CHAPTER IV
RESULTS AND DISCUSSION

4.1 Clinoptilolite Characterization

4.1.1 BET Surface Area

The specific area of clinoptilolite was calculated from the 5-points adsorption isotherm of N_2 gas on clinoptilolite using a BET surface analyzer. From the BET results, it was found that the surface area of clinoptilolite is $9.45 \pm 0.5 m^2/g$

4.1.2 Chemical Composition

Based on X-ray diffraction analysis as shown in Figure 4.1, it was found that the commercial clinoptilolite contains a majority of clinoptilolite with a small amount of ammonium aluminum phosphate (less than 10%) and a trace amount of heulandite. K^+, Na^+ and Ca^{2+} are the naturally present exchangeable cations that found in clinoptilolite.
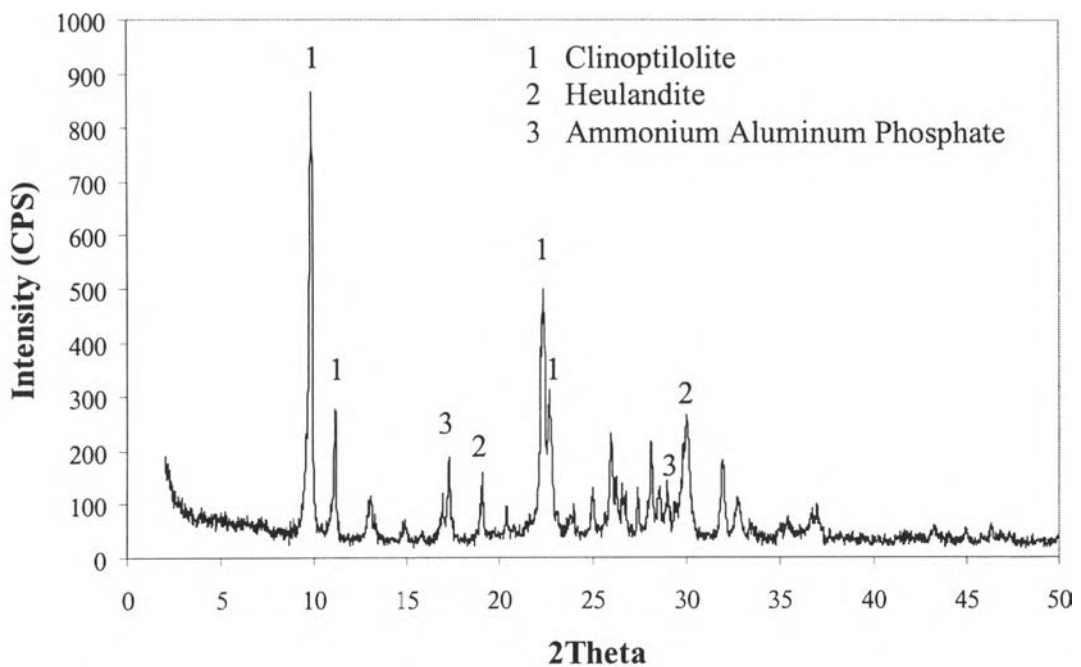

Figure 4.1 XRD pattern of clinoptilolite.

