# CHAPTER IV
RESULTS AND DISCUSSION

4.1 Adsorbents Characterization

4.1.1 BET Surface Areas

The specific surface areas of all adsorbents except activated carbon were determined by BET 3-parameters to fit an adsorption isotherm. The surface areas of all zeolite adsorbents are shown in Figure 4.1 while the surface area of activated carbon was reported by the supplier. The surface areas of all zeolites were in the same range of approximately 550 m^2/g. The surface area of activated carbon was 1,100 m^2/g.
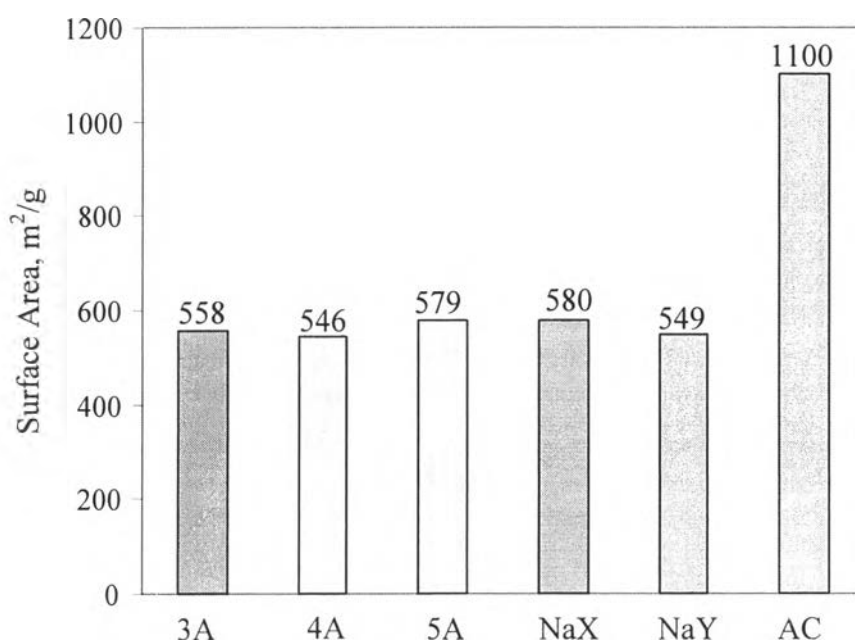

Figure 4.1 BET characterization of adsorbents: 3A, 4A, 5A, NaX and NaY zeolites and activated carbon (AC, coconut shell based carbon).

According to the results, the effect of surface areas to diphenylmercury (DPM) adsorption on all zeolites was unimportant for comparison of ability to remove DPM from n-heptane solution while the area of activated carbon which shown twice as much as the area of zeolites might

enhance the ability of removing DPM. Thus, the concentration of DPM per gram of adsorbents was used to compare the ability of removing DPM in the studies.

4.1.2 Chemical Composition

The X-ray diffraction patterns of all adsorbents are shown in Figure 4.2. It was found that the commercial zeolite adsorbents contain a majority of aluminosilicate indicated by most of the peaks of high relative X-ray intensities in the range of 2Theta between 5° and 50°, referred to the provided diffraction patterns from the computer database. Besides, aluminum oxide (Al_2O_3)as a binder also presents in the commercial zeolite adsorbents with a small amount. K^+, Na^+, and Ca^{2+} are the naturally present exchangeable cations that found in zeolite adsorbents.
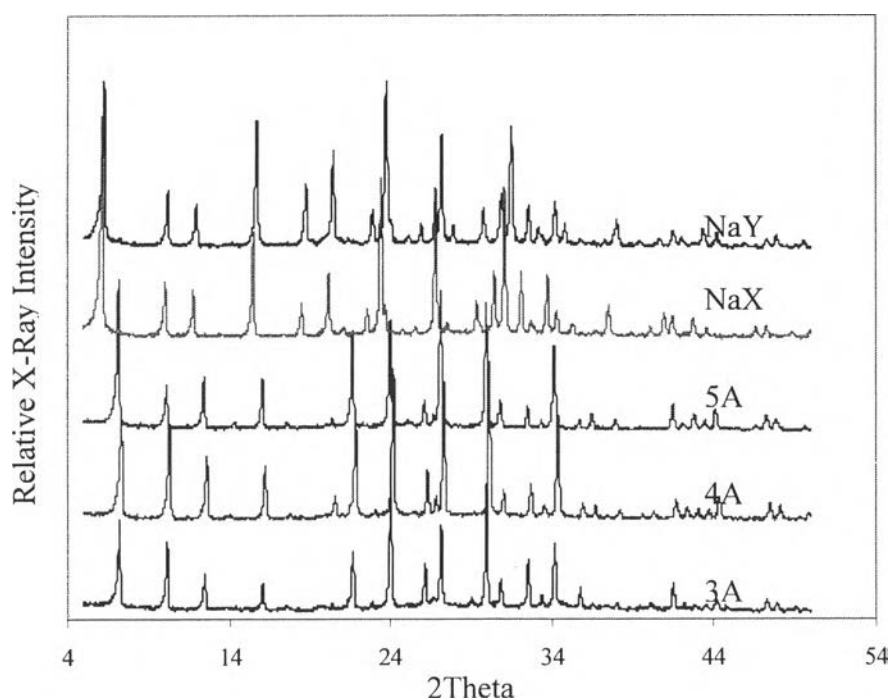
Figure 4.2 X-Ray diffraction patterns of zeolite adsorbents.

