

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Thermogravimetric Analysis (TGA)

The water content in adsorbent can reduce the capacity and accuracy of DPM adsorbent (Nampri, 2005). The moisture content must be controlled and less than 5% by weight is recommended. Then, it is necessary to dry all adsorbents before use. The weight losses of adsorbents with temperature were investigated by thermogravimetric analysis technique (TGA) to determine the temperature for the treatment of adsorbent. TGA results of all adsorbents are shown in Figure 4.1. The results show that all zeolites (Omega, Beta, and L all are powder) lost weight in the temperature range of 30°C to 150°C and became constant around 350°C. The moisture including impurity was released and decreased continuously. At temperature of 250°C, the values were slightly dropped and remained the same for long period of time. The results showed the losses of weight for zeolites Beta, Omega, and L at 16.2, 13.9 and 12.4 % (wt) respectively. Therefore, the pre-treatment temperature for zeolites L, Beta and Omega were 200°C, 350°C and 350°C, respectively. However in this work all zeolites were treated at 350°C for 2 hrs and cooled to room temperature in a desiccator.

For the commercial adsorbent CMG273 (pellet), the weight loss decreased from the beginning, when temperature reached 350°C, the curve dropped steeply. The result indicated that the loss of some chemical occurred. Since the adsorbent CMG273 is oxygen and moisture sensitive, it was kept in an evacuated desiccator and used directly.

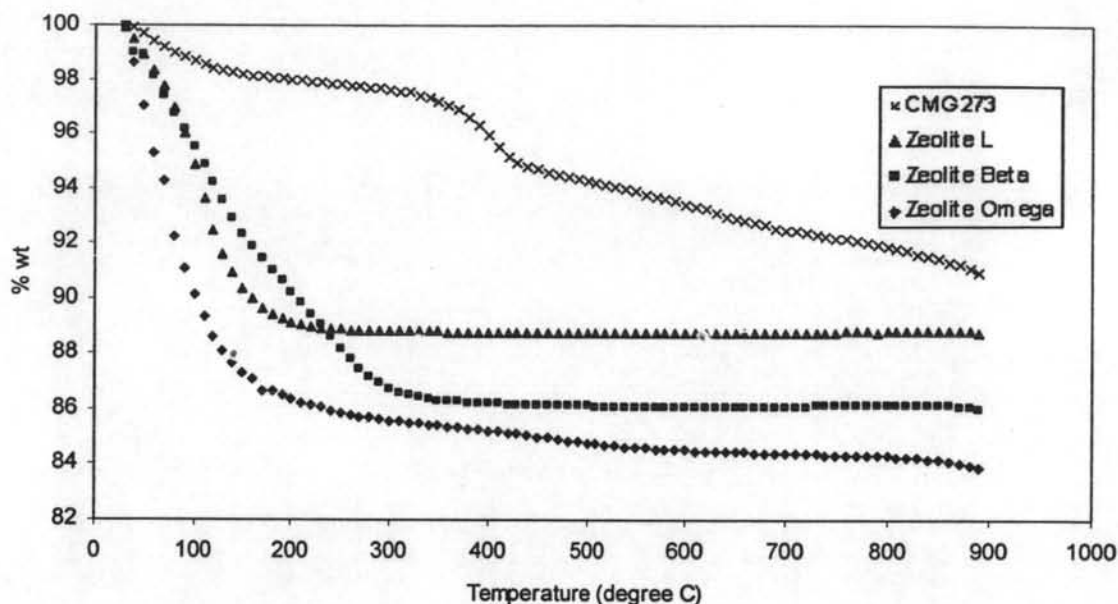


Figure 4.1 TGA results for all adsorbents: Zeolite Omega, Beta, L and CMG273.

4.2 Stability of DPM in Borosilicate Glass Containers

Losses of mercury due to adsorption on the wall of container were studied. The stability of DPM in a glass vial (borosilicate) of 2 ml capacity was performed for 7 days. The results of storing 2 ppm DPM in n-heptane is shown in Figure 4.2. The concentration of DPM was dropped slightly after one week storage with less than 1.5 % loss. However, the loss was a variation within the analytical error. It is, therefore, reasonable to use borosilicate glass vials for storage DPM solution.

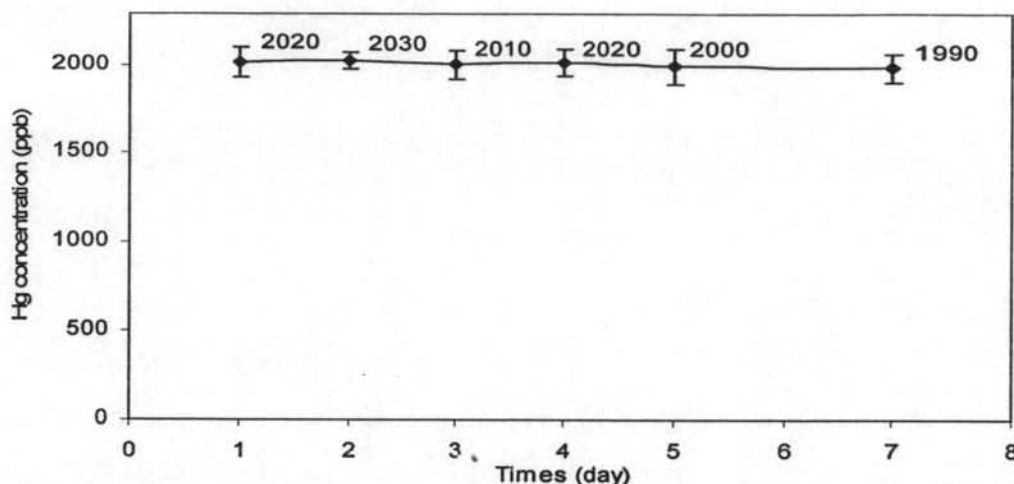


Figure 4.2 Adsorption of diphenylmercury in n-heptane in a storage borosilicate glass vials at room temperature.

4.3 Kinetic Studies

4.3.1 Kinetic Studies of Diphenylmercury Adsorption in n-Heptane

The adsorption kinetics of DPM on zeolites Omega, Beta, L and CMG273 was studied. The experiments were conducted with two concentrations (2 ppm and 5 ppm) of DPM. Figure 4.3 shows DPM adsorption per gram of adsorbent at 30°C, 40°C and 50°C. The zeolite Omega, Beta, L and CMG273 reached the equilibrium around 10, 12, 50 and 180 minute, respectively. At low concentration (2 ppm) and 30°C, more than 70%, 60% and 35% of DPM adsorption could be archived with in first minute on the zeolite Omega, Beta, and L, respectively. In addition, the adsorption on all zeolites was decrease as increase adsorption temperature. For CMG273, and 30°C, the DPM adsorption was gradually increased and required more than 2 hours to achieve 70% adsorption, and the adsorption increased with increasing temperature. At high concentration (5 ppm), the adsorption increased in all adsorbents. At the same concentration of DPM in n-heptane and 30°C, the adsorption capacity was in the order of Beta > CMG273 > Omega > L, which at 50°C, CMG273 > Beta > Omega > L.

It was noted that the size of adsorbent (powder for zeolites and pellet for CMG273) caused the different rates of adsorption. For CMG273, initial rate of diffusion may be slow due to presence of macro pore resistance (pellet form) along with micro pore resistance. However, powder form of zeolites has macro pore diffusion, but micro pore resistance is responsible for high rate of removal.

