CHAPTER IV
RESULTS AND DISCUSSION

4.1 Blank Test

The experiment setup of the blank test was performed the same as kinetic of adsorption studies in a batch system without adding the adsorbent. The temperature of heavy naphtha was controlled at 50°C. In a span time of 6 h, the sample was regularly taken to analyze mercury concentration by mercury analyzer (NIC SP-3D) every hour. It was found that the concentrations of heavy naphtha are rather constant. The small variation of the concentrations of heavy naphtha may be caused by analytical error. Therefore, the result from blank test can confirm the reliability of mercury adsorption capacity of each zeolite.

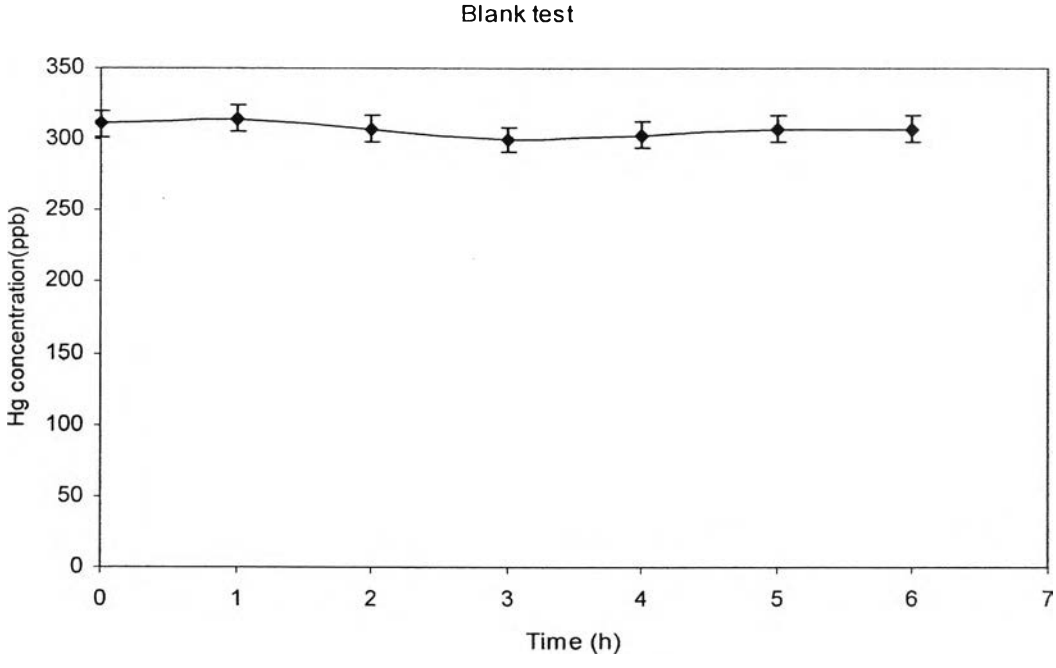
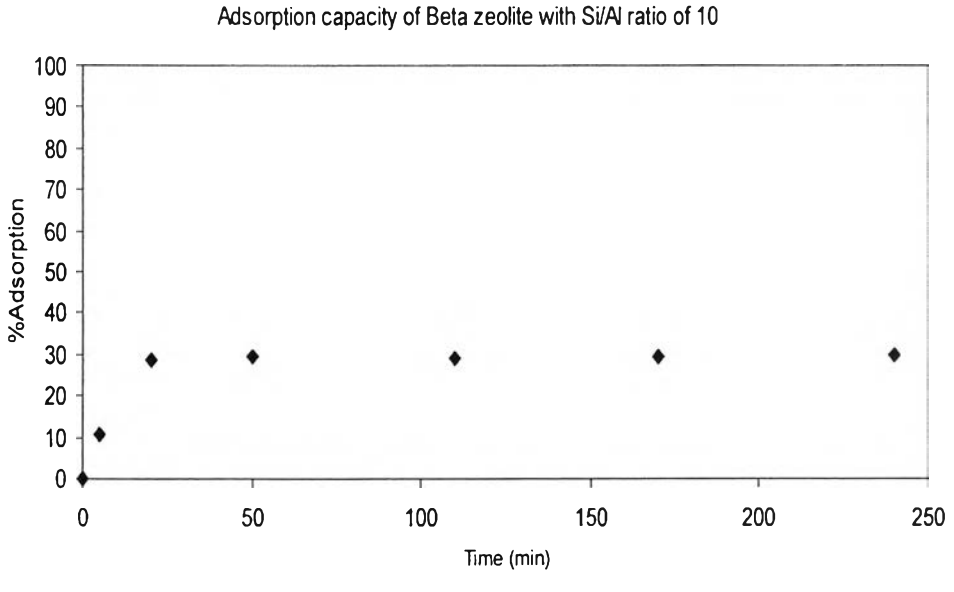


Figure 4.1 Blank test for mercury adsorption study at 50°C for 6 h.

