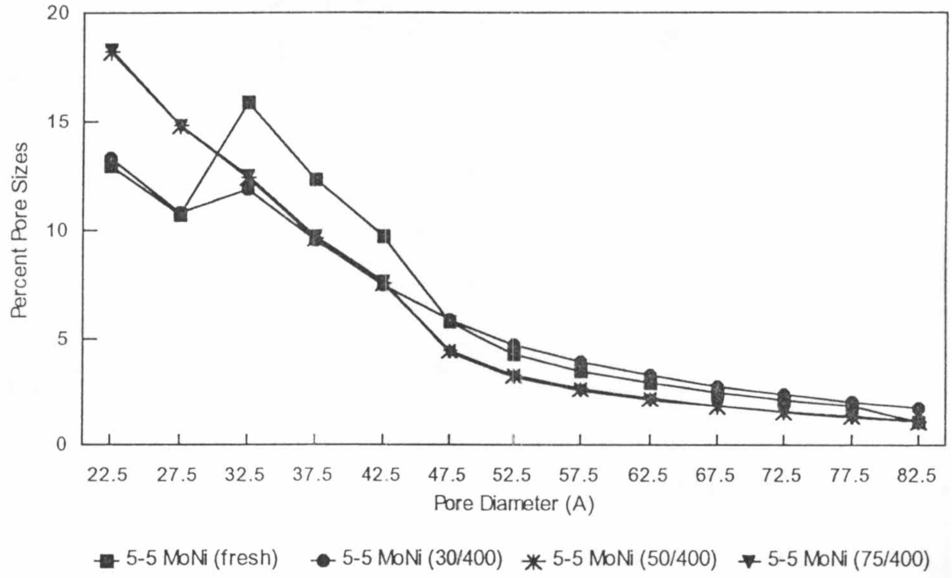

Figure 4.85 Comparison of pore sizes distribution between fresh and spent 5-5 MoNi adsorbents.

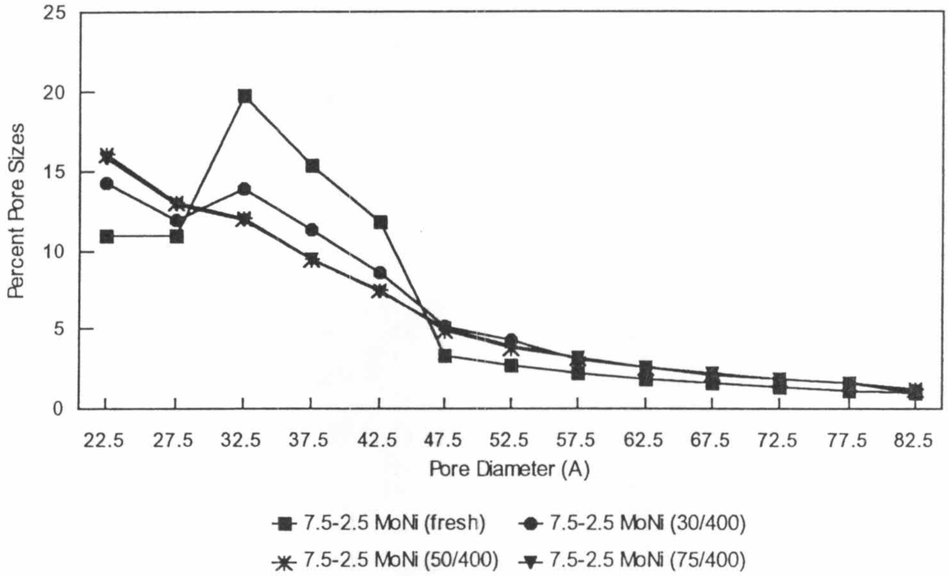

Figure 4.86 Comparison of pore sizes distribution between fresh and spent 7.5-2.5 MoNi adsorbents.