4.2 CTAB Adsorption on Clinoptilolite

The adsorption isotherm of cetyltrimethylammoniumbromide (CTAB) on clinoptilolite at 30°C is shown in Figure 4.2. The maximum sorption of CTAB on clinoptilolite is approximately 200 µmol of CTAB per gram of clinoptilolite (0.2 mmole/g). This sorbed amount is approximately twice the zeolite's external cation exchange capacity (0.1 mequiv/g).
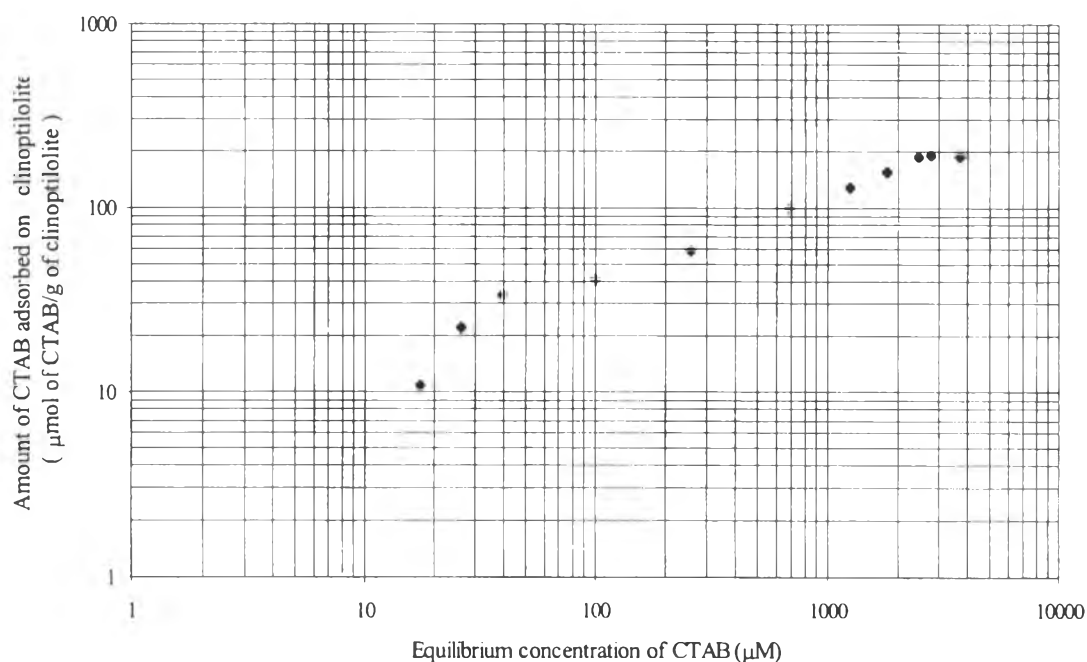

Figure 4.2 Adsorption isotherm of CTAB on clinoptilolite at 25°C.

Figure 4.3 shows the zeta potential of clinoptilolite as a function of CTAB adsorption. This figure simply reflects the extent of adsorption and the orientation of adsorbed CTAB on clinoptilolite. Starting from having a net negative charge, the surface potential became less negatively charge as CTAB loading increased and eventually became positive. The net negative charge on the zeolite was neutralized when the CTAB loading reached 100 µmol/g, which indicated a complete monolayer adsorption of CTAB on clinoptilolite (Rosen, 1989). This surface adsorption is half of the bilayer coverage which should make the zeolite surface becomes neutral as seen in this figure.
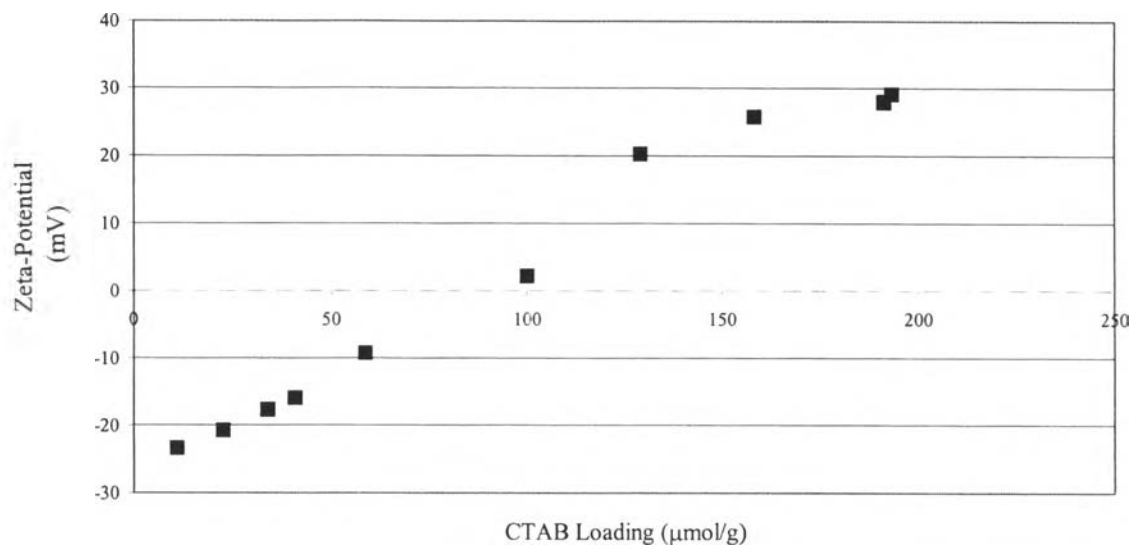
Figure 4.3 Zeta potential of clinoptilolite as a function of CTAB loading.