4.2 Kinetic Studies

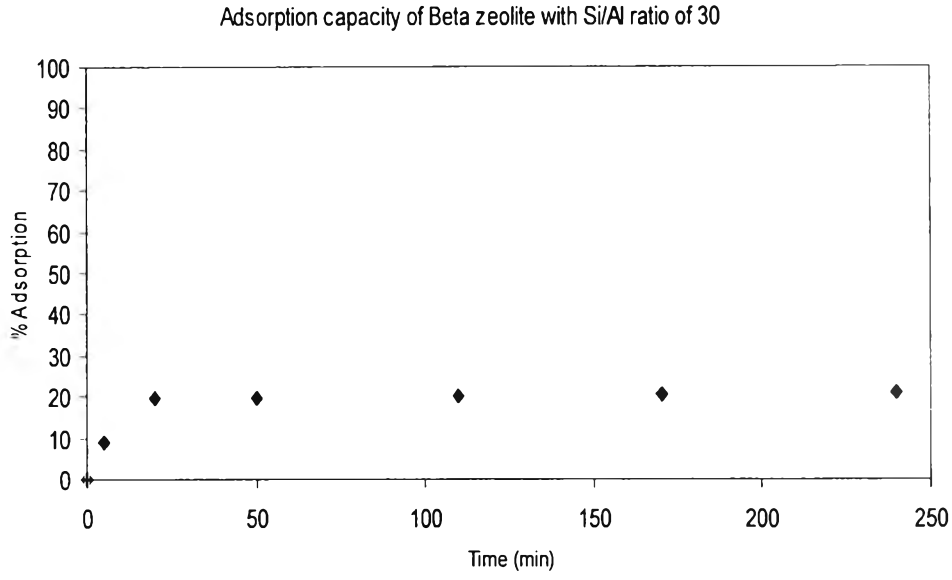
4.2.1 Kinetic Studies of Mercury Adsorption in Heavy Naphtha on Zeolites

The kinetic of adsorption of mercury in heavy naphtha on Beta zeolite with Si/Al ratio of 10, 30, and 100, X zeolite, Y zeolite and ZSM-5 zeolite were studied. The initial mercury concentration of heavy naphtha was about 300 ppb. The adsorption was carried out in a batch system at temperature of 50°C. For Beta zeolite, the mercury adsorption reached the equilibrium at 20, 20, and 50 minutes for the zeolite with Si/Al ratios of 10, 30, and 100, respectively as shown in Figure 4.2. At equilibrium, about 30%, 20% and 15% mercury adsorption were obtained by Beta zeolite with Si/Al ratios of 10, 30, and 100, respectively. It was clearly seen that for Beta zeolite, the lower the Si/Al ratio, the higher the mercury adsorption capacity. This may be due to the lower the Si/Al ratio of Beta zeolite can provide more sites for interacting with mercury compound.



(a)

Figure 4.2 Kinetic of adsorption of mercury 300 ppb in heavy naphtha on a) zeolite Beta Si/Al ratios of 10, b) zeolite Beta Si/Al ratios of 30, c) zeolite Beta Si/Al ratios of 100.



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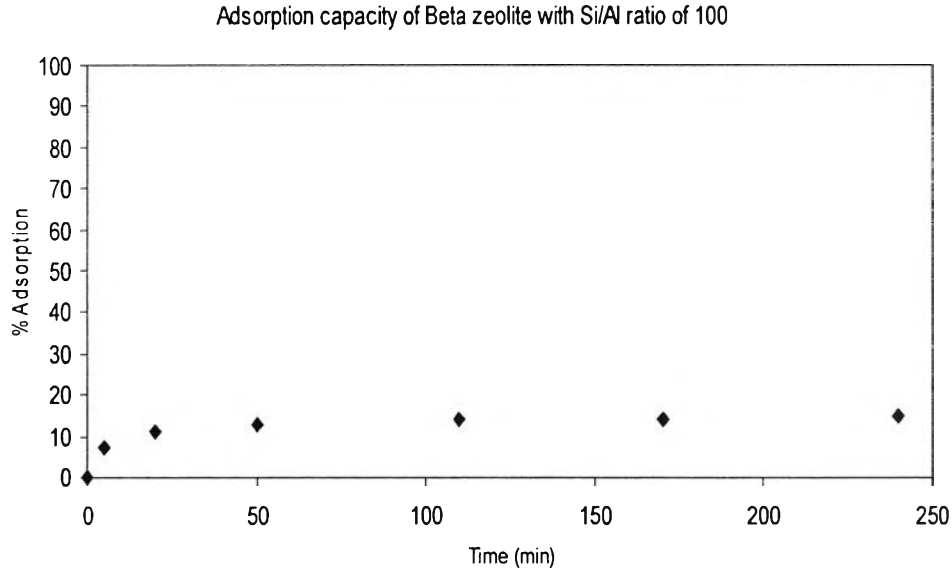
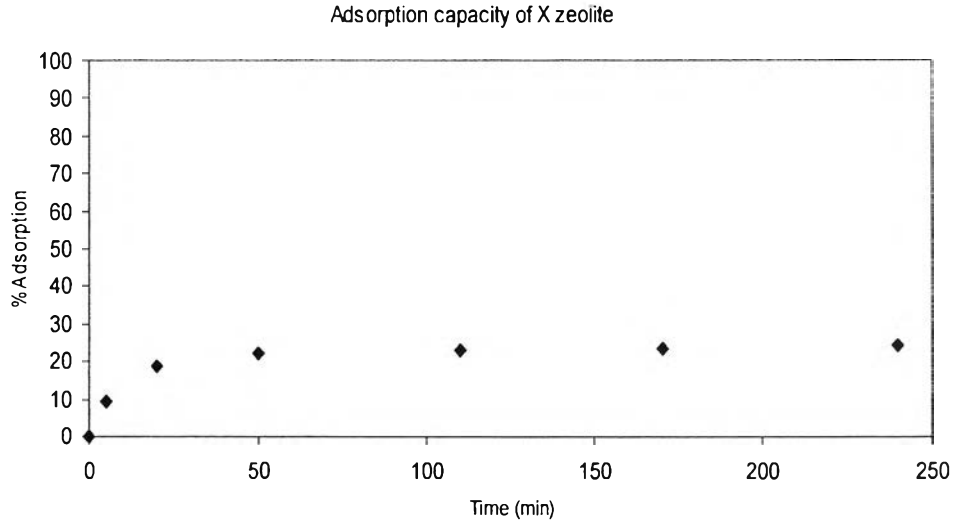


(c)

Figure 4.2 (cont'd) Kinetic of adsorption of mercury 300 ppb in heavy naphtha on a) zeolite Beta Si/Al ratios of 10, b) zeolite Beta Si/Al ratios of 30, c) zeolite Beta Si/Al ratios of 100.