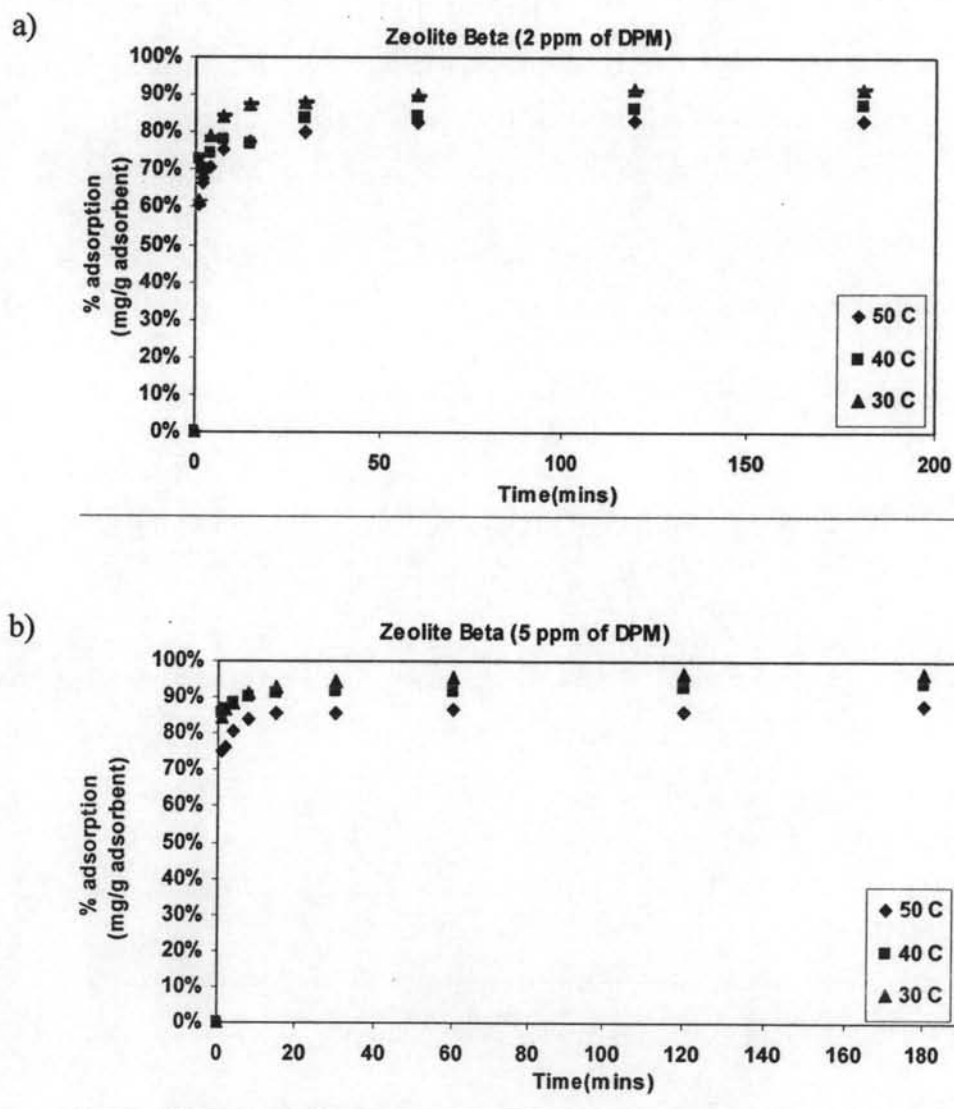


Figure 4.3 Adsorption kinetics of DPM 2 ppm on Zeolite a) Omega, c) Beta, g) L and f) CMG273 and DPM 5 ppm on Zeolites b) Omega, d) Beta, f) L and h) CMG27

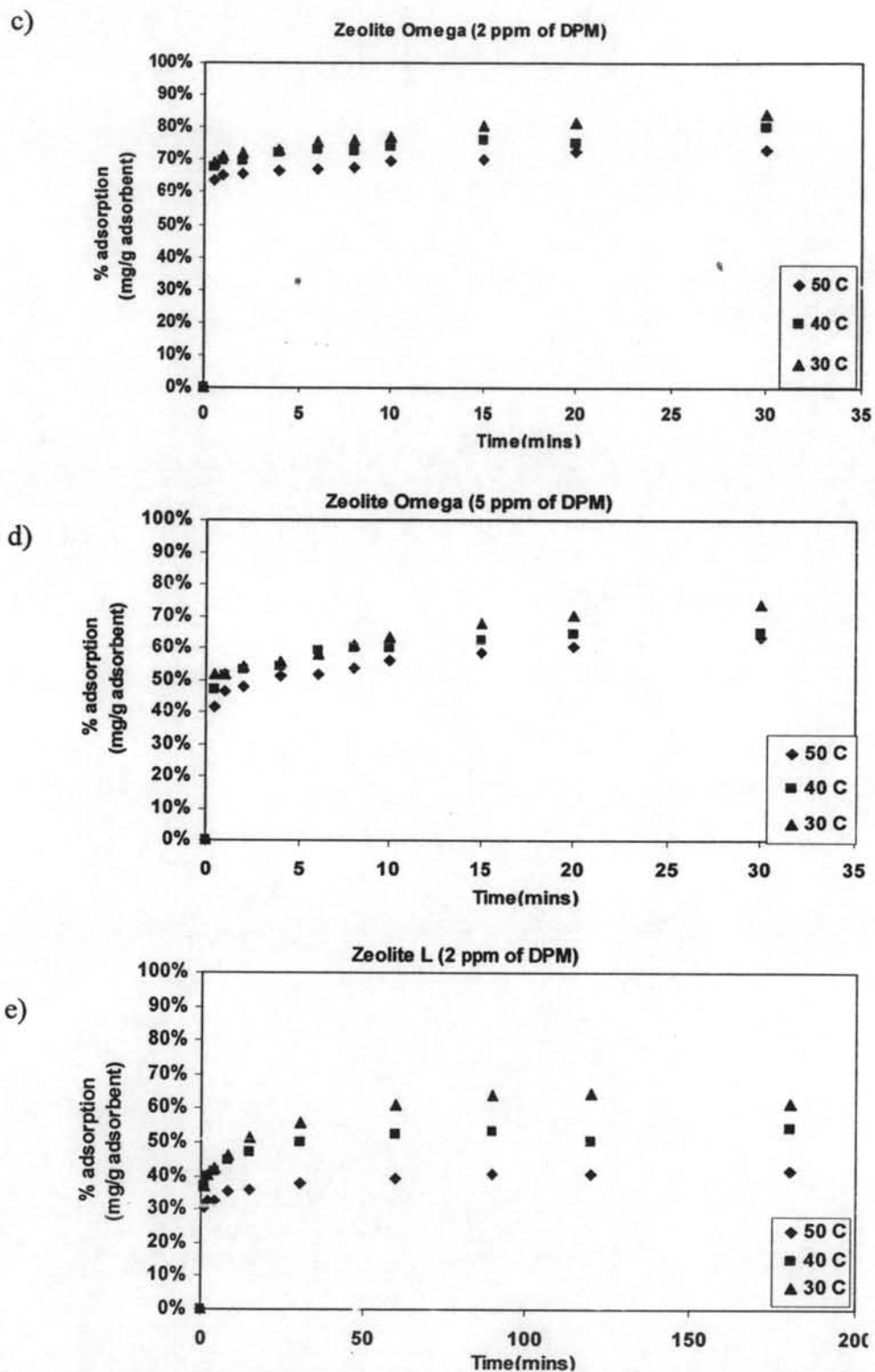


Figure 4.3 (cont'd) Adsorption kinetics of DPM 2 ppm on Zeolite a) Omega, c) Beta, g) L and f) CMG273 and DPM 5 ppm on Zeolites b) Omega, d) Beta, f) L and h) CMG273.

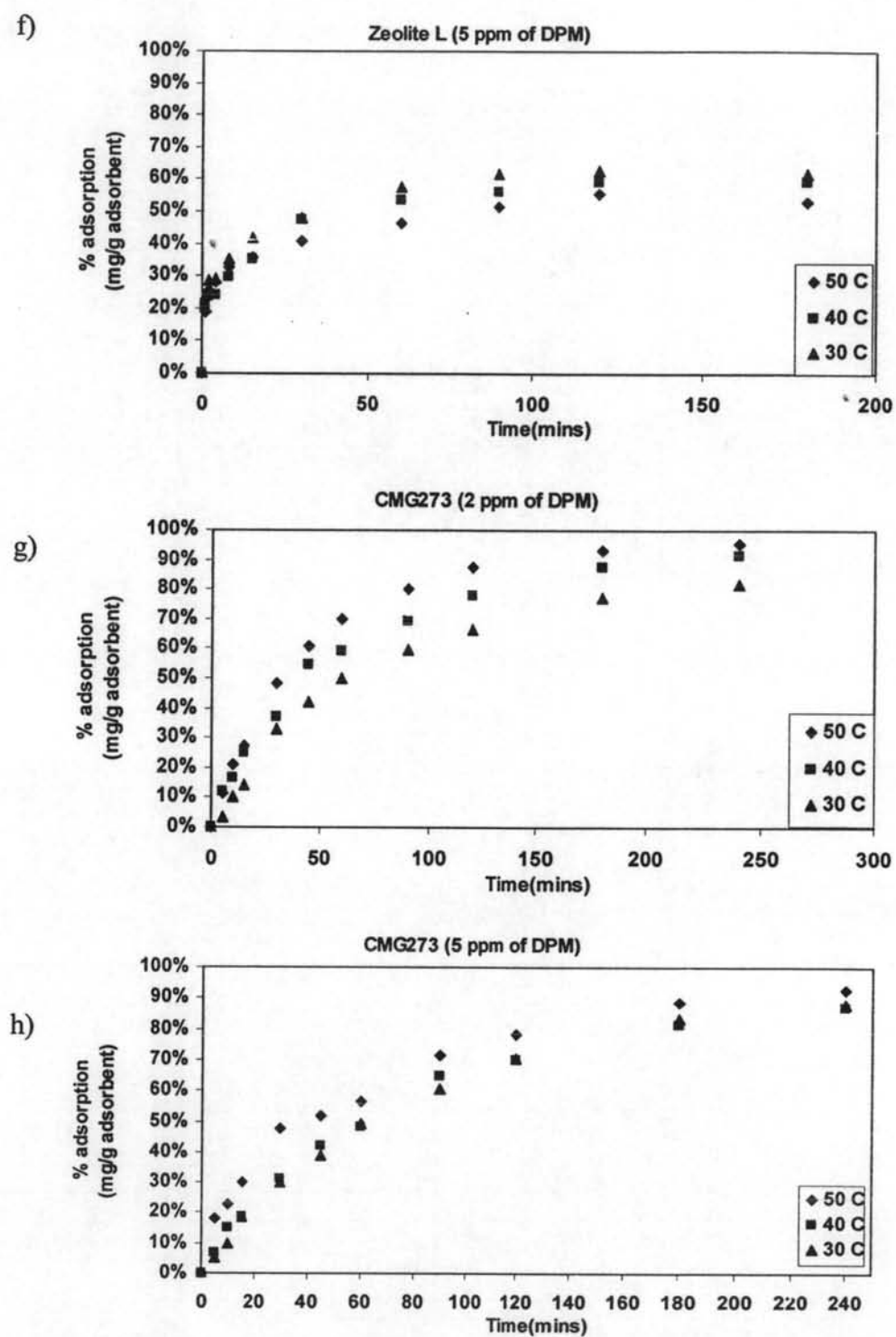


Figure 4.3 (cont'd) Adsorption kinetics of DPM 2 ppm on Zeolite a) Omega, c) Beta, g) L and f) CMG273 and DPM 5 ppm on Zeolites b) Omega, d) Beta, f) L and h) CMG273.