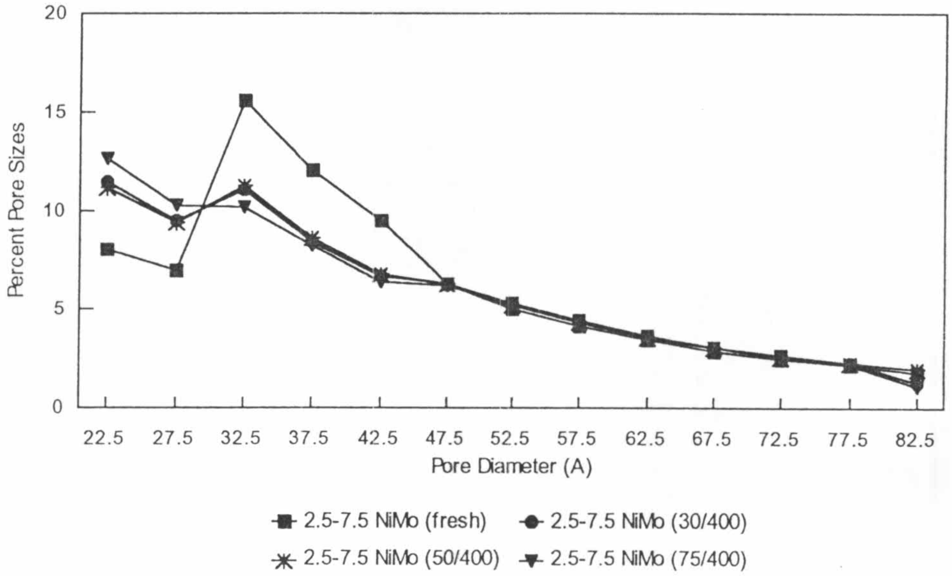

Figure 4.87 Comparison of pore sizes distribution between fresh and spent 2.5-7.5 NiMo adsorbents.

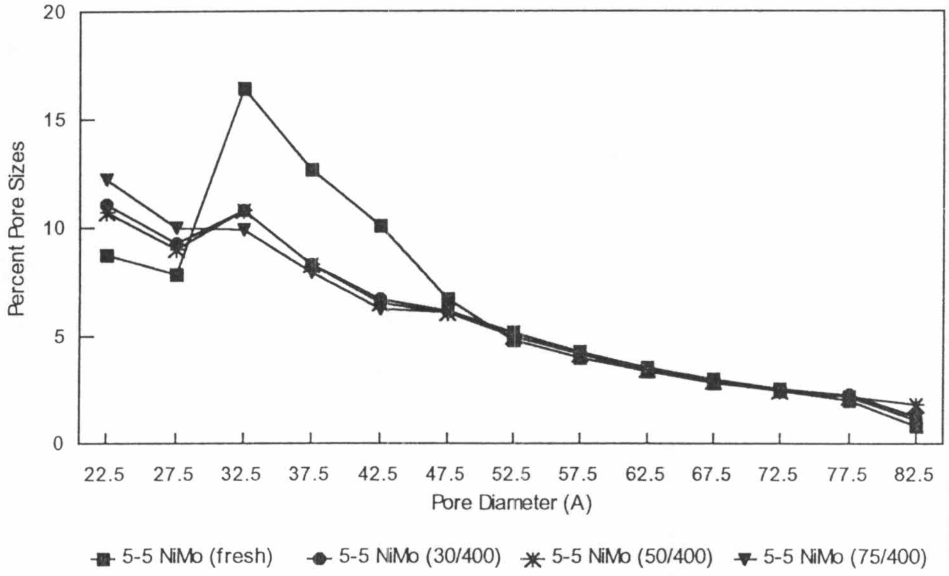

Figure 4.88 Comparison of pore sizes distribution between fresh and spent 5-5 NiMo adsorbents.