The mercury adsorption of X zeolite and Y zeolite which are large pore zeolites gave similar trends. The adsorption rapidly increased and reached the equilibrium state at 50 minutes. At that state, X and Y zeolites adsorbed 25% and 20%, respectively of mercury from heavy naphtha. Besides, for ZSM-5 zeolite, a medium pore zeolite, its mercury adsorption reached only 7% after 50 minutes.



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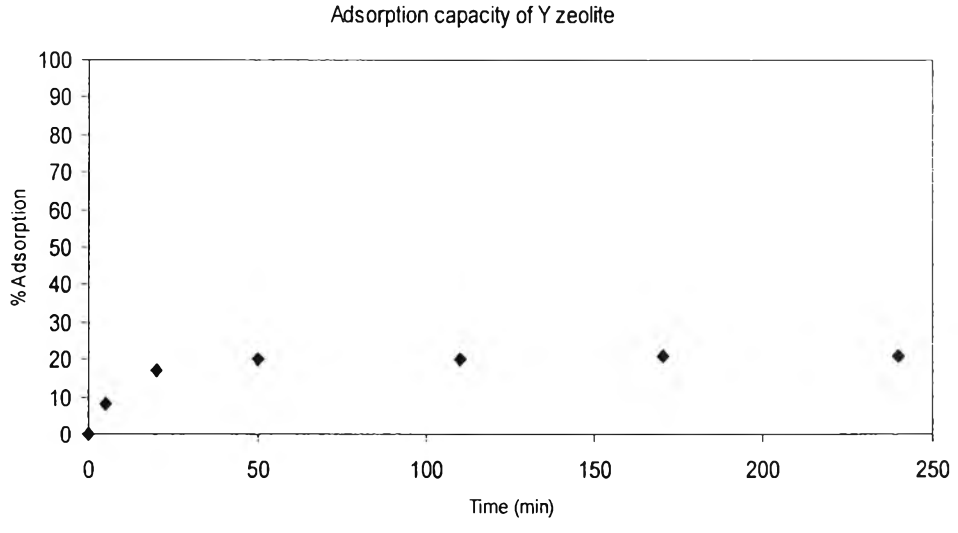
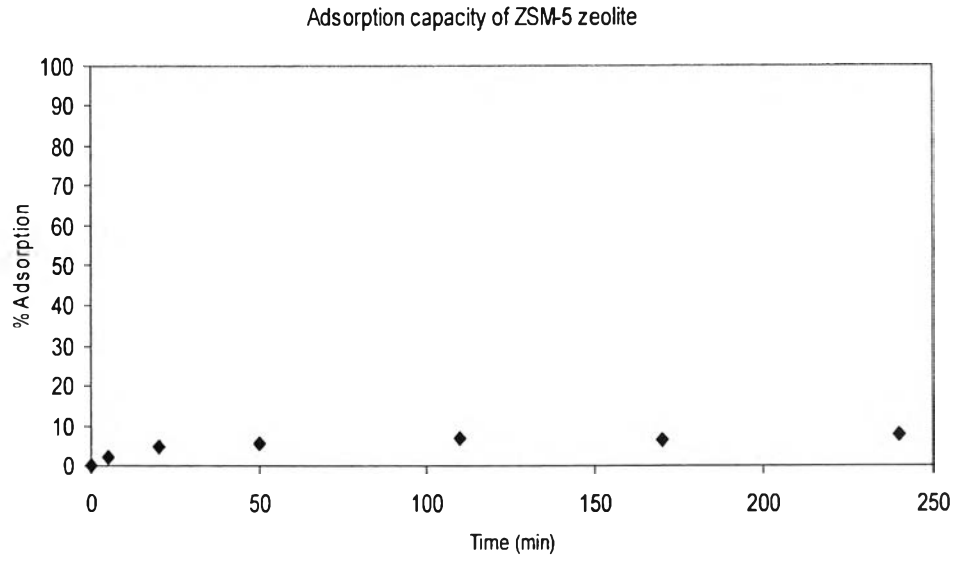


(b)

Figure 4.3 Kinetic of adsorption of mercury 300 ppb in heavy naphtha on a) X zeolite, b) Y zeolite and c) ZSM-5 zeolite.



(c)

Figure 4.3 (cont'd) Kinetic of adsorption of mercury 300 ppb in heavy naphtha on a) X zeolite, b) Y zeolite and c) ZSM-5 zeolite.

4.2.2 Correlation of Adsorption Kinetic of Mercury on Zeolites

The kinetic models applied to the batch experimental data are composed of the Lagergren equation pseudo 1st and 2nd order and the Elovich equation. The correlation coefficients (R^2) of these kinetic models are shown in Table 4.1.

By plotting $\log(q_e-q_t)$ vs time in case of the Lagergren equation pseudo 1st order, the plots have poor linearity for all zeolites as shown in terms of the correlation coefficient (R^2). In addition, the application of the Elovich equation by plotting q_t vs lnt is also shown poor linearity for almost all cases but it well fit with Beta zeolite with Si/Al of 100 and ZSM-5 zeolite which showed poor mercury adsorption capacity. For plotting t/q_e vs t, it is obviously fit with the experimental data. The correlation coefficients (R^2) were very close to 1 in all cases. Table 4.2 shows q_e and Ke_2 computed from the Lagergren pseudo 2nd order equation and q_e from experimental data. It was found that q_e obtained from equation is very close to that from experimental data. Therefore, this equation is suitable to

apply for kinetic of adsorption of natural mercury in heavy naphtha on Beta zeolite with Si/Al ratio of 10, 30, 100, X zeolite, Y zeolite and ZSM-5 zeolite.