4.3.1.1 Correlation of Adsorptions Kinetics of DPM on Zeolite Omega, Beta, and L

The linear equation of Lagergren, both pseudo 1st and 2nd order and Elovich were applied to the experimental data (batch) for zeolites Omega, Beta, and L. The correlation coefficients (R^2) of all three kinetic models were calculated as shown in Table 4.1 and Table 4.2.

The rate of adsorption was first tested with the pseudo 1st order mechanism by plotting $\log(q_e - q_t)$ vs time. The plots have poor linearity for zeolites Omega, Beta, and L as shown in terms of the correlation coefficients (R^2) value for both concentrations and temperature at 30, 40 and 50°C. Pseudo 2nd order equation was applied by plotting t/q_e vs t . The plots were shown an excellent fitting with the data. The correlation coefficients (R^2) were close to 1 (more than 0.99) in all cases. The application of the Elovich equation to the kinetics data of DPM adsorption on zeolite Omega, Beta, and L showed poor fitting. The correlation coefficients (R^2) of the Elovich equation were comparable with the pseudo 1st order.

Table 4.1 Correlation coefficients (R^2) of the three kinetic adsorption models for 2 ppm DPM in n-heptane solution

Adsorbent	R^2								
	Pseudo 1 st order			Pseudo 2 nd order			Elovich		
	30 °C	40 °C	50 °C	30 °C	40 °C	50 °C	30 °C	40 °C	50 °C
Omega	0.7236	0.4587	0.7171	0.9999	0.9983	0.9994	0.9198	0.8848	0.8951
L	0.9454	0.5955	0.7488	0.9985	0.9984	0.9994	0.9648	0.9588	0.9881
Beta	0.8721	0.5202	0.7818	1.0000	0.9993	1.0000	0.8086	0.8710	0.9410

Table 4.2 Correlation coefficients (R^2) of the three kinetic adsorption models for 5 ppm in DPM n-heptane solution

Adsorbent	R^2								
	Pseudo 1 st order process			Pseudo 2 nd order process			Elovich		
	30 °C	40 °C	50 °C	30 °C	40 °C	50 °C	30 °C	40 °C	50 °C
Omega	0.8392	0.8782	0.8392	0.9959	0.9978	0.9971	0.8939	0.9745	0.9699
L	0.9789	0.9633	0.9425	0.9981	0.9978	0.9957	0.9690	0.9605	0.9775
Beta	0.7417	0.4038	0.4160	1.0000	0.9999	0.9999	0.9672	0.9489	0.8611

The equilibrium rate constant (k_{e2}) and adsorption capacity (q_e) for zeolites Omega, Beta, and L were then calculated from the pseudo 2nd order rate model and are summarized in Tables 4.3 and 4.4.

Table 4.3 Pseudo 2nd order parameters for kinetics of adsorption of 2 ppm DPM at in n-heptane

Adsorbent	k_{e2} (g adsorbent/mg DPM/min)			q_e (mg DPM /g adsorbent)		
	30 °C	40 °C	50 °C	30 °C	40 °C	50 °C
Omega	7.3704	9.8732	12.1486	0.2655	0.2413	0.2209
L	2.6569	3.6411	4.0729	0.1955	0.1671	0.1294
Beta	4.1415	3.3441	4.4054	0.2961	0.2824	0.2691

Table 4.4 Pseudo 2nd order parameters for kinetics of adsorption of 5 ppm DPM in n-heptane

Adsorbent	k_{e2} (g adsorbent/mg DPM/min)			q_e (mg DPM /g adsorbent)		
	30°C	40°C	50°C	30°C	40°C	50°C
Omega	1.6358	3.4661	2.1293	0.5560	0.4989	0.4954
L	0.3717	0.3189	0.4373	0.4989	0.4622	0.4175
Beta	2.8337	3.6173	3.6166	0.7188	0.6927	0.6425

From Tables 4.3 and 4.4, the adsorption capacity at equilibrium (q_e), for all adsorbents, was decreased slightly with increased temperatures, which exhibit the phenomena of physical adsorption of diphenylmercury molecule. The physical adsorption indicates the possibility of regeneration of used adsorbent using conventional methods.

On the contrary, equilibrium rate constant (k_{e2}), for all adsorbents, increased with temperature. It shows that the rate of DPM adsorption can be improved by increasing temperature.

4.3.1.1 Correlation of Adsorption Kinetics of DPM on Adsorbent CMG273

For adsorption kinetics of DPM in n-heptane on CMG273, three kinetic model, the pseudo 1st, 2nd order and Elovich equation were also applied to these data. It was found that the adsorption kinetics data were fitted very well for all models. The parameters from each model calculated and compared with the experimental result as shown in Tables 4.5 and 4.6.

A comparison of q_e values (experimental and those obtained from the pseudo 1st, 2nd and Elovich equation) showed that the values q_e from the pseudo 1st order equation were in good agreement with the experimental data in both ranges of concentrations (2 ppm and 5 ppm). The q_e that calculated from pseudo 2nd order was higher than experimental data and much higher for an Elovich (b value) equation in two ranges of DPM concentration. However, the differences still existing might be due to the uncertainty inherent in obtaining the experimental q_e values and also due to the actual process being not in conformity with simple first order or second order kinetics.

Table 4.5 Experimental and computed q_e and k_e of DPM (2 ppm in n-heptane) kinetics adsorption on CMG273

Temperature (°C)	Experimental data (mg/g)	Pseudo 1 st order			Pseudo 2 nd order			Elovich		
		q_e (mg/g)	K_{e1}	R ²	q_e (mg/g)	K_{e2}	R ²	a	b (mg/g)	R ²
30	0.250	0.2565	0.0158	0.9842	0.3866	0.0228	0.9825	0.0112	14.9925	0.9680
40	0.285	0.2768	0.0168	0.9942	0.3483	0.0550	0.9958	0.0167	14.1844	0.9696
50	0.282	0.2766	0.0213	0.9827	0.3384	0.0705	0.9999	0.0190	14.0056	0.9764

Table 4.6 Experimental and computed q_e and k_e of DPM (2 ppm in n-heptane) kinetics adsorption on CMG273

Temperature (°C)	Experimental data(mg/g)	Pseudo 1 st order			Pseudo 2 nd order			Elovich		
		q_e (mg/g)	K_{e1}	R ²	q_e (mg/g)	K_{e2}	R ²	a	b (mg/g)	R ²
30	0.665	0.7096	0.0156	0.9899	0.9854	0.0096	0.9927	0.0284	5.7504	0.9849
40	0.652	0.6519	0.0147	0.9928	0.8597	0.0153	0.9950	0.0309	6.0827	0.9791
50	0.699	0.6094	0.0146	0.9975	0.7987	0.0321	0.9974	0.0525	6.4185	0.9847

4.3.2 Adsorption Kinetics of Diphenylmercury in Treated Heavy Naphtha

The adsorption kinetics of DPM in n-heptane on zeolites Omega, Beta was found very fast and, also, these zeolites have shown highest adsorption capacity for DPM. Thus, zeolites Omega and Beta were selected for further adsorption of spiked DPM in heavy naphtha. Non contaminated heavy naphtha spiked with 2 ppm of DPM was carried out at 30°C and the results are presented in Figure 4.4.

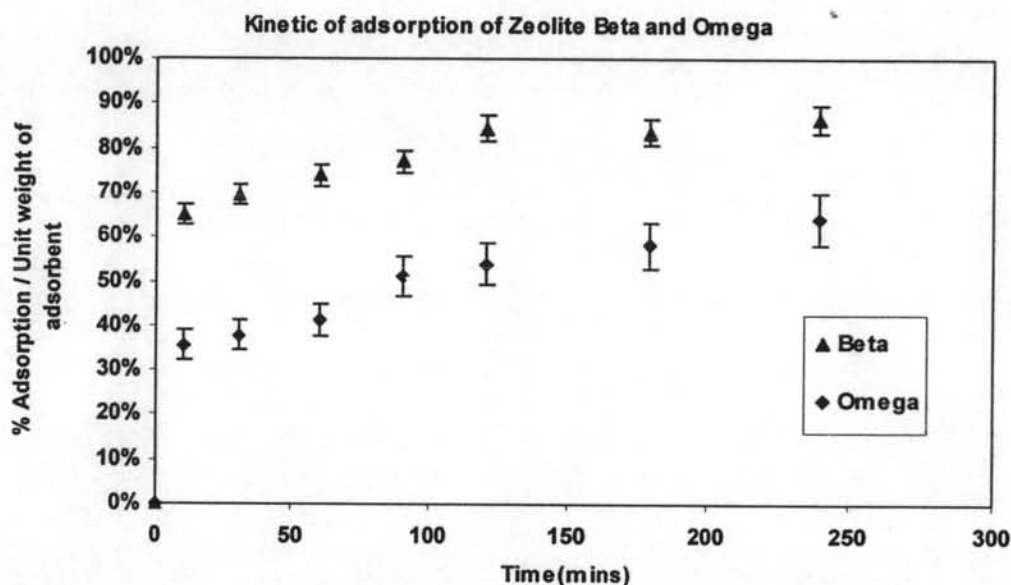


Figure 4.4 Adsorption kinetics of DPM in heavy naphtha on Zeolite Beta and Omega.