4.1.3 Thermo Gravimetric Analysis

In order to minimize the effect of water and control the amount of water adsorbed on adsorbents not exceeding 5% by weight, weight losses in adsorbents upon temperature were investigated by thermo gravimetric technique to indicate the proper temperature for treating the adsorbents before use. TGA results of the adsorbents are shown in Figure A1 in Appendix B. The summary of TGA results is shown in Table 4.1.

**Table 4.1** Thermo gravimetric analysis results

Solids	Water contents (% wt)
3A	15.346
4A	17.368
5A	17.047
NaX	20.429
NaY	19.167
Activated Carbon	10.769

From the results in Figure A1 in Appendix B, it was clear that to control the water contents less than 5% in 3A, 4A, 5A, NaX, and NaY zeolites and activated carbon, the adsorbents should be treated at least at the temperature of 300°C, 350°C, 300°C, 300°C, 300°C, and 120°C, respectively. However, for all experiments, zeolite adsorbents were treated at 350°C while the activated carbon was treated at 120°C for 6 h. The adsorbents were cooled down by placing in a desiccator.

4.2 Adsorption of Diphenylmercury on Plastic (HDPE) Containers

Results of storage tests for both 2.0 mg/l and 5.0 mg/l of DPM concentrations are shown in Figure 4.3. The plastic (HDPE) containers gave good stability over the course of one week although the overall loss in mercury concentration slightly occurred, approximately by 5% loss, after storing for 5 days. Although Bloom (2000) concluded that polyethylene containers are unsuitable for storage of mercury in petroleum, it is reasonable

to use plastic (HDPE) containers for the collection and storage of organomercury, especially diphenylmercury in this study.
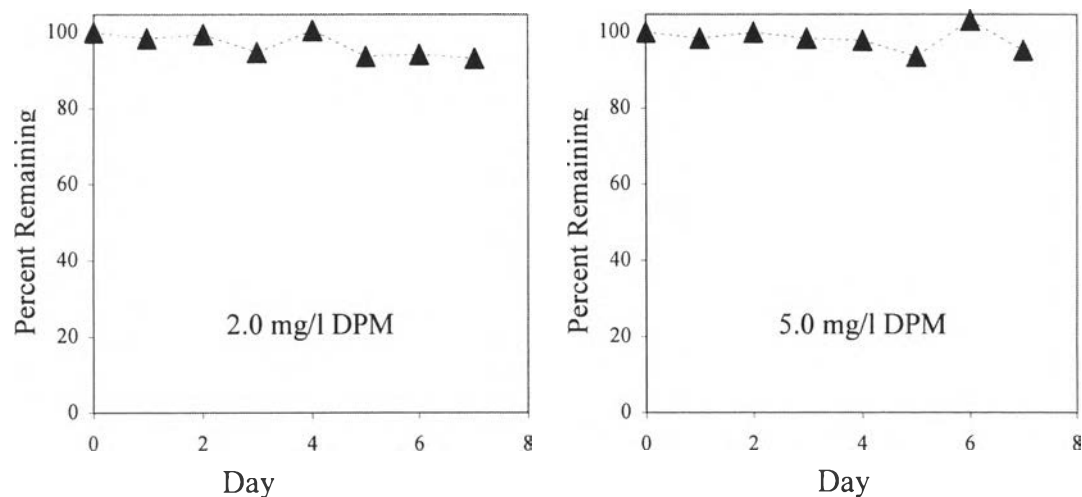
Figure 4.3 Adsorption of diphenylmercury in n-heptane in plastic (HDPE) containers.