Table 4.1 Correlation coefficient (R^2) of the kinetic adsorption models

Adsorbent	Correlation coefficient (R^2)		
	Pseudo 1st order	Pseudo 2nd order	Elovich
Beta zeolite with Si/Al of 10	0.5887	0.9990	0.6685
Beta zeolite with Si/Al of 30	0.7876	0.9996	0.7274
Beta zeolite with Si/Al of100	0.8646	0.9994	0.9641
X zeolite	0.7934	0.9997	0.8887
Y zeolite	0.8918	0.9997	0.8592
ZSM – 5 zeolite	0.7109	0.9854	0.9493

Table 4.2 Experimental q_e and computed q_e and Ke from pseudo 2nd order equation

Adsorbent	q_e (experimental data)	Pseudo 2nd order	
	(mg/g)	q_e (mg/g)	Ke_2
Beta zeolite with Si/Al of 10	0.0221	0.0226	9.66
Beta zeolite with Si/Al of 30	0.0155	0.0158	13.58
Beta zeolite with Si/Al of 100	0.0109	0.0111	11.83
X zeolite	0.0180	0.0184	7.70
Y zeolite	0.0156	0.0161	9.40
ZSM – 5 zeolite	0.0057	0.0057	10.36

4.3 Adsorption Study of Hg^0 in Heavy Naphtha

The adsorption of Hg^0 on Beta zeolite with Si/Al ratios of 10, 30, and 100, X zeolite, Y zeolite and ZSM-5 zeolite was investigated under the condition based on the adsorption kinetic studies. The initial concentration of Hg^0 in heavy naphtha was 300 ppb. Table 4.3 shows Hg^0 adsorption capacity of the adsorbents and it was found that Hg^0 can be removed less by the adsorbents. These can be confirmed by Ullah, (2006) which claimed that Hg^0 has no affinity toward Beta zeolite and only little amount of Hg^0 was adsorbed by X and Y zeolite.

Table 4.3 Hg^0 adsorption capacity of Beta zeolite with Si/Al ratios of 10, 30, and 100, X zeolite, Y zeolite and ZSM-5 zeolite

Adsorbent	%Adsorption
Beta zeolite with Si/Al of 10	5.88
Beta zeolite with Si/Al of 30	5.95
Beta zeolite with Si/Al of 100	3.61
X zeolite	8.54
Y zeolite	6.17
ZSM-5 zeolite	7.41

4.4 Adsorption Isotherm Studies

The adsorption isotherm studies for Beta zeolite with Si/Al ratios of 10, 30, and 100, X zeolite, Y zeolite and ZSM-5 zeolite were examined under the condition based on the adsorption kinetic studies. The experiments were done by varying the concentrations of mercury in heavy naphtha as 300, 200, 100 and 50 ppb. The Langmuir Isotherm model was selected to explain the adsorption behavior. The equation can be defined as:

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

where q = the quantity of molecules adsorbed on the solid phase (mg/g of adsorbent)

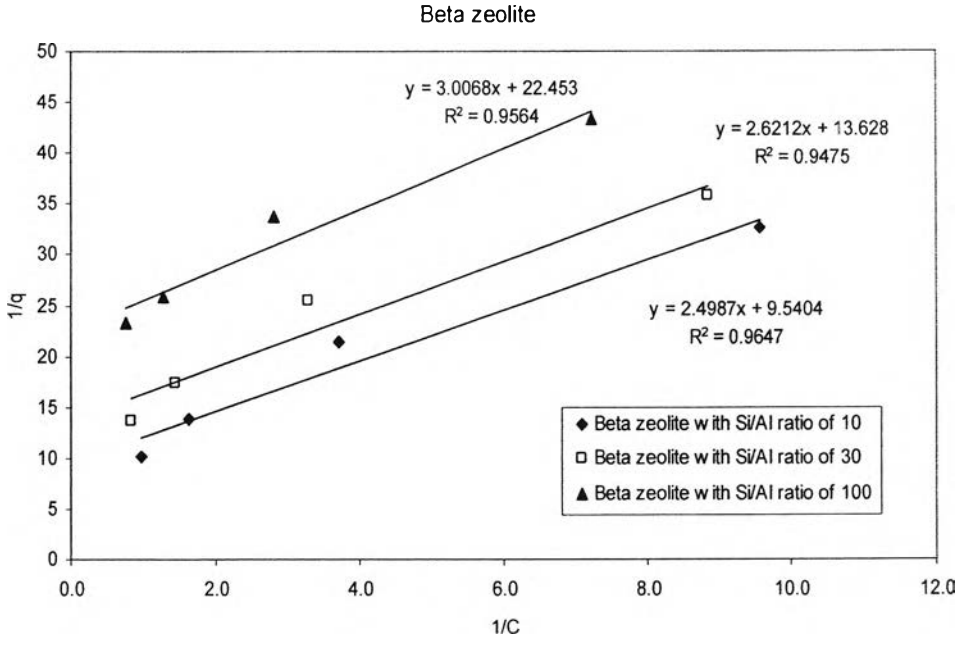
q_{max} = the maximum quantity adsorbed on solid phase

b = adsorption / desorption constant

C = equilibrium concentration of mercury in liquid phase.