4.3 Characterization of Surfactant-Modified Zeolite (SMZ)

After CTAB adsorption at the monolayer coverage on clinoptilolite, the surface was further modified by adsorbing palmitic acid through hydrophobic interaction. The resulting SMZ was then subjected to surface characterization techniques including SEM and FTIR

4.3.1 Surface Morphology of SMZ

The scanning electron micrographs of clinoptilolite and SMZ are shown in Figures 4.4 and 4.5, respectively. The clinoptilolite surface, as seen in Fig. 4.4, clearly reveals its crystalline structure. In contrast, the surface of SMZ did not show the crystalline structure but rather is amorphous and heterogeneous as a result of the sorption of CTAB and palmitic acid on clinoptilolite.
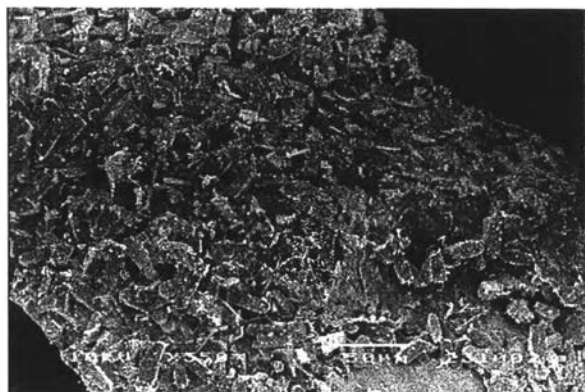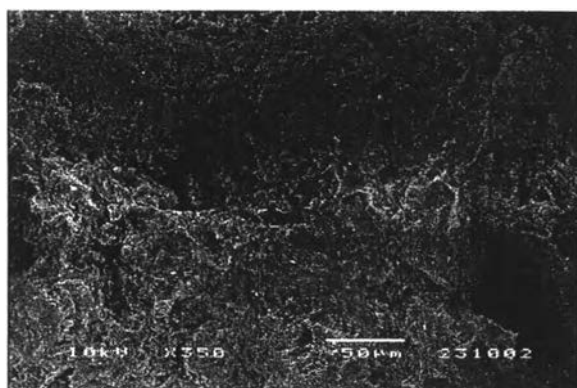
Figure 4.4 SEM image of clinoptilolite.

Figure 4.5 SEM image of surfactant-modified zeolite (SMZ).

4.3.2 Surface Functional Groups on SMZ

FTIR spectra of clinoptilolite and SMZ are shown in Figures A5 and A6 in Appendix. Some relevant IR adsorption frequencies of clinoptilolite and SMZ are also shown in Table 4.1. The spectra show the OH stretching of aluminum hydroxide at 3636 cm^{-1} can be clearly seen in both clinoptilolite and SMZ samples. In contrast, the characteristic vibrational frequency of quaternary amine salt (2922 cm^{-1}) and C=O stretching (1680 cm^{-1}) of carboxyl group appeared only in SMZ. These spectra reflect the presence of palmitic acid on clinoptilolite. Moreover, the C-H stretching of aliphatic group (2852 cm^{-1}), which found in CTAB and palmitic acid also appeared only in SMZ.

Table 4.1 Some fundamental IR adsorption frequencies of the clinoptilolite and SMZ.