A reduction in adsorption capacity was seen in both zeolites Omega and Beta. Moreover, the rate of adsorption was also slow, more than 2 hours to reach equilibrium. A drop in the adsorption capacity and the decreased in adsorption rate may be due to the complexity of hydrocarbon species in heavy naphtha.

In order to understand behavior of adsorption, the pseudo 2nd order rate model (equation 2.13) was applied. The best fitting with R^2 better than 0.98 were obtained (Figure 4.5). The rate constant (k_{e2}) and equilibrium

capacity (q_e) were calculated from the slope and intercept and listed in Table 4.7.

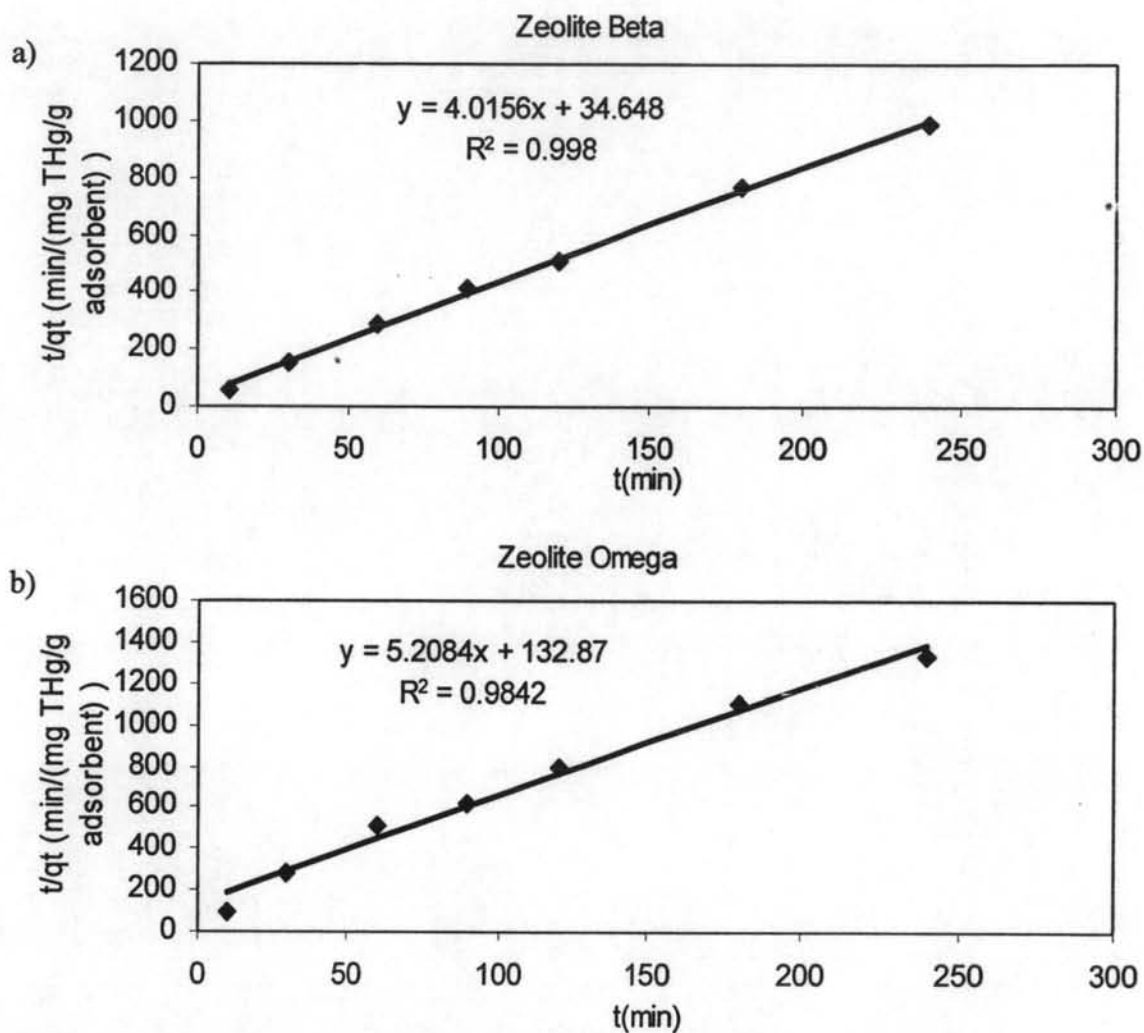


Figure 4.5 The pseudo 2nd order coefficients for adsorption of DPM in heavy naphtha a) Zeolite Beta and b) Omega.

Table 4.7 Pseudo 2nd order parameters for kinetics of adsorption of DPM in heavy naphtha

Adsorbent	k_{e2} (g adsorbent/mg Hg /min)	q_e (mg Hg /g adsorbent)
	30 °C	30 °C
Beta	0.4645	0.2490
Omega	0.2039	0.1921

Nampri, (2005) studied the effect of various hydrocarbons species (such as toluene, xylene, ethylbenzene and cyclohexane) on adsorption of DPM in n-heptane on zeolites X and Y. He also found a decrease in the adsorption capacity and the rate and proposed that various hydrocarbon matrices act as a competitor with diphenylmercury on adsorption sites of zeolites X and Y. Similar phenomena are observed for zeolites Omega and Beta; however the reduction in capacity was not found the same for both zeolites. Higher adsorption may be due to better compatibility of zeolite Beta (higher Si/Al ratio in Table 3.1) for a non polar DPM molecule.

4.3.3 Adsorption Kinetics of Natural Mercury species in Real Heavy Naphtha

Heavy naphtha fraction was obtained from distillation column. The fraction still containing elemental mercury and other organomercury species (Shafawi *et al.*, 2000) was use in this experiment. Total mercury in the heavy naphtha was analyzed and 800 ppb was obtained. The adsorption mercury species in the heavy naphtha was performed with zeolite Omega and Beta at 30°C. Figure 4.6 shows the adsorption of mercury species in the heavy naphtha fraction on zeolite Omega and Beta. Adsorption of total mercury as high as 40% and 30% were obtained on zeolite Bata and Omega, respectively, at 4 hours period. The adsorption of zeolite Beta and Omega was due to organomercury species as demonstrated by DPM adsorption, while the elemental mercury has no affinity toward zeolite Beta and Omega (Ullah, 2006). The exact type of organomercury that present in this heavy naphtha

fraction is not known, but 60 to 80 % of the metallic mercury in similar heavy naphtha was observed by IFP.

The pseudo 2nd order rate model (equation 2.12) was again used to explain the behavior of adsorption. The R^2 were greater than 0.98 and presented in Figure 4.7 and the capacity (q_e) and the adsorption rate (k_{e2}) in Table 4.8, very low adsorption capacity but a high value for rate constant. The capacity and rate of adsorption of organomercury species was much less than the adsorption of DPM in n-heptane and spiked DPM in heavy naphtha.

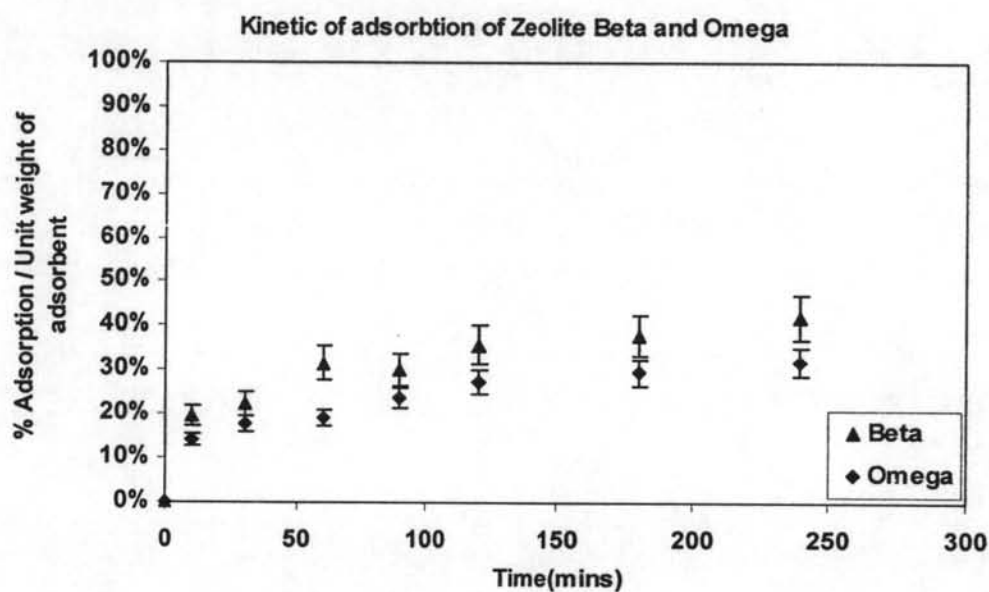


Figure 4.6 Kinetics of adsorption of natural mercury species heavy naphtha of zeolites Beta and Omega at 30°C and at atmospheric pressure.