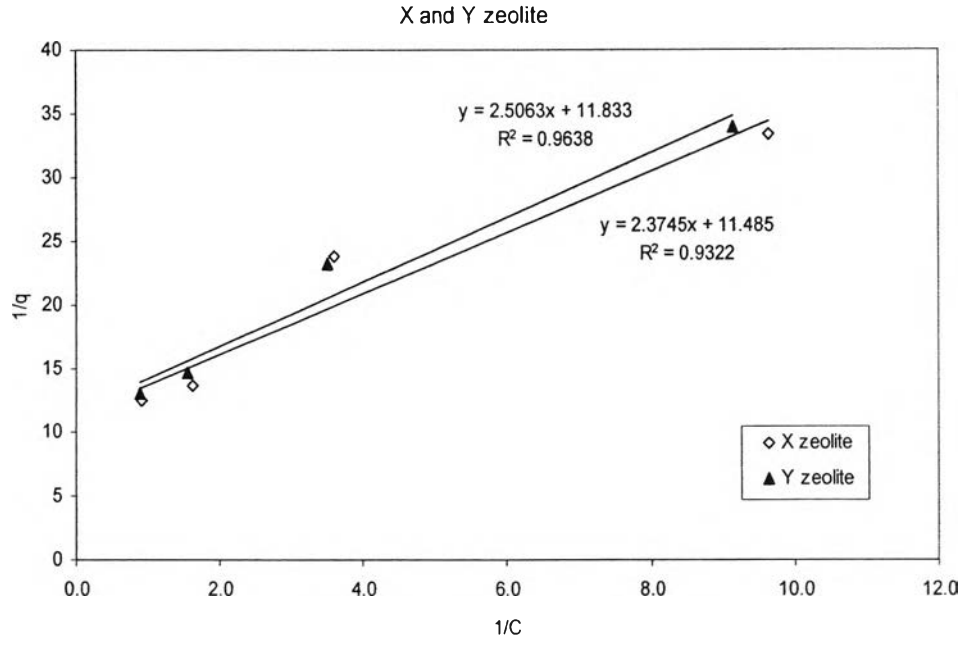
The equation 4.1 can be rearranged for linearization as:

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



(a)

Figure 4.4 Langmuir linearization model of a) Beta zeolite with Si/Al ratios of 10, 30 and 100 b) X and Y zeolite and c) ZSM-5 zeolite.



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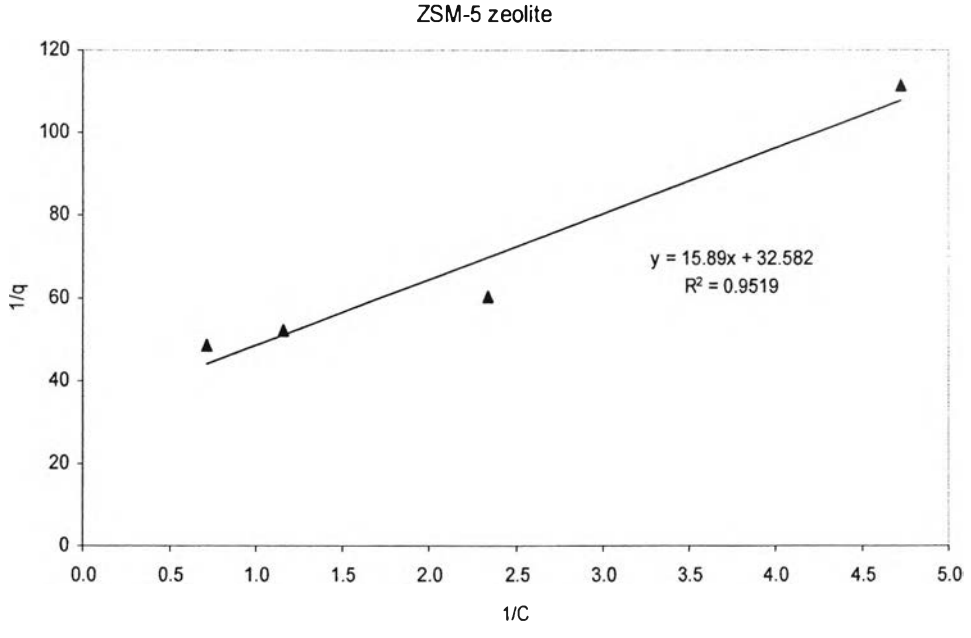
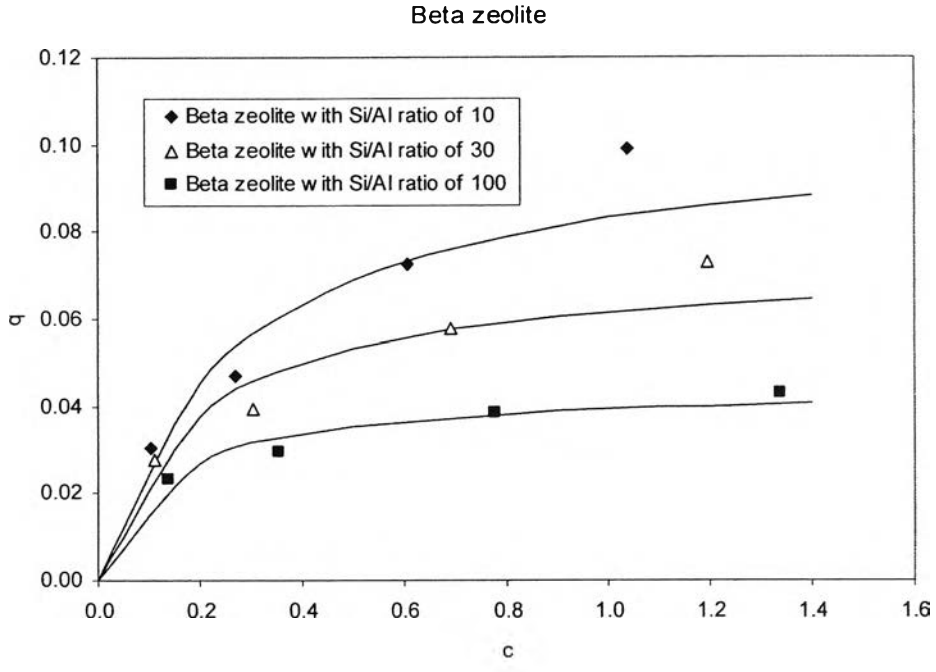


(c)

Figure 4.4 (cont'd) Langmuir linearization model of a) Beta zeolite with Si/Al ratios of 10, 30 and 100 b) X and Y zeolite and c) ZSM-5 zeolite.