4.3 Kinetic Studies of Diphenylmercury

The adsorption kinetics of DPM on all adsorbents are shown in Figure 4.4. It did not follow the simple first order with respect to DPM concentration. The rate of mercury removal is rapid on the initial contact and slows down as the contact time is increased. In fact, the improvement in mercury removal is quite limited and almost reaches the equilibrium when the contact time reached to about 200 minutes for most selected adsorbents, except for zeolite NaX and NaY that still preformed well until 400 minutes of contact time. It is noted that a very high level of mercury removal was not achieved even through the feed contains only one species of organomercury, diphenylmercury, in condensate due to the demand of removing mercury to a very few ppb levels although the use of NaY which shown the greatest capability of removing mercury among selected adsorbents. However, it gave some evidence that organomecury like diphenylmercury can be removed by using a proper adsorbent while Yamada *et al.* (1994) reported that
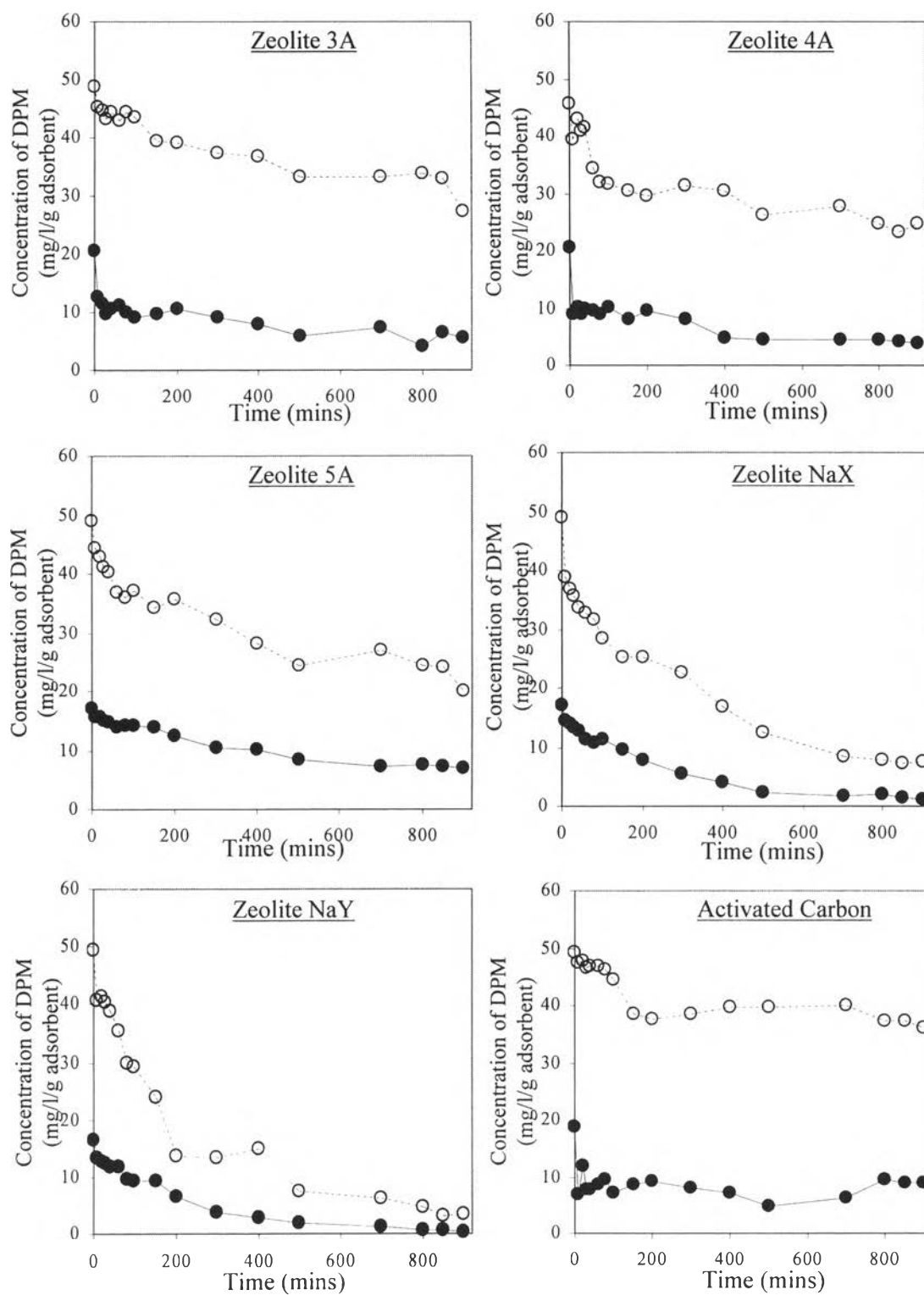
Figure 4.4 Kinetics of diphenylmercury adsorption on various adsorbents.

----o---- 5.0 mg/l DPM ——●—— 2.0 mg/l DPM

organomercury can not be adsorbed on any type of adsorbent and not be extracted with any type of agent.

From the results, it is obvious that contact time must be allowed at least 600 minutes to reach the equilibrium of adsorption process for all kind of adsorbents. The NaY and NaX zeolites gave a very good trend to remove mercury while 3A, 4A, and 5A zeolites and activated carbon show less efficient to remove mercury, respectively.

D.M. Ruthven (1984) shows that the kinetics of adsorption can be resumed by the following expression.

$$\frac{q_t}{q_\infty} = 2\left(\frac{A}{V}\right)\left(\frac{D_c t}{\pi}\right)^{1/2} \tag{4.1}$$

Where: A/V is the ratio of the external area-to-particle, and for a spherical particle, it is simply as $3/r_c$.

r_c is the crystallite size.

D_c is the intracrystalline diffusivity.

q (q_t, q_∞) is mass adsorbed (at time t and at t →∞).

A plot of fractional uptake versus $\sqrt{t}$ should therefore yield a straight line through the origin with the slope of $2(A/V)(D_c/\pi)^{1/2}$. These results are presented in Figure 4.5.
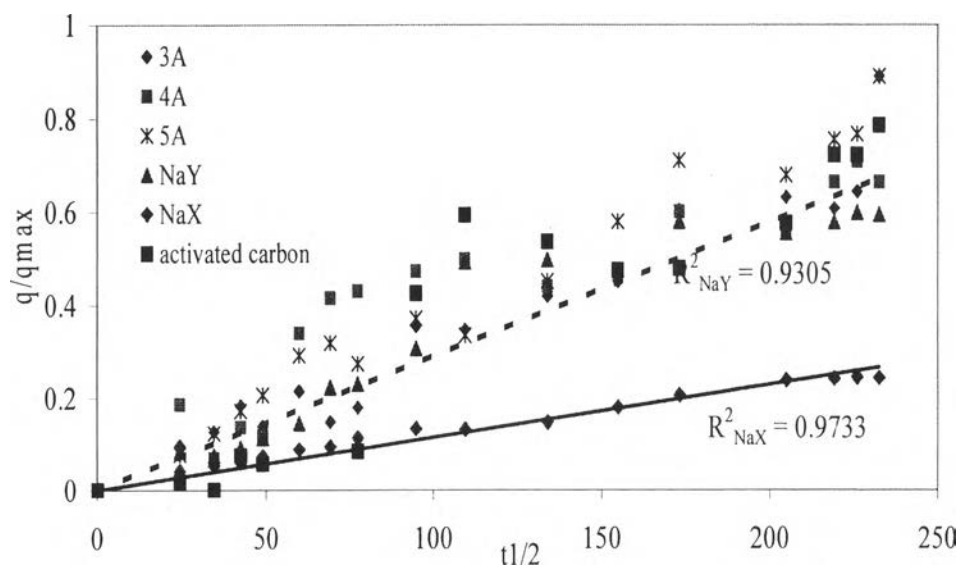
Figure 4.5 Evolution of q/q_{max} ratio versus time.