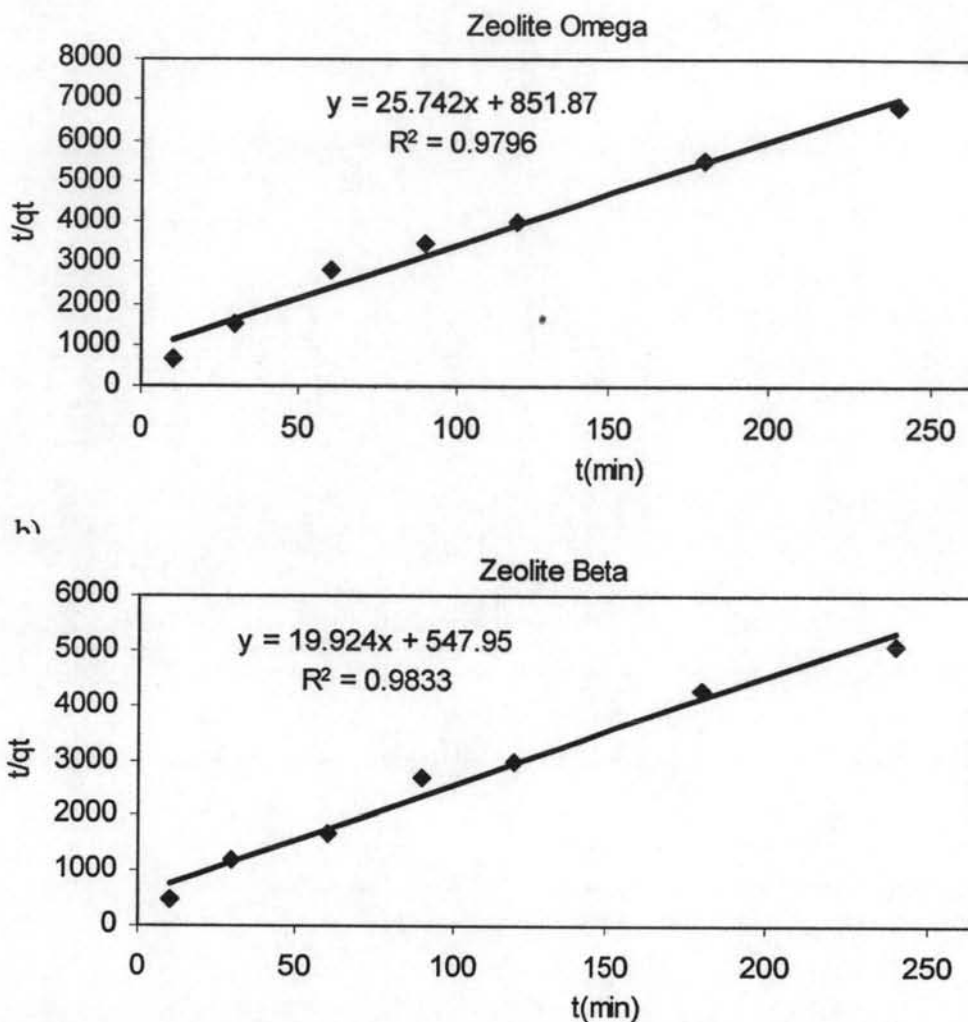


Figure 4.7 The pseudo 2nd order coefficients for adsorption of DPM in heavy naphtha a) Zeolite Omega and b) Beta.

Table 4.8 Pseudo 2nd order parameters for kinetics of mercury species adsorption in heavy naphtha

Adsorbent	k_{e2} (g adsorbent/mg Hg /min)	q_e (mg Hg /g adsorbent)
	30 °C	30 °C
Beta	0.7245	0.0502
Omega	0.7779	0.0388

A drop in capacity could be explain due to presence of higher level of metal mercury while somewhat higher rate constant was seen due to the presence of small quantities of other mercury species (such as organic and inorganic forms) in real feedstock.

4.4 Isotherm of Adsorption Studies

4.4.1 Isotherms for Diphenylmercury Adsorption in n-Heptane

The adsorption isotherms for zeolites Omega, Beta, L and CMG273 were performed at temperatures 30°C, 40°C and 50°C. The experiments were done by varying the concentrations of DPM in the range of 2 to 5 ppm and equilibrium time was set at 6 hours (based on the kinetic study). Langmuir Isotherm was found suitable and was used to correlate solid and liquid phase concentrations.

The Langmuir Model can be explained as follows:

$$q = \left(\frac{bC}{1 + bC} \right) q_{\max} \quad (4.1)$$

where q is the quantity of molecules adsorbed on the solid phase (mg/g of adsorbent), q_{\max} is the maximum quantity adsorbed on solid phase, b is adsorption / desorption constant and C is the fluid phase concentration.

Equation 4.1 can be linearized as follows:

$$\frac{1}{q} = \frac{1}{q_{\max}} + \left(\frac{1}{bq_{\max}} \right) \frac{1}{C} \quad (4.2)$$

Figure 4.8 shows the liner plots of Langmuir model equation for zeolites Omega, Beta, L and CMG273 in a), c), e) and g), respectively. The adsorbtion capacity (q_{\max}) and the adsorption rate constant (b) obtained from the interception and slope, respectively are shown in Table 4.9.

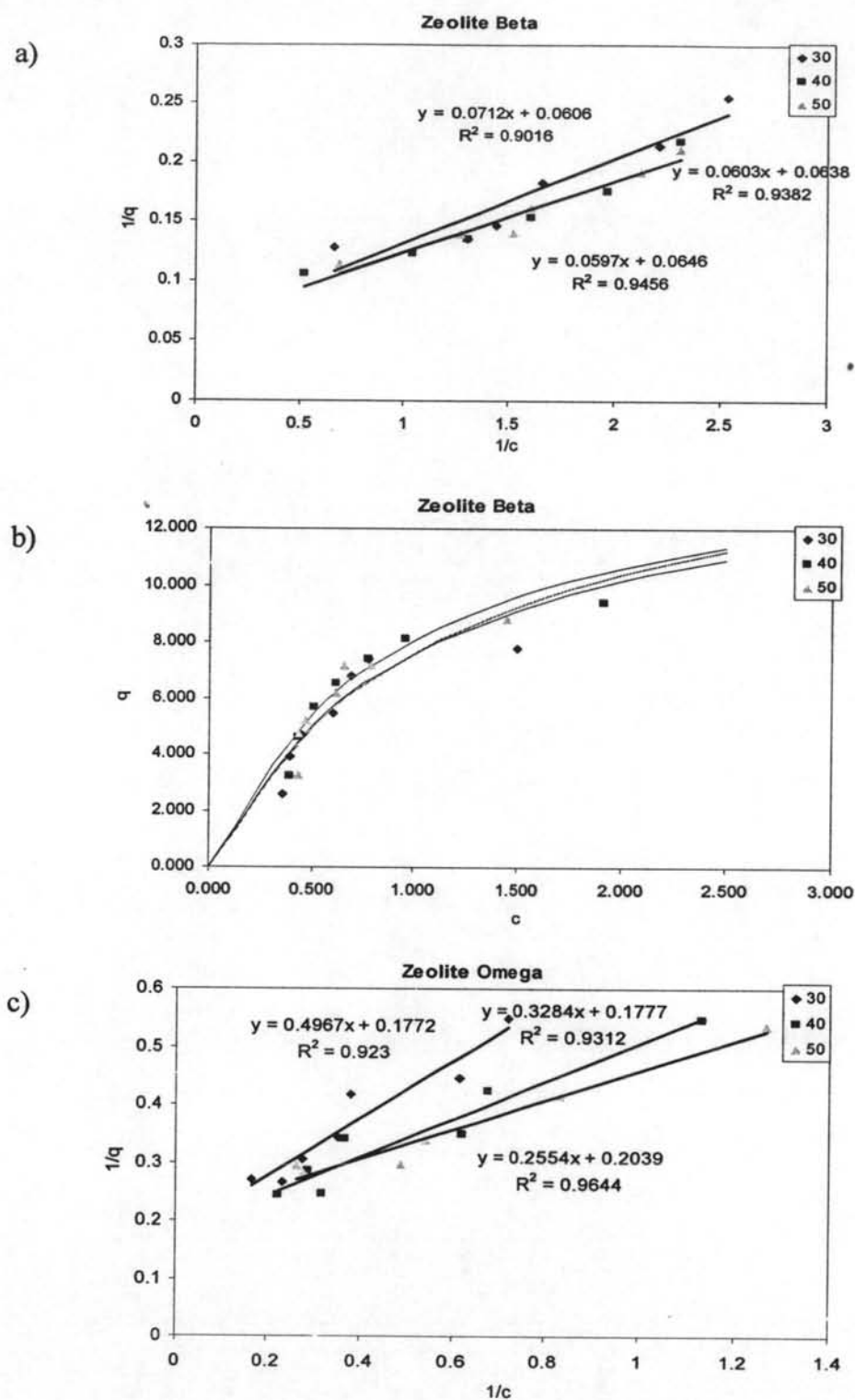
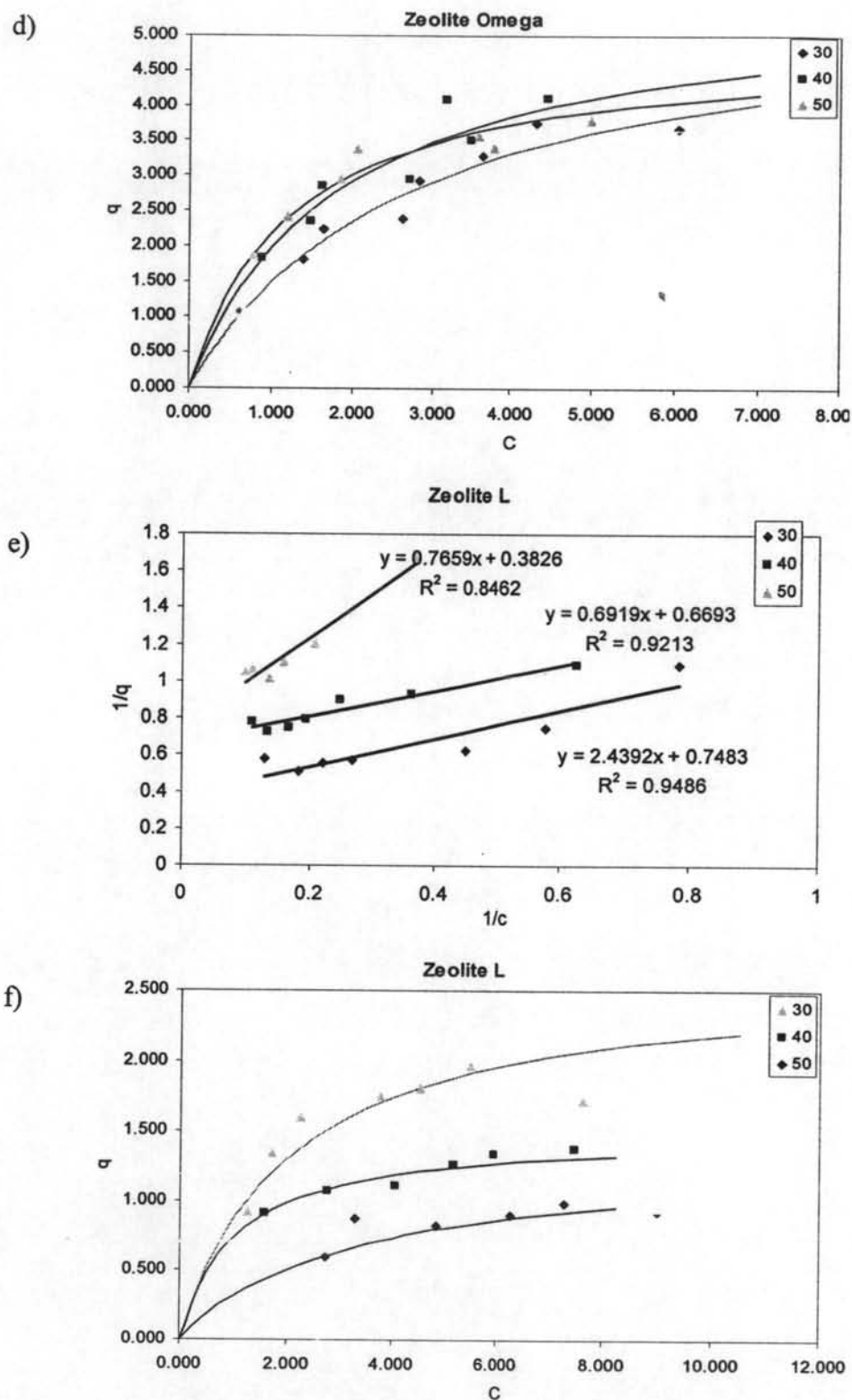