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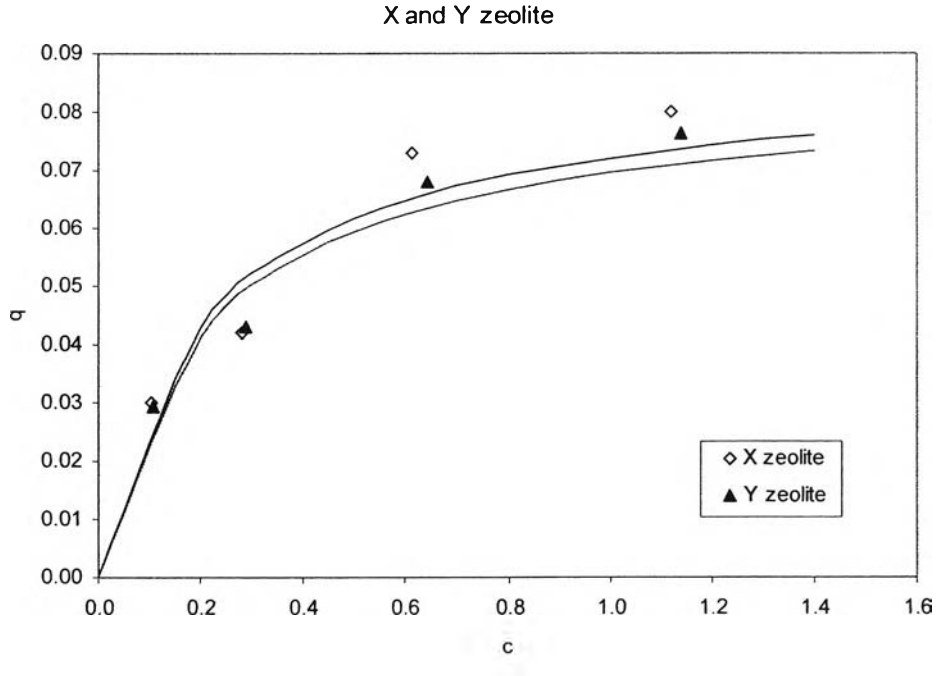
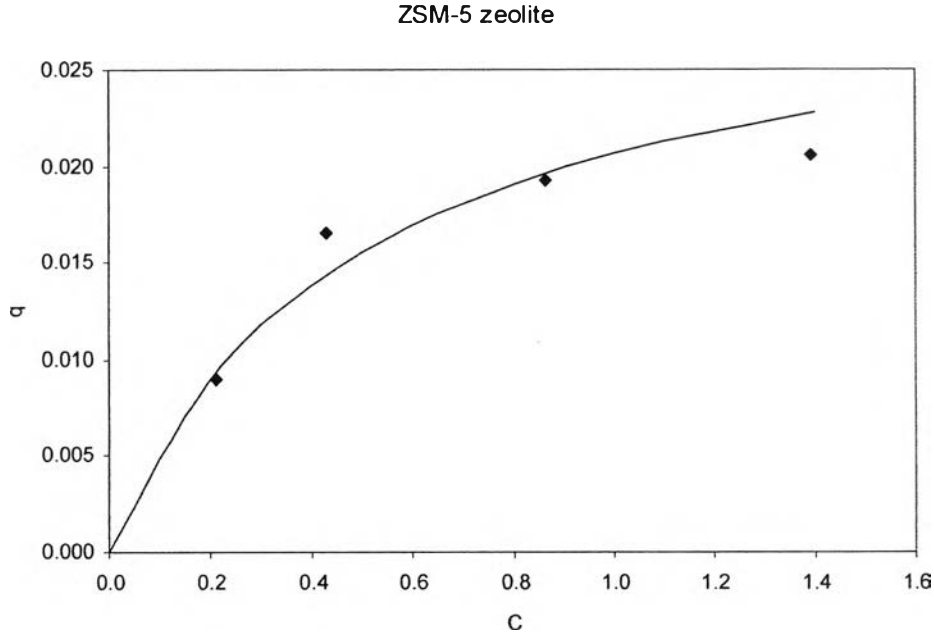


(b)

Figure 4.5 Fitting of Langmuir Isotherm model with experimental data of a) Beta zeolite with Si/Al ratios of 10, 30 and 100 b) X and Y zeolite and c) ZSM-5 zeolite.



(c)

Figure 4.5 (cont'd) Fitting of Langmuir Isotherm model with experimental data of a) Beta zeolite with Si/Al ratios of 10, 30 and 100 b) X and Y zeolite and c) ZSM-5 zeolite.

Figure 4.4 shows the plots between 1/q and 1/C that give $1/q_{max}$ and $1/bq_{max}$ as the intercept and slope, respectively. In addition, Figure 4.5 shows the fitting of the Langmuir Isotherm model with the experimental data of all zeolites.

From the slope and interception of the plots between 1/q and 1/C, the maximum capacity (q_{max}) and b shown in Table 4.3 were acquired from calculation. The maximum capacity value of all zeolites and b were substituted in equation 4.1 in order to construct the plots between C and q from Langmuir Isotherm model as shown in Figure 4.5. It was found that the relationship of C and q from Langmuir Isotherm model and experimental data are fit. Therefore, the model could be used to predict the adsorption of natural mercury in heavy naphtha on Beta zeolite with Si/Al ratios of 10, 30, 100, X zeolite, Y zeolite and ZSM-5 zeolite.