The slope could give the D_c constant. Since we don't have any precision of the crystallite size of the zeolite and it is known that, as synthesized, commercial molecular sieve zeolite crystals are quite small (typically 1.5-10 μm) reported by Ruthven (1984), the calculations were performed with two size of crystallite: 1.5 μm and 10 μm. The results for the NaX and NaY zeolites are presented in Table 4.2.

Table 4.2 Calculation of intracrystalline diffusivity constant

Solids	D_c (cm^2/s) with 1.5 μm of crystallite size	D_c (cm^2/s) with 10 μm of crystallite size
NaX	2.6×10^{-15}	1.2×10^{-13}
NaY	1.4×10^{-14}	6.4×10^{-13}

On the following data shown in Table 4.3, there are some intracrystalline diffusivity constants reported in the literature.

**Table 4.3** Survey of literature for intracrystalline diffusivity constant

Adsorbents	Compounds	Temperature (°C)	Diffusivity Constant (cm^2/s)	References literature
NaY, CeY, HY	1.1-Methyl naphthalene cumene	28	3×10^{-13} to 16×10^{-13}	Satterfield *et al.* (1971)
	2.Benzene	25		

The calculated diffusivity constants are closed to the ones found in the literature where the calculation of diffusivity constants based on the weighted average crystallite size of 10.1 μm. However, these constants are very low

specially the one of NaX zeolite. Therefore, a limitation of the diphenylmercury adsorption is due to the diffusivity.

4.4 Effect of Pore Size on Diphenylmercury Adsorption

The effect of pore size on the adsorption of diphenylmercury with 3A, 4A, 5A, NaX and NaY zeolites is shown in Figure 4.6. At 2.0 mg/l, the weight percent of DPM removal is 45.23, 54.19, 54.19, 84.48, and 84.91, respectively. At 5.0 mg/l, the weight percent of DPM removal is 29.76, 44.65, 46.53, 79.26, and 79.58, respectively. For the activated carbon, the weight percent of DPM removal is 52 and 30 at 2.0 mg/l and 5.0 mg/l, respectively. It should be noted that NaX and NaY zeolites, which have the biggest pore opening within the concerned group, show very good performing in removing diphenylmercury.
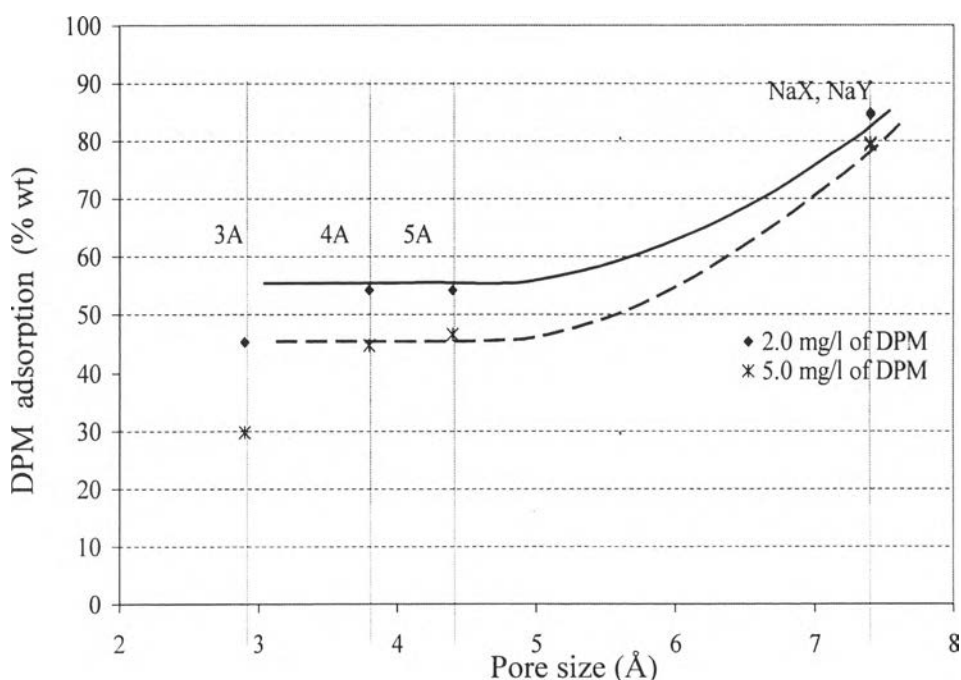

Figure 4.6 Effect of zeolite pore opening size on diphenylmercury adsorption.