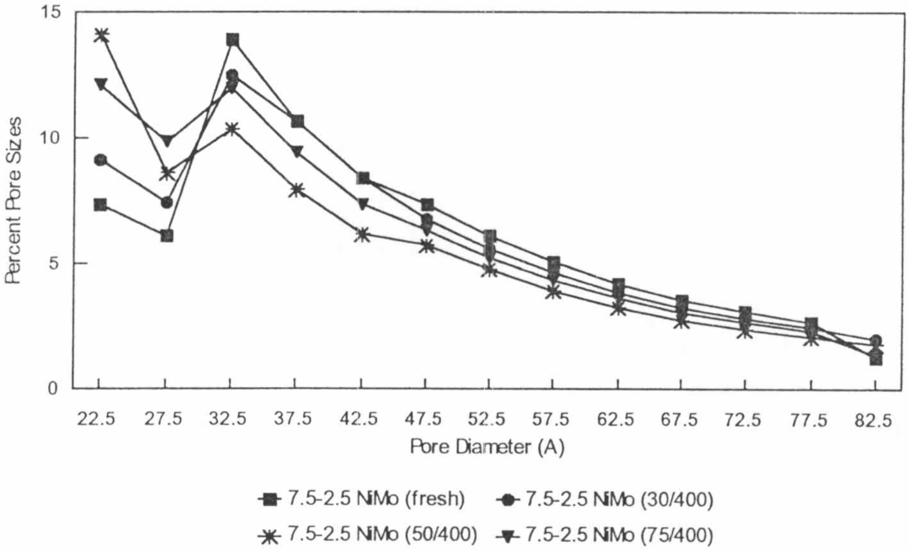

Figure 4.89 Comparison of pore sizes distribution between fresh and spent 7.5-2.5 NiMo adsorbents.

penetrate deeper to absorbed on alumina phase and causes the small pore size to change.

Effect of Nickel on Different Bimetallic Adsorbents

This section is conducted to study the presence of nickel on different adsorbents. The efficiency of arsenic removal is studied by comparison of experiments using MoNi/Al_2O_3 and NiMo/Al_2O_3 adsorbents. The ability of adsorbents on arsenic removal is considered to compare with the quantity of remaining arsenic in each experiment. The less remaining arsenic in product is the high ability of adsorbent for arsenic removal.

Figures 4.89 through 4.94 are comparison of remaining arsenic which used MoNi/Al_2O_3 and NiMo/Al_2O_3 at the temperature ranging from 30°C to 75°C. Figures 4.89 and 4.90 show the comparison of remaining arsenic which used 7.5-2.5 MoNi/Al_2O_3 and 2.5-7.5 NiMo/Al_2O_3 as the adsorbents. When nickel loading in 7.5-2.5 MoNi/Al_2O_3 and 2.5-7.5 NiMo/Al_2O_3 is equally (2.5%), the efficiency of arsenic removal in 7.5-2.5 MoNi/Al_2O_3 is higher than 2.5-7.5 NiMo/Al_2O_3. This effect can be explained in term of reactivity of nickel. In MoNi/Al_2O_3, alumina support is first impregnated with molybdenum and the latter is impregnated with nickel. This indicates that the outer surface of alumina is mostly sheltered with nickel surface. Thus arsenic can be adsorbed on this surface. Comparison of NiMo/Al_2O_3, the outer surface is mostly sheltered with molybdenum phase. This causes the efficiency of arsenic decreasing comparison to that one.

Figures 4.91 and 4.92 show the comparison of remaining arsenic which used 5-5 MoNi/Al_2O_3 and 5-5 NiMo/Al_2O_3 as the adsorbents. Figures 4.93 and 4.94 show the comparison of remaining arsenic which used 2.5-7.5 MoNi/Al_2O_3 and 7.5-2.5 NiMo/Al_2O_3 as the adsorbents. These results agree with the reasons that described above. The efficiency of arsenic removal on bimetallic adsorbents at the same nickel loading increases in the order 7.5-2.5 MoNi/Al_2O_3 > 2.5-7.5 NiMo/Al_2O_3,

5-5 MoNi/Al_2O_3 > 5-5 NiMo/Al_2O_3 and

2.5-7.5 MoNi/Al_2O_3 > 7.5-2.5 NiMo/Al_2O_3.