Clinoptilolite	SMZ	Assignment
3636	3636	O-H stretching of aluminum hydroxide
-	2852	C-H stretching of aliphatic group
-	2922	Quarternary amine salt
-	1680	C=O stretching of carboxyl group

All frequencies in cm^{-1}

4.4 Kinetics of Cadmium Adsorption on Clinoptilolite and SMZ

The kinetics of cadmium adsorption by unmodified clinoptilolite is shown in Figure 4.6. It can be seen that the adsorption of cadmium by clinoptilolite was fast at the beginning. Approximately 40% of the total amount of adsorbed cadmium ions was taken up by clinoptilolite during the first 30 min. After that the adsorption was gradually slowed down and reached equilibrium within approximately 250 min.
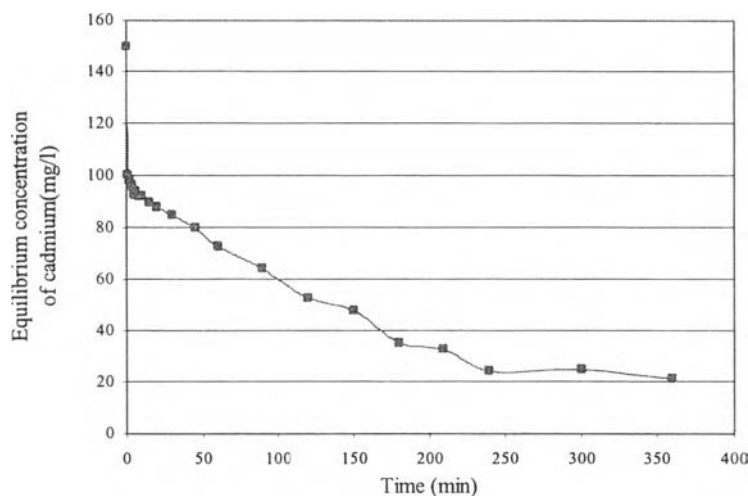

Figure 4.6 Kinetics of cadmium adsorption on clinoptilolite at pH 8 and initial concentration of cadmium = 150 mg/l.
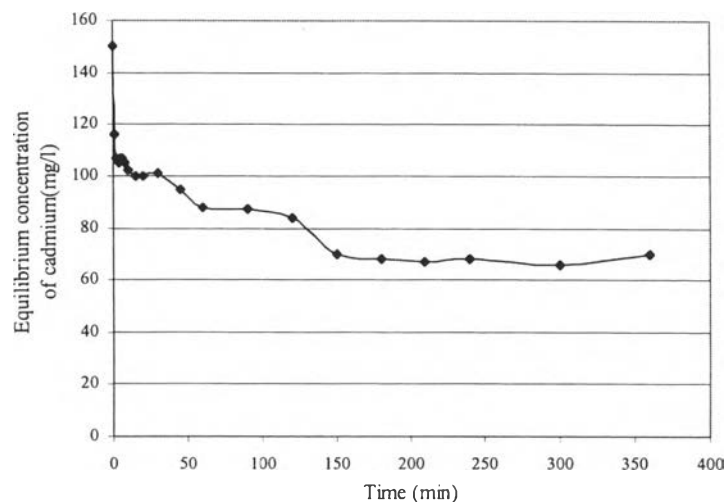
Figure 4.7 Kinetics of cadmium adsorption on SMZ at pH 8 and initial concentration of cadmium = 150 mg/l.

Figure 4.7 shows the kinetics of cadmium adsorption on SMZ. In general, the kinetic data were shown to be quite similar to the adsorption of cadmium on unmodified clinoptilolite. The results indicated that the adsorption of cadmium on SMZ occurred rapidly. Approximately 60 % of the total amount of cadmium adsorbed was taken up by SMZ during the first 30 min. It is clearly seen that the adsorption reached equilibrium within approximately 200 min.

When comparing the adsorption of cadmium by unmodified clinoptilolite and SMZ, one can see that the surface modification using cationic surfactant and palmitic acid did not have any adverse effect on the rate of adsorption of cadmium by SMZ. The adsorption rate of cadmium by SMZ was shown to be comparable to that of the unmodified clinoptilolite which was in the range of 0.3-0.4 mg/g·min. From the total amount of adsorbed cadmium by the adsorbent, a large fraction of cadmium (60%) were adsorbed by SMZ during the first 30 min while only 40% of the total adsorbed amount was adsorbed in the latter part of the adsorption course until equilibrium was reached. This can be attributed to the adsorption mechanism of SMZ which is expected to be the complexation mechanism as previously observed in the adsorption of cadmium on the surfactant-modified clay complexes (Malakul *et al.*, 1998). In contrast, the adsorption of cadmium by unmodified

clinoptilolite is expected to be through simple ion-exchange mechanism. This will be further discussed in the next section.