Table 4.4 Physical parameters for Langmuir Isotherm of Beta zeolite with Si/Al ratios of 10, 30, and 100, X zeolite, Y zeolite and ZSM-5 zeolite

Adsorbent	q_{max} (mg/g)	b
Beta zeolite with Si/Al of 10	0.0210	3.8183
Beta zeolite with Si/Al of 30	0.0147	5.1991
Beta zeolite with Si/Al of 100	0.0089	7.4674
X zeolite	0.0175	4.8368
Y zeolite	0.0170	4.7213
ZSM-5 zeolite	0.0062	2.0505

4.5 Speciation of Mercury in Heavy Naphtha

Mercury species in heavy naphtha was investigated by GC – ICP MS. To complete the analysis, two injections were required. The first sample, untreated heavy naphtha, was directly injected to GC – ICP MS in order to detect the non polar species, e.g. metallic mercury (Hg^0) or organic mercury. Besides, to analyze the polar species, the second sample which was heavy naphtha treated by the Grignard reaction as shown in equation 4.1 and 4.2 was injected to GC – ICP MS.

$$\text{AlkylHgCl} + \text{BuMgCl} \rightarrow \text{AlkylBuHg} + \text{MgCl}_2 \quad (4.1)$$

$$\text{Hg}^{2+} + 2\text{BuMgCl} \rightarrow \text{Bu}_2\text{Hg} + 2\text{MgCl}_2 \quad (4.2)$$

From Table 4.5, Hg^0 and ionic mercury were the main species found in the heavy naphtha. Since the adsorbents have less efficiency in Hg^0 adsorption that already claimed in section 4.3, ionic mercury is the main specie of mercury adsorbed on the adsorbents.

Table 4.5 Speciation of mercury in heavy naphtha

Total Hg (μg/kg)	Hg^0 (μg/kg)	Ionic Hg (μg/kg)
530	210	320

4.6 Continuous System Studies

The experiments were done in a continuous flow system at IFP, Lyon, France. Only Beta zeolite with Si/Al ratio of 10 and X zeolite which gave the best performance in removal mercury from heavy naphtha were selected to examine the adsorption capacity in the continuous system. The breakthrough curves of the two zeolites are shown in Figure 4.6.

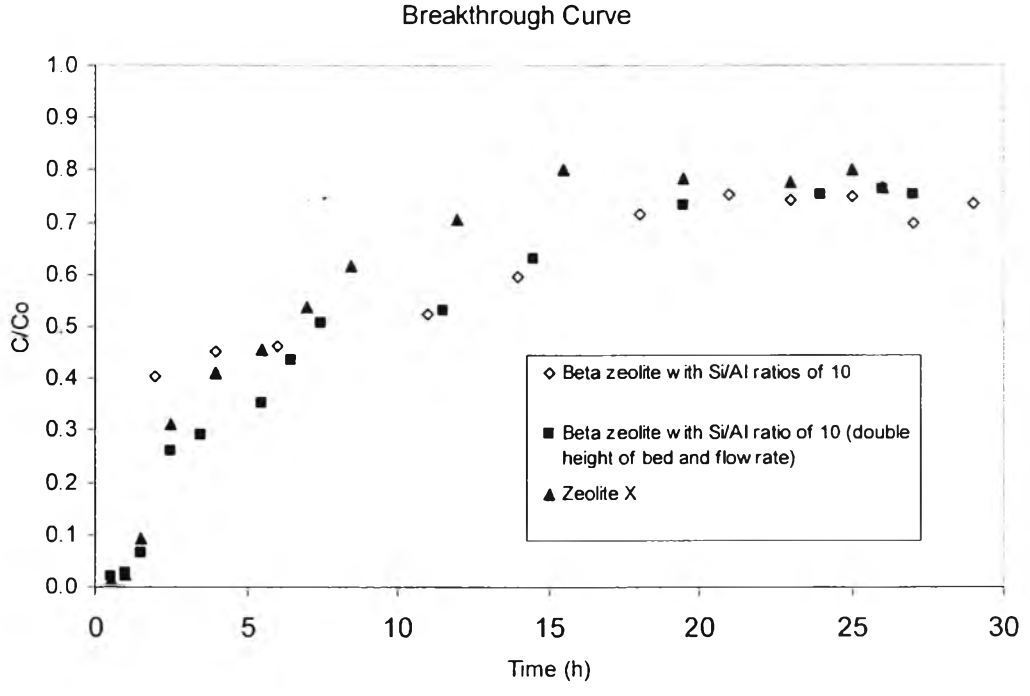


Figure 4.6 Breakthrough curve, plotting between the ratios of mercury concentration in effluent to feed versus time.

Each experiment was performed for 30 h. From Figure 4.7, Beta zeolite with Si/Al ratio of 10 and X zeolite showed the similar pattern of breakthrough curves. However, Beta zeolite with Si/Al ratios of 10 exhibited better mercury adsorption capacity than X zeolite that the breakthrough curve reached maximum of mercury adsorption capacity at 20 and 15 h, respectively. Moreover, these results can confirm higher maximum adsorption capacity of Beta zeolite with Si/Al ratio of 10 obtained from adsorption isotherms studies. Besides, for Beta zeolite with Si/Al ratio of 10, another condition which doubles flow rate and height of bed was also performed. It was found that its breakthrough curve is still the same so there is no effect of external mass transfer limitation for mercury adsorption in case of Beta zeolite with Si/Al ratio of 10.