The diphenylmercury molecule model presented in Figure 4.7, the narrowest intramolecular distance corresponding to H-H length across a

benzene ring is 4.64 Å and the widest part, corresponding to H-H distance across the two benzene rings, is 12.70 Å whereas the pore opening of 3A, 4A and 5A zeolites are 2.9, 3.8 and 4.4 Å, respectively. Therefore, the adsorption on the 3A, 4A and 5A zeolites are most likely due to the adsorption on the external sites (at the surface zeolites and inside the mesopores). For the 5A zeolite, a part of DPM molecule could perhaps get inside the supercage through the pore opening while the pore opening (7.4 Å) for the NaX and NaY zeolites is sufficient to allow the DMP molecules to adsorb on the adsorption sites located in the supercage cavities.
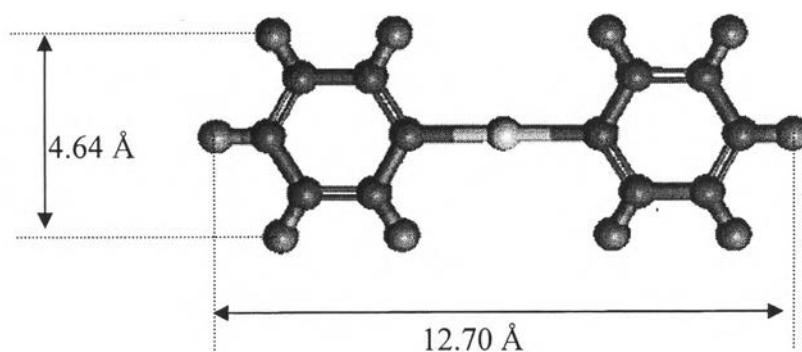

Figure 4.7 Diphenylmercury molecule model.

4.5 Isotherms of Diphenylmercury Adsorption on Adsorbents

From the previous results, it can be seen that there are two different phenomena based on the location of surface adsorption. The first one is the group of a small pore size such as 3A, 4A and 5A zeolites since the diphenylmercury adsorption is due mainly to the adsorption on the external sites. The second one is constituted by NaX and NaY zeoiltes with a high pore opening which the diphenylmercury molecules can penetrate inside the supercage of the zeolites through the pore channels. Figure 4.8 shows the plots of diphenylmercury adsorption versus equilibrium diphenylmercury concentration. Thus, two adsorption models were used to describe the

adsorption phenomena: pure Langmuir adsorption model called Langmuir and Bi-Langmuir model where there are two different kinds of adsorption sites.
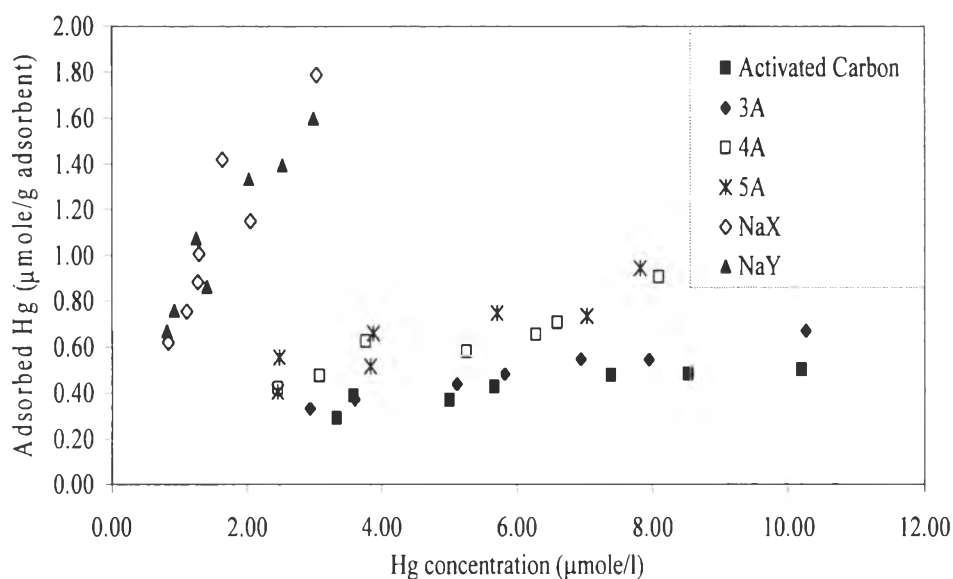
Figure 4.8 Diphenylmercury adsorption versus equilibrium diphenylmercury concentration (experimental results).

4.5.1 Langmuir Model

The pure Langmuir model hypothesizes the followings. There is only one kind of adsorption sites that each site is equivalent to another and can adsorb only one molecule on one distinct adsorption site, and the adsorption energy is the same for all the adsorption sites.

The model determines the fraction or the ratio of the number of adsorbed molecules on the total number of molecules required for a complete monolayer, defined as Θ. At the equilibrium, the adsorption speed (R_{Ad}) and desorption speed (R_{De}) are equal;

$$R_{Ad} = k_A(1-\Theta)C \cdot L \qquad (4.2)$$

$$R_{De} = k_D\Theta \cdot L \qquad (4.3)$$

where   C is equilibrium concentration of diphenylmercury.

L is total site for a complete monolayer.

k_A and k_D are adsorption and desorption constants, respectively.

Therefore, the two previous equations can be rearranged as following.

$$\theta = \frac{bC}{(1+bC)} \qquad (4.4)$$

where   b is called adsorption/desorption constant.

The experimental data which can be measured is the quantity of molecules adsorbed on the solid called q (mol/m^2 or mol/g of adsorbent). Thus, the equation 4.4 can be rewritten as the following.

$$q = \left(\frac{bC}{1+bC}\right)q_{max} \qquad (4.5)$$

And it can be rearranged to satisfy the first order linear relationship.

$$\frac{1}{q} = \frac{1}{q_{max}} + \left(\frac{1}{bq_{max}}\right)\frac{1}{C} \qquad (4.6)$$