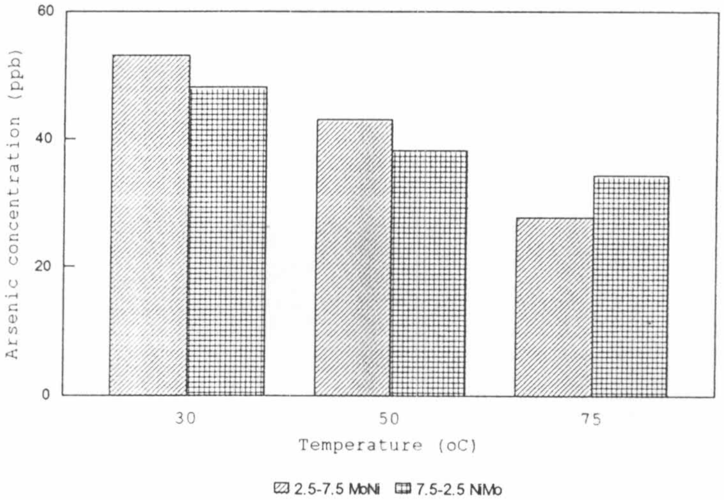

Figure 4.90 Comparison of remaining phenylarsine oxide in study the effect of 7.5% nickel on MoNi and NiMo adsorbents.

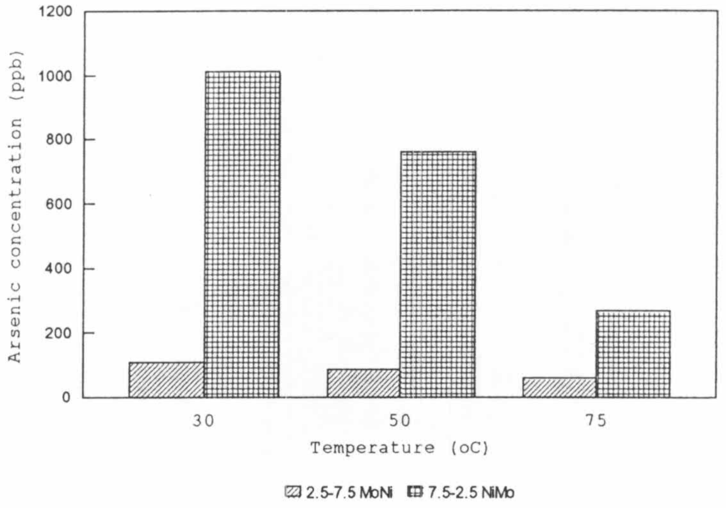

Figure 4.91 Comparison of remaining arsenic oxide in study the effect of 7.5% nickel on MoNi and NiMo adsorbents.

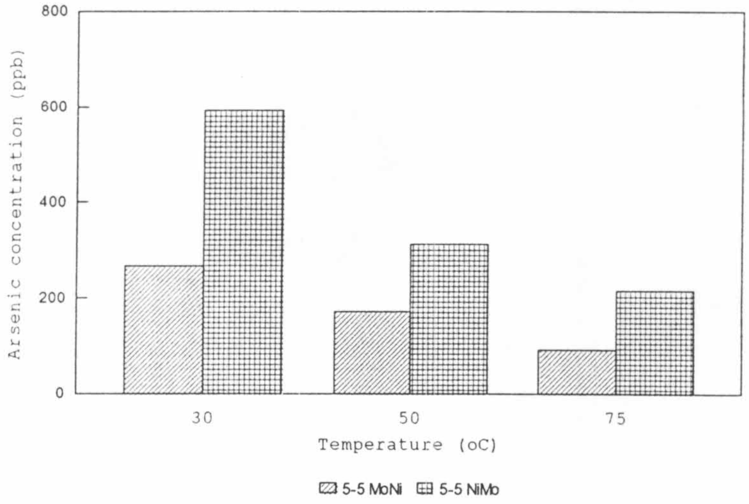

Figure 4.92 Comparison of remaining phenylarsine oxide in study the effect of 5% nickel on MoNi and NiMo adsorbents.