Figure 4.8 Langmuir linearization model of zeolites a) Omega, c) Beta, e) L and g) CMG 273 and fittings of Langmuir Isotherm with data of zeolites b) Omega, d) Beta, f) L and h) CMG 273.



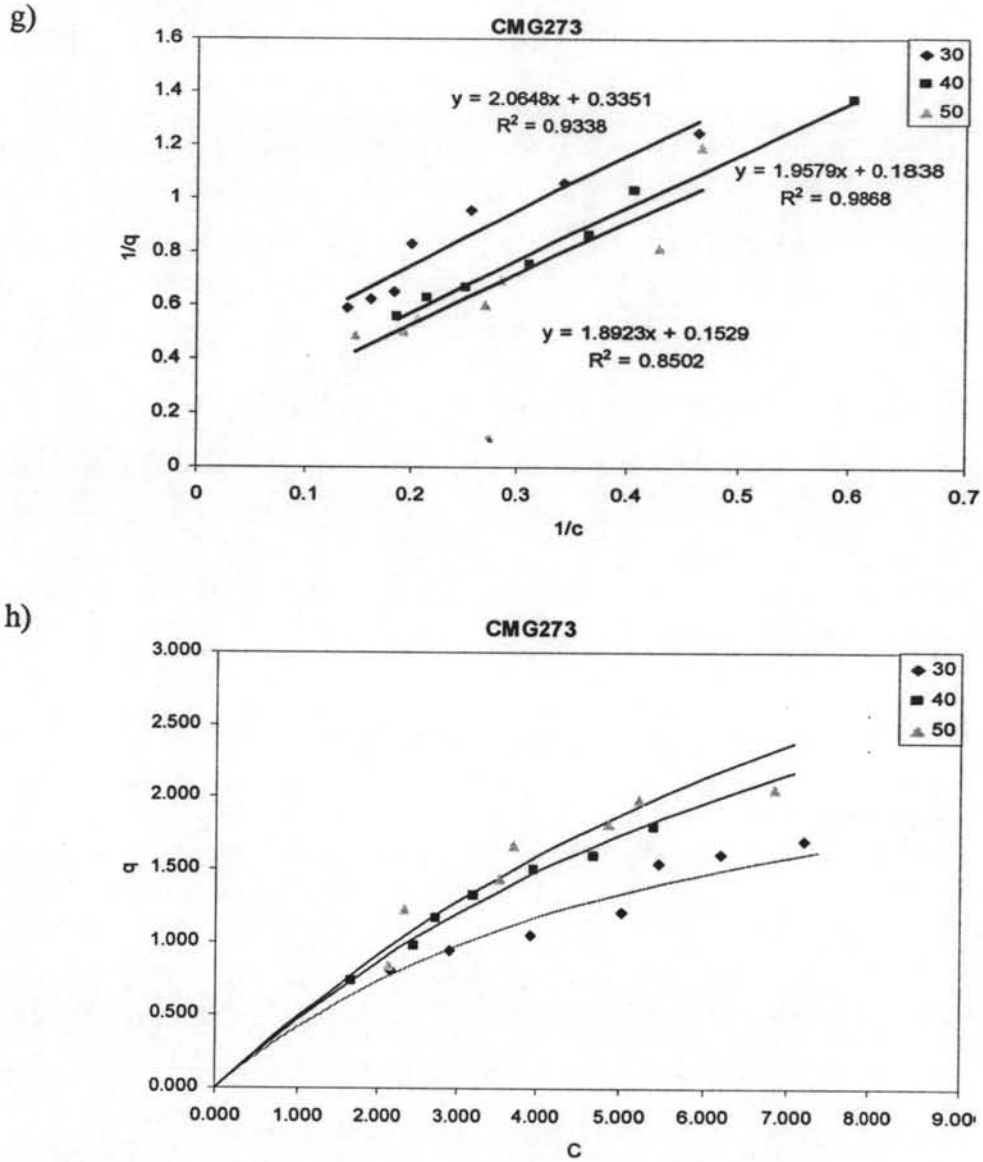


Figure 4.8 (con'd) Langmuir linearization model of zeolites a) Omega, c) Beta, e) L and g) CMG 273 and fittings of Langmuir Isotherm with data of zeolites b) Omega, d) Beta, f) L and h) CMG 273.

The maximum capacities (q_{max}) of all adsorbents are temperature dependent. With increasing temperature from 30 to 50°C, the DPM adsorption capacity of zeolite Beta and Omega slightly decreased by 7% and 13%, respectively. For zeolite L, the capacity strongly depended on the temperature, 43% of DPM adsorption capacity was reduced with increasing the temperature from 30 to 40°C and further decrease of 7% with increasing the temperature from 40 to 50°C. For all zeolites, it indicated that the physisorption is the main phenomenon. On the contrary, for CMG273 the adsorption capacity was dramatically increased for 45% with increased the temperature from 30 to 40°C, and further decrease of 17% with increasing the temperature from 40 to 50°C indicating the chemisorptions, and perhaps also physisorption.

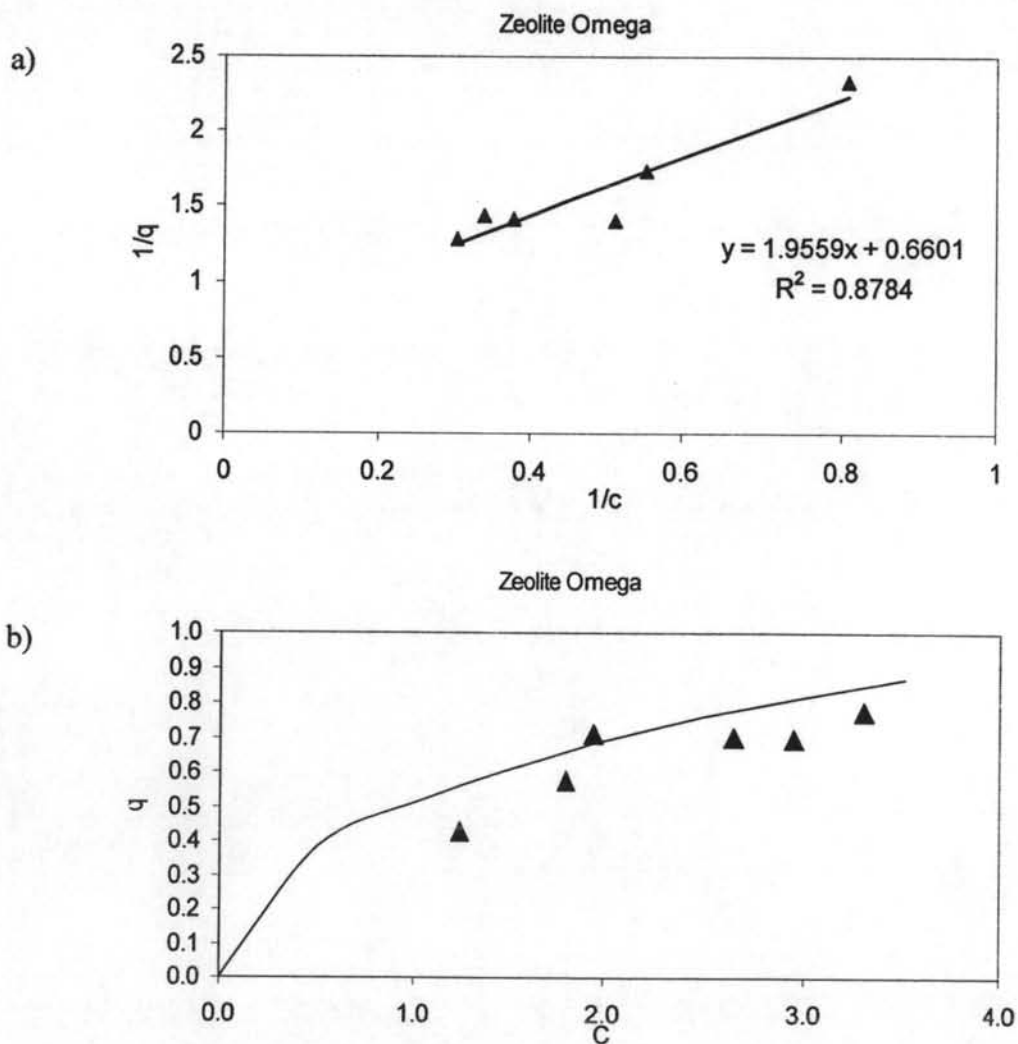
The values of q_{max} and b (in Table 4.9) were placed into equation 4.1 to obtain the adsorption curve presenting in the figure 4.8 b), d), f) and h) respectively. These adsorption model could be use to predict the adsorption of DPM on different adsorbent.