Figure 4.9 shows the results obtained from the experimental results.
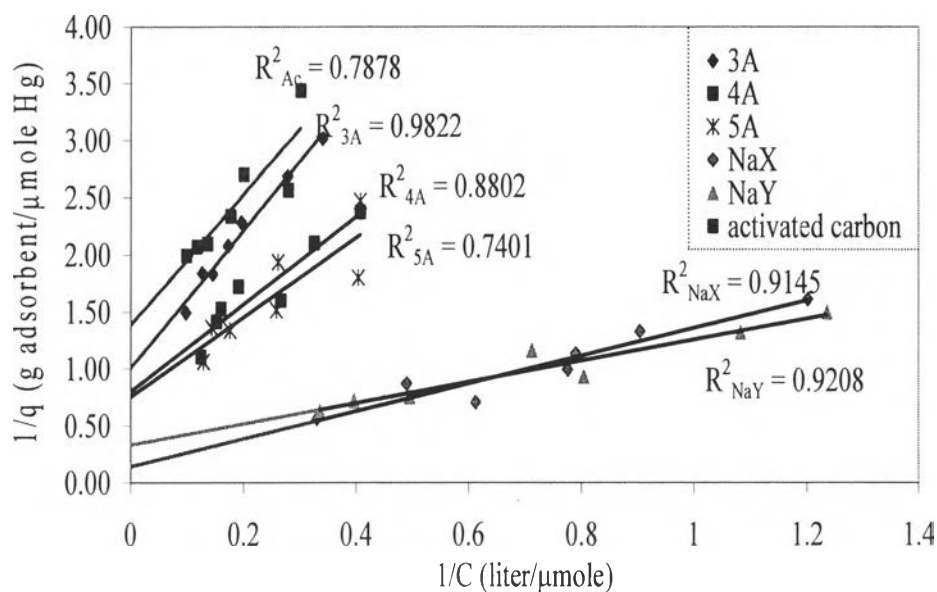
Figure 4.9 Determination of the one site Langmuir model coefficients.

From the slope and the intercept of the curves with the y axe, q$_{max}$ and the adsorption coefficient (b) can be calculated as shown in Table 4.4.

Table 4.4 Langmuir model coefficients versus types of solids

Solids	q_{max} (μmole/g adsorbent)	b
Activated Carbon	0.721	0.24235
3A	0.992	0.16699
4A	1.246	0.20968
5A	1.326	0.21578
NaX	7.069	0.11627
NaY	3.022	0.35801

There is a good agreement between the experimental results and the one site Langmuir model as seen in Figure 4.10 after inserting the adsorption parameters shown in Table 4.4 into the Equation 4.5 for the comparison.
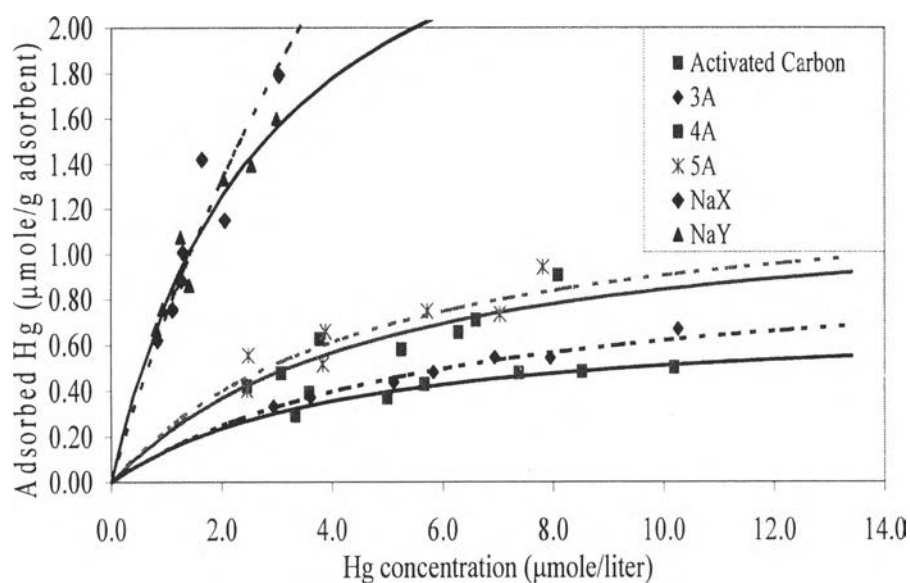
Figure 4.10 Comparison between experimental results and the one site Langmuir model.

It is necessary to check if the maximum quantity of mercury adsorbed (q_{max}) on the different solids is "theoretically" possible or if the calculation results are not in accordance with the reality.

The calculations were performed based on NaY characteristics, provided by IFP. Since the binder or clay quantity is around 26.7% of the adsorbent mass and the unit cell formula of NaY is known, the quantity of cages is around 2.77×10^{20} cages/ g of zeolite, the calculation of which is shown in Appendix A. Besides, it is known that this kind of solid can get a maximum of 3 molecules of para-diethylbenzene adsorbed inside one supercage (information provided by IFP). From geometry point of view, as the diphenylmercury is composed of two aromatics rings, this kind of solid could get around one molecule of diphenylmercury per cage.

Based on these characteristics and the q_{max} calculated previously, the number of diphenylmercury molecules adsorbed inside one supercage of the NaX was around 0.01 molecule indicating that the greatest part of the zeolite supercages were free of diphenylmercury molecules. This low value could be due to the restriction of the diffusivity of the molecules inside the zeolite or the rotation probability of the diphenylmercury molecules in order to expose the side that can penetrate inside the supercage of zeolites.

However, the diphenylmercury, as seen previously, cannot penetrate inside the zeolite supercages of the 3A and 4A zeolites and only probably slightly for the 5A zeolite. Therefore, the adsorption is due mainly to the external surface or the binder.