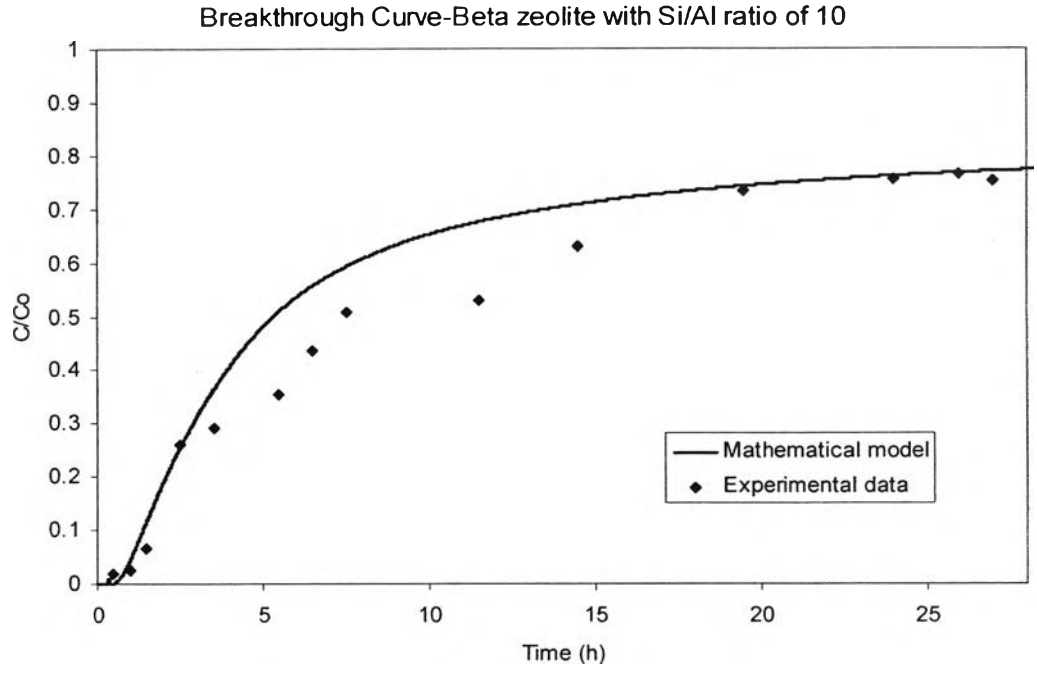
4.7 Mathematical Model of Mercury Adsorption

From equation 2.12, the terms of loss by chemical adsorption and loss by deactivation were ignored so the equation can be rearranged as shown below.

$$\frac{\partial C}{\partial t} = \left\{ -\frac{\partial \upsilon C}{\partial z} \right\} + \left\{ D_L \frac{\partial^2 C}{\partial z^2} \right\} - \left\{ \frac{(1-\varepsilon)}{\varepsilon} \frac{\partial q}{\partial t} \right\} \tag{4.3}$$

The method of lines, mentioned in section 2.6.3.1 was used for solving partial differential equation by converting it to ordinary differential equation.

The mathematical model was constructed on the assumption that ionic mercury was the only specie adsorbed on the adsorbents. The parameters required to solve the model including porosity of the bed (ε) 0.2, superficial velocity (υ) 1.13 cm/min. Moreover, q_{max} and b of Beta zeolite with Si/Al ratio of 10 and X zeolite from the adsorption isotherm study in Table 4.4 were also used in the model. Figure 4.7 shows breakthrough curve obtained by the mathematical model and experimental data from the continuous system studies. In order to acquire the accurate model, the correction factor for loss of mercury in the system was also needed. It can be seen from Figure 4.7 that both breakthrough curves from the model are quite different from the experimental data. This may be due to the complexity of ionic mercury existing in heavy naphtha.



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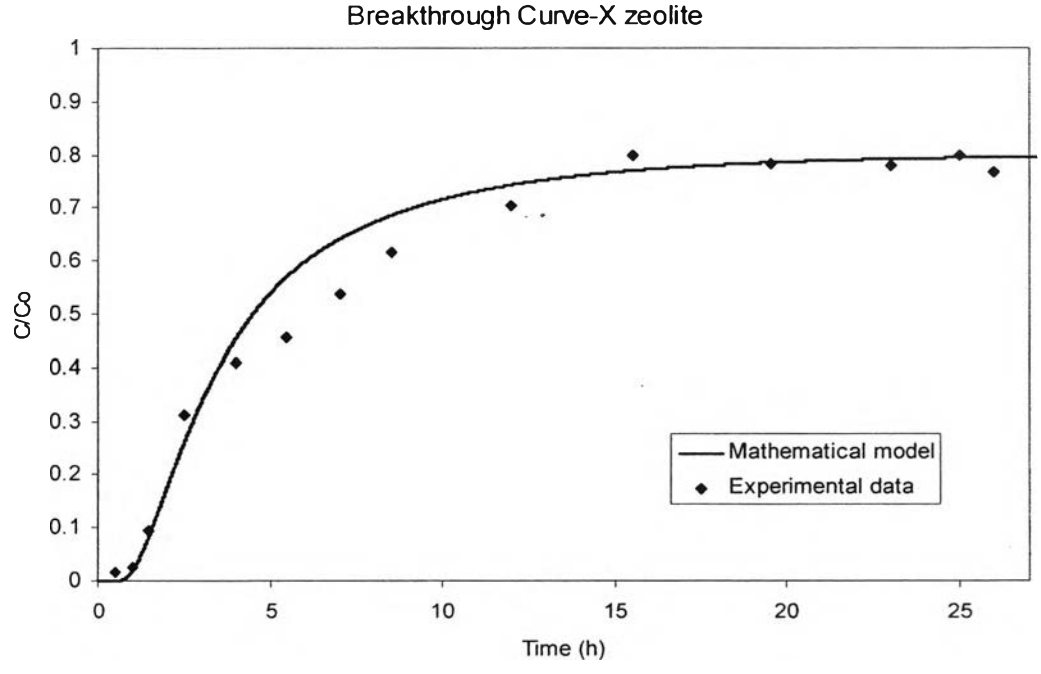

(b)

Figure 4.7 Breakthrough curve from mathematical model a) Beta zeolite with Si/Al ratio of 10 b) X zeolite.