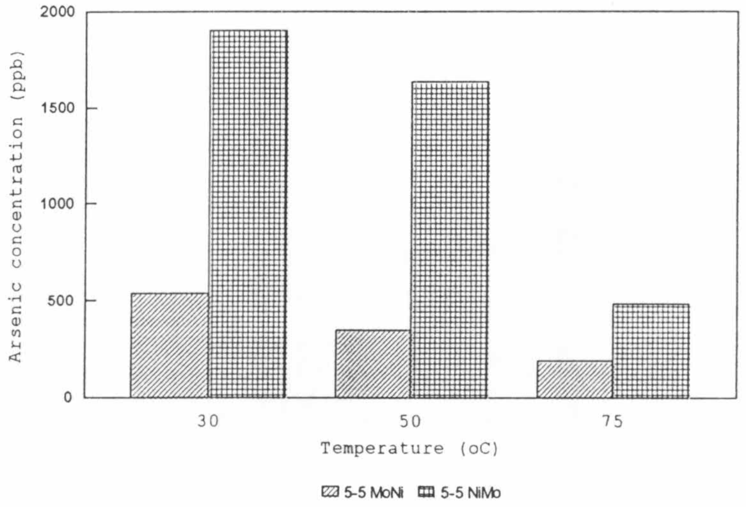

Figure 4.93 Comparison of remaining arsenic oxide in study the effect of 5% nickel on MoNi and NiMo adsorbents.

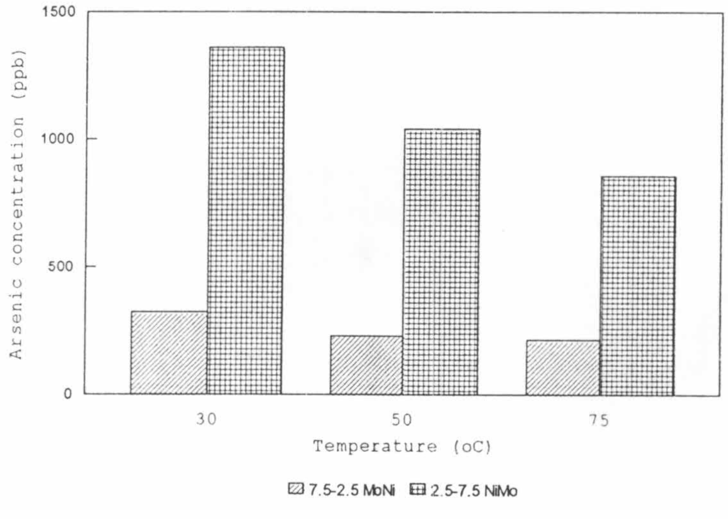

Figure 4.94 Comparison of remaining phenylarsine oxide in study the effect of 2.5% nickel on MoNi and NiMo adsorbents.

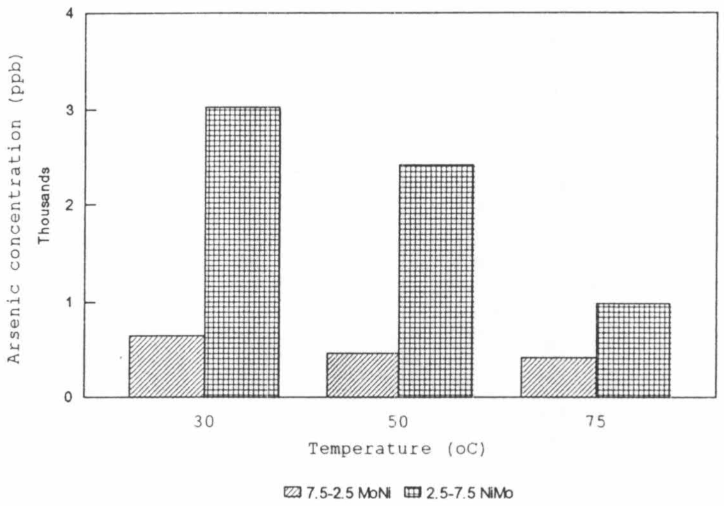

Figure 4.95 Comparison of remaining arsenic oxide in study the effect of 2.5% nickel on MoNi and NiMo adsorbents.