Noticeably, the NaX and NaY zeolites have a high maximum diphenylmercury adsorption capacity compared to the 3A and 4A zeolites. The result was probably due to the fact that the diphenylmercury could penetrate inside supercages of these zeolites and adsorbed inside the supercages. Therefore, the adsorption of the NaX and NaY zeolites was perhaps related to two phenomena (adsorption on the external surface or binder similar to 3A and 4A zeolites and adsorption inside the zeolite supercages). In this case, a model with two kinds of adsorption sites is required. This model would be also based on the Langmuir isotherm expression.

For the 5A zeolite, there is perhaps a part of adsorption due to the supercage sites, but the extent is not known and would be calculated.

4.5.2 Bi-Site Langmuir Model

The model hypothesizes the followings. There are two kinds of adsorption sites, and the diphenylmercury can be adsorbed equally. The two kinds of sites were referred to site I located at the external surface area and site II located inside the supercage of zeolites. However, with this assumption, the adsorption on the activated carbon could not be modeled with bi-Langmuir model because the activated carbon has no supercages as zeolites do.

Thus, from the equation 4.5, it can be expressed by the following.

$$q = \left(\frac{b_1 C}{1 + b_1 C} \right) q_{1\,max} + \left(\frac{b_2 C}{1 + b_2 C} \right) q_{2\,max} \qquad (4.7)$$

It was assumed for site I of the NaX, NaY and also 5A zeolites that the adsorption parameters were equivalent to those of the 4A zeolite. Therefore, q_{1max} and b_1 were known. Consequently, the q_{2max} and b_2 can be then determined and shown in Table 4.5.

Table 4.5 Bi-site Langmuir model coefficients versus types of solids

Solids	q_{1max} (μmole/g adsorbent)	b_1	q_{2max} (μmole/g adsorbent)	b_2
3A	0.992	0.16699	0	0
4A	1.246	0.20968	0	0
5A	1.246	0.20968	1.884	0.1060
NaX	1.246	0.20968	5.421	0.1048
NaY	1.246	0.20968	2.052	0.4033

Figure 4.11 shows the comparison between the one site model and the bi-site model for the 5A zeolite.
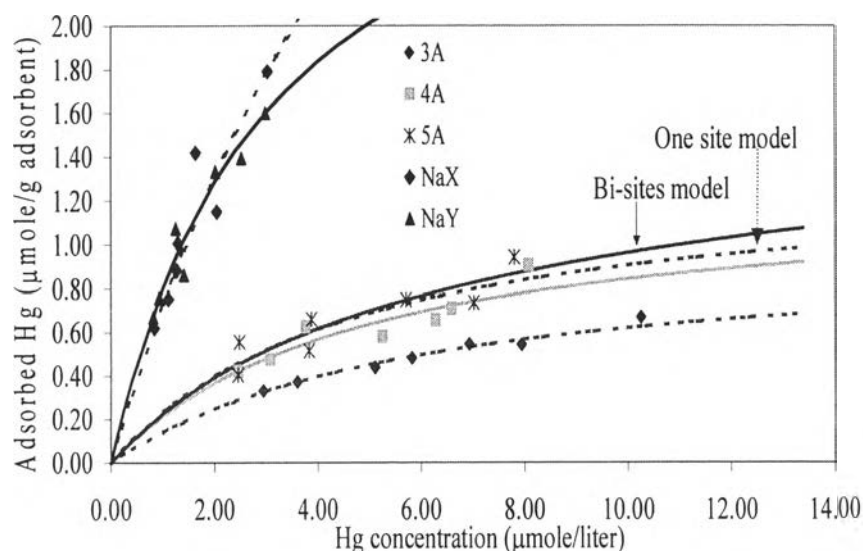
Figure 4.11 Comparison between experimental results and bi-site Langmuir model.

For the 3A and 4A zeolites, all the diphenylmercury adsorption is due to the external adsorption sites, site I. For the other zeolites (5A, NaX and NaY), there is a contribution of the two kinds of sites to the diphenylmercury adsorption. The contribution of each part has been calculated, with the model coefficients presented in Table 4.5, for each solid as shown in Table 4.6.

**Table 4.6** Contribution of each kind of sites to the total diphenylmercury adsorption

Soilds	Adsorption due to the external site, (%),"site I"	Adsorption due to the internal site, (%),"site II"
3A	100	0
4A	100	0
5A	89-93	7-11
NaX	27-30	70-73
NaY	26-30	70-74

It can be seen that for the 5A zeolite, in case of a bi-site Langmuir adsorption model, only 10% of the total diphenylmercury adsorption could be due to the supercage sites (internal sites). The adsorption occurred mainly on the external surface of the zeolite. In this case, the adsorption could be assumed as a one site model adsorption such as 3A and 4A zeolites.

On zeolites with bigger pore aperture such as NaX and NaY, the adsorption of the diphenylmercury occurred mainly on the supercage sites.