Table 4.9 Physical parameters for Langmuir Isotherm

Adsorbents	Temp(°C)	q_{max} (mg Hg/g Ad)	b
Beta	30	5.86	2.40
	40	5.56	2.98
	50	5.49	3.05
Omega	30	5.64	0.36
	40	5.63	0.54
	50	4.90	0.80
L	30	2.61	0.50
	40	1.49	0.97
	50	1.34	0.31
CMG273	30	2.98	0.16
	40	5.44	0.09
	50	6.54	0.08

4.4.2 Isotherms for Diphenylmercury (DPM) Adsorption in Heavy Naphtha

The adsorption isotherms of DPM in heavy naphtha on zeolites Omega and Beta were studied at the temperature 30°C and The experiments were done by varying the concentrations of DPM in the range of 2 to 5 ppm at the equilibrium time of 6 hours (based on the kinetic study). The R^2 coefficient of Langmuir model was generated, the value of q_{max} and b (Table 10) were placed in the langmuir model and the results are presented in Figure 4.9.



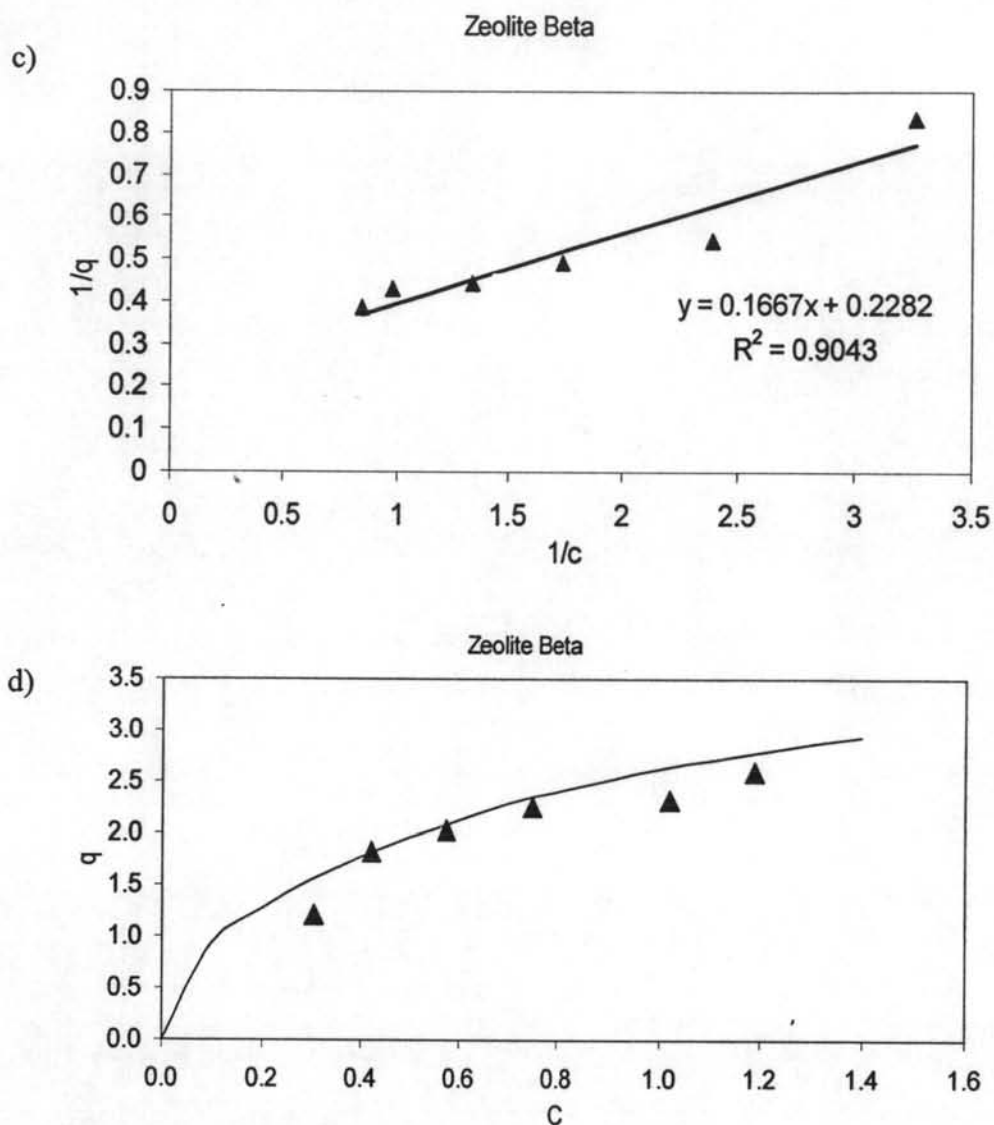


Figure 4.9 Langmuir model linearization of zeolites a) Omega, c) Beta and fittings of Langmuir Isotherm with data of zeolite b) Omega and d) Beta.

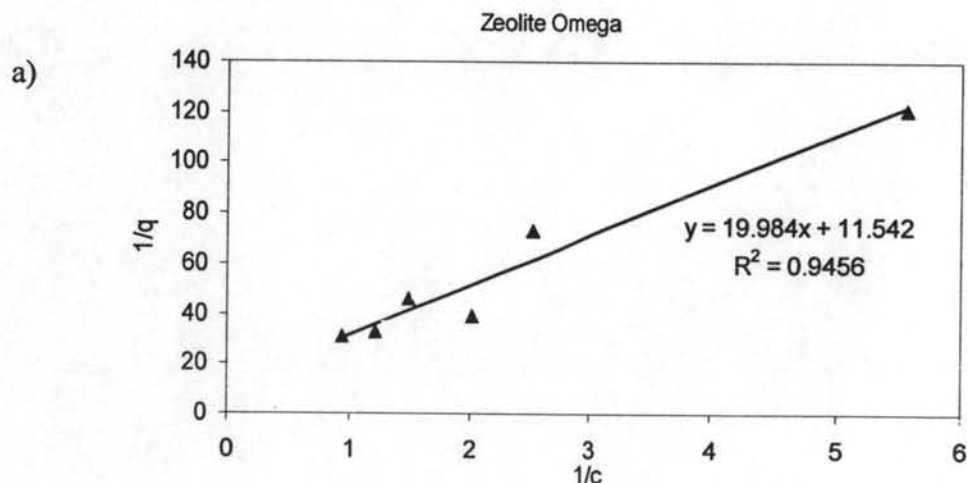
The result shows better efficiency in DPM adsorption on zeolite Beta than Omega. However, due to the complexity of hydrocarbon species in heavy naphtha, the efficiency of DPM adsorption of zeolite Beta and Omega were dropped 25% and 40% respectively as compared to the adsorption in n-heptane.

Table 4.10 Langmuir isotherm parameters for adsorption of DPM in heavy naphtha

Adsorbents	q_{max} (mg Hg /g)	b
Beta	4.38	1.36
Omega	1.51	0.34

4.4.3 Adsorption Isotherm of Natural Mercury species in Heavy Naphtha

The condition was set the same as in section 4.4.2. The experiment was done by varying the concentrations of natural mercury species by diluting the contaminated heavy naphtha by treated heavy naphtha (Hg free) to obtain the concentrations at 100, 200, 300, 400, 500, 600, 700 to 800 ppb and equilibrium time was set at 6 hours (based on the kinetic study). Langmuir model can be fitted well with the data and its parameters were calculated as shown in Table 4.9.