4.6 Breakthrough Curves Study

Since the experiments were limited by time, only half way of the breakthrough curves for each adsorbent were presented in Figure 4.12.
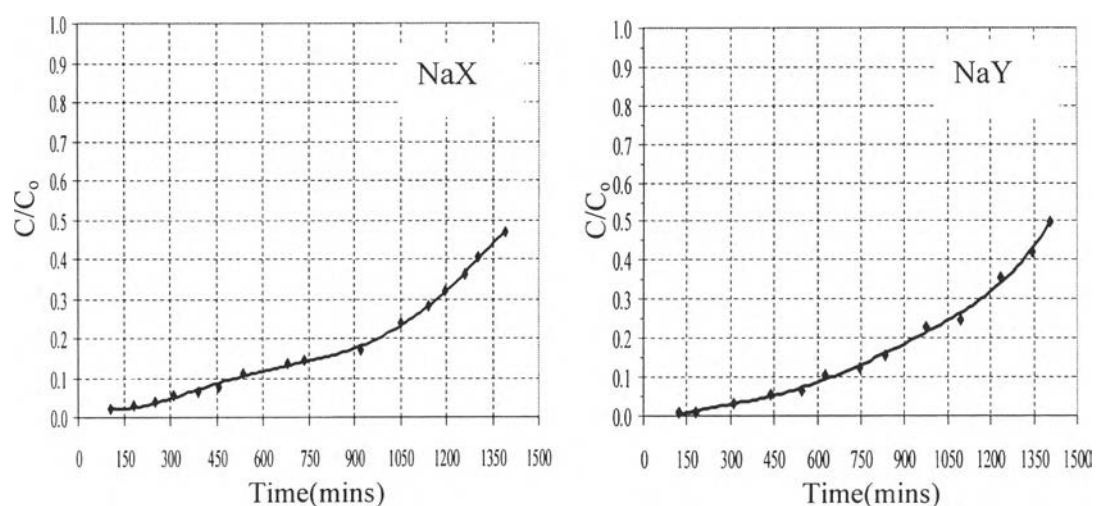
Figure 4.12 Breakthrough curves, plotting the ratio of the effluent concentration of DPM ,C, to initial concentration, C_o (2100 ppb), versus time for NaX and NaY zeolites in continuous system tested in unit U844.

In general, the breakthrough time is set at 0.05 of the ratio of the effluent concentration to the initial concentration, C/C_o. For NaX zeolite, it was found that the breakthrough time is 315 mins while the breakthrough time of NaY is 440 mins. The mercury removal efficiency of NaX and NaY zeolites is almost the same. The mercury removal efficiency of NaY reached to 99%,

whilst the mercury removal efficiency of NaX reached to 98%. Thus, in practical manner, using NaY to remove diphenylmercury is more preference than using NaX. However, it should be noted that the results from the small pilot tests are always pessimistic with respect to larger pilot operations due to the low ratio of the internal diameter of the reactors with respect to the average catalyst particle size. This value was less than 10 for the small pilot operations, thus some bypasses of the impurities were expected. In larger pilot units or industrial units, as the diameter ratio is increased significantly above ten, by- pass is substantially reduced and performance increases.

Cussler (1997) presented a very useful relation for a breakthrough curve in case of irreversible adsorption in a packed bed of length l as the following equation.

$$\frac{C}{C_o} = e^{\left(-1 + \frac{kal}{v}\left(\frac{C_o vt}{q_o(1-\varepsilon)} - 1\right)\right)} \tag{4.8}$$

Where: v is feed flow rate

q_o is the saturation concentration in the adsorbent

l is the length of the bed

k is the mass transfer coefficient

a is the adsorbent area per bed volume

ε is a void fraction

The equation was made with two assumptions: (1) the accumulation within the solution is much less than the accumulation within the tapping mass solid and (2) the adsorption is irreversible so that the equilibrium concentration near the trapping mass solid surface is zero. Therefore, if the plot of the logarithm of concentration of the breakthrough curve is linear with time, the adsorption process on the trapping mass solid can be said to be irreversible adsorption or chemisorption even though a few points at the begining of the breakthough curve are applied.
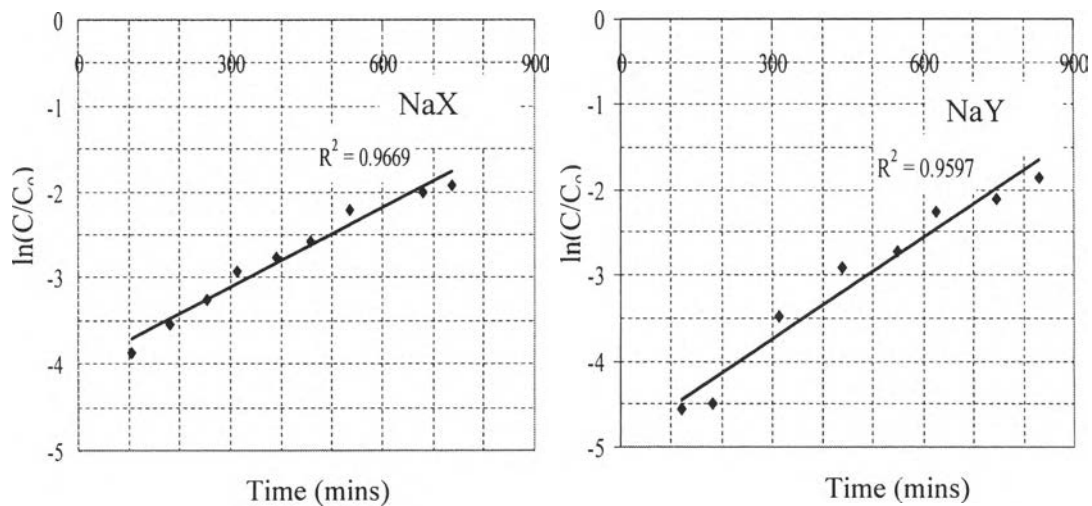
Figure 4.13 Logarithm of concentration versus time.

Figure 4.13 shows the plot of the logarithm of concentration of the breakthrough curve versus time. Since the logarithm of concentration varies with time, the possibility of the irreversible adsorption or chemisorption rather than physisorption of diphenylmercury on both NaX and NaY zeolites is existing. However, the relevant support for this conclusion needs to be extended for further study.