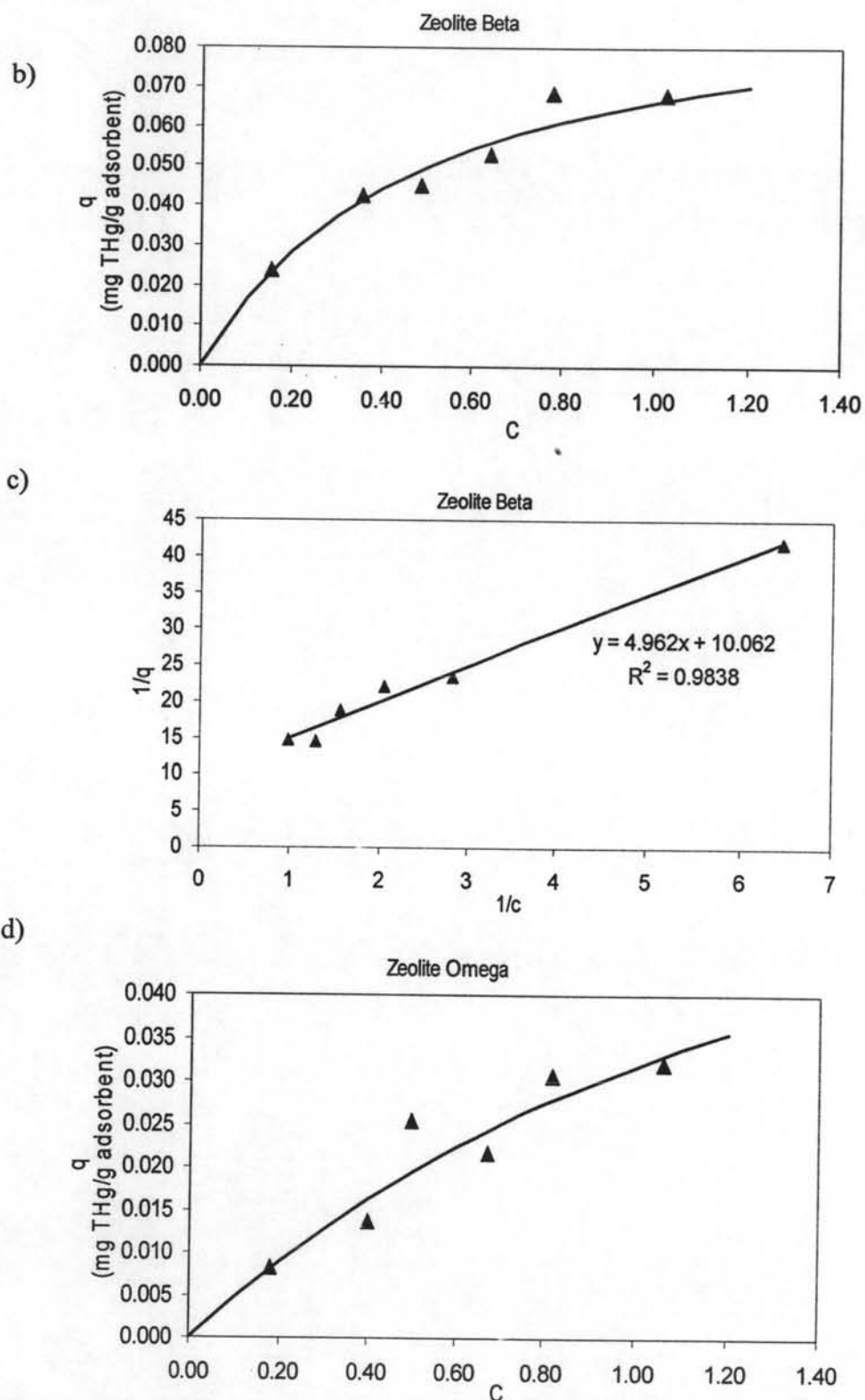


Figure 4.10 Langmuir model linearization of zeolites a) Omega, c) Beta and fittings of Langmuir Isotherm with data of zeolite b) Omega and d) Beta for adsorption natural mercury species in heavy naphtha at 30°C.

Zeolites Beta and Omega showed significant adsorption of mercury species in heavy naphtha, but much lower than the adsorption of DPM in heavy naphtha due to the differences in mercury species that were presented in the heavy naphtha. At present, there is no information about the organomercury species in heavy naphtha. However, mostly metallic mercury was found in heavy naphtha with minor amount of organomercury species.

Table 4.11 Langmuir isotherm parameters for adsorption of Mercury Removal in Heavy Naphtha

Adsorbents	q_{max} (mg Hg/g)	b
Beta	0.099	2.028
Omega	0.087	0.577

4.5 Continuous System Studies

Base on high efficiency of DPM adsorption in the batch system, zeolite Beta was selected for further studied in a continuous system. The commercial adsorbents, alumina (Al_2O_3) and CMG273 were compared for their efficiency on removal DPM in heavy naphtha.

The experiment was carried out using the facilities at the IFP, France. Due to the time limit, complete breakthrough curve could not achieved in all adsorbents. The breakthrough curves for three adsorbents are shown in Figure 4.11.

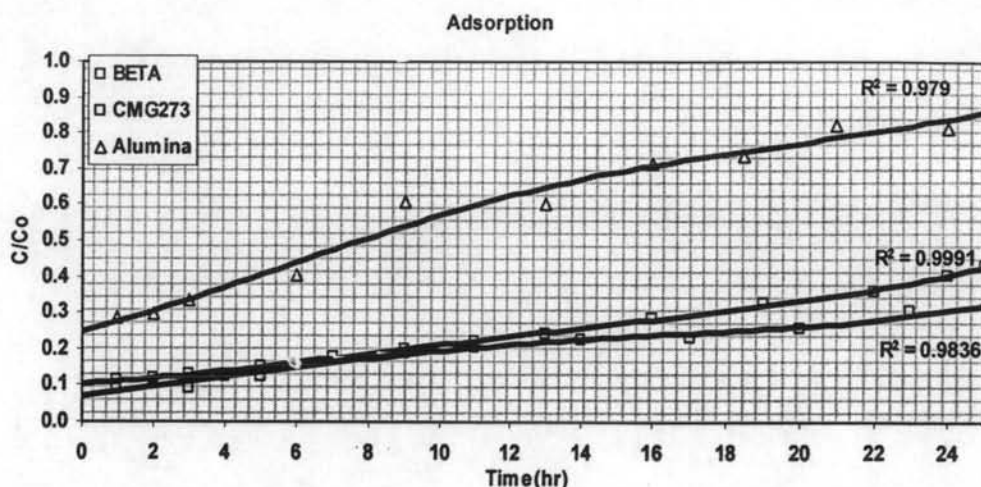


Figure 4.11 Adsorption isotherm of DPM in heavy naphtha operated in continuous system at 30°C and 7 bar.

According to Figure 4.11, the removal of DPM by alumina impregnated with copper sulfide ($\text{CuS}/\text{Al}_2\text{O}_3$ or CMG273) was higher than alumina without copper sulfide. It can be clearly said that copper sulfide which impregnated on alumina can improve the efficiency in removing DPM in heavy naphtha.

4.6 Effect of Si/Al ratio and Structure in Adsorption DPM of Zeolites

DPM molecule is a symmetric molecule and their polarity is very low, the results show that DPM preferred to adsorb on zeolite Beta which has high Si/Al ratio compared to others. Figure 4.12 compares the maximum capacity (q_{max}) in adsorption of DPM in n-heptane as function of Si/Al.

The result also shows that the capacity in adsorption of DPM of channels structure zeolite is higher than cage structure zeolite. There is not enough information that can say whether the structure will affect the improvement of removing mercury. Since the capacity of zeolites X, Y (cage structure) and zeolite L, Omega (channel structure) are comparable. Besides, the pore opening of all zeolites in this studied are in the same range.

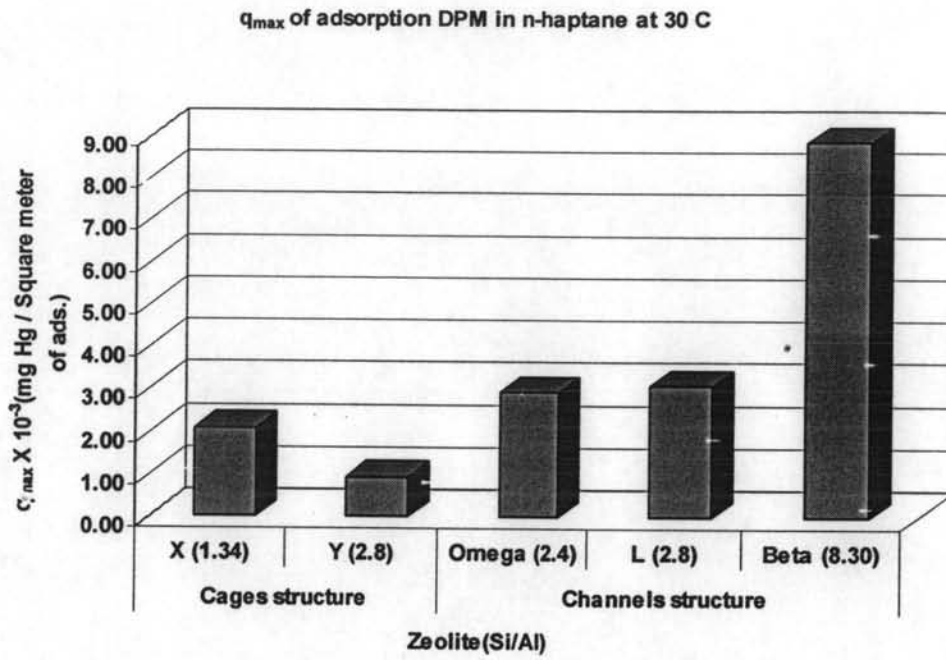


Figure 4.12 Adsorption capacities (mg Hg / Square meter of surface area of zeolite) in function of Si/Al ratio and type of structure.