4.5 Effect of pH on Cadmium Adsorption

4.5.1 Cadmium Adsorption on Clinoptilolite

Figure 4.8 shows the adsorption isotherms of cadmium on clinoptilolite at pH 4, 7 and 8. It should be noted that in this pH range, the majority of cadmium present in the system is in a divalent form (Cd^{2+}). The results show that pH had little effect on cadmium removal by clinoptilolite. The amount of cadmium adsorbed on clinoptilolite slightly increased with increasing pH of the system from 4 to 7.
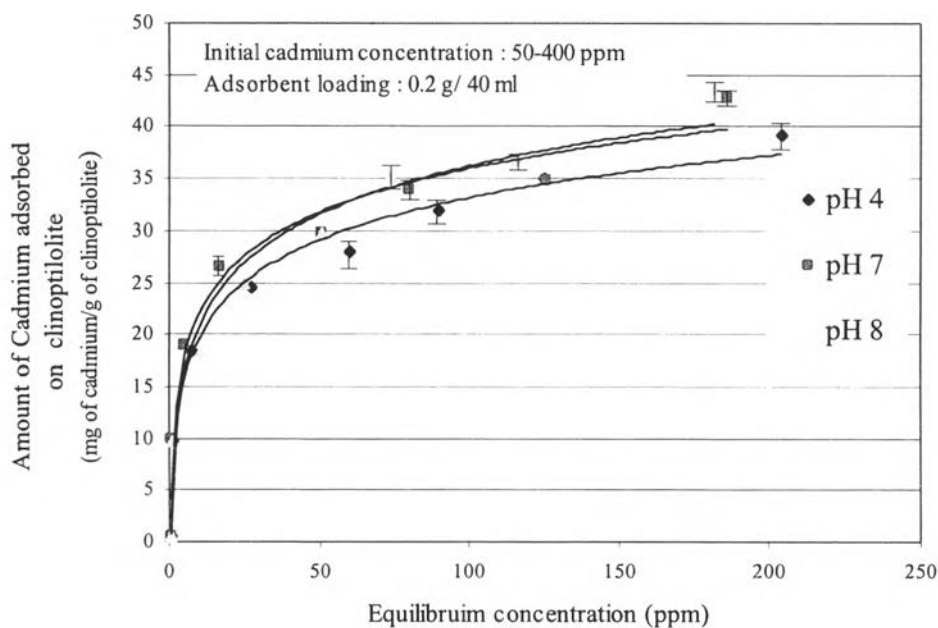

Figure 4.8 Adsorption isotherms of cadmium on clinoptilolite at pH 4, 7 and 8.

The results can be explained that the functional groups on clinoptilolite surface can dissociate at higher pH values, thus resulting in higher negative charges on the surface of clinoptilolite which could contribute to the increased cadmium adsorption (Ouki and Kavannagh, 1999). However, it can be seen from Figure 4.9 that the amount of cadmium adsorbed on clinoptilolite at pH 7 and 8 were quite

close. This is probably due to an insignificant change in the negative charges on the surface of clinoptilolite when pH was increased from 7 to 8.

4.5.2 Cadmium Adsorption on SMZ

The adsorption isotherms of cadmium on SMZ at pH 4, 7 and 8 are illustrated in Figure 4.9. In contrast to the unmodified clinoptilolite, the results obtained from the adsorption of cadmium by SMZ clearly revealed a more significant pH effect. This is a result of the different surface functional group on SMZ as compared to the unmodified clinoptilolite. After the surface modification with cationic surfactant and metal ligand, the carboxylic group of the palmitic acid became the surface functional group of SMZ for metal adsorption. The influence of pH on Cd^{2+} adsorption of SMZ is attributed to the chemistry of the functional group on SMZ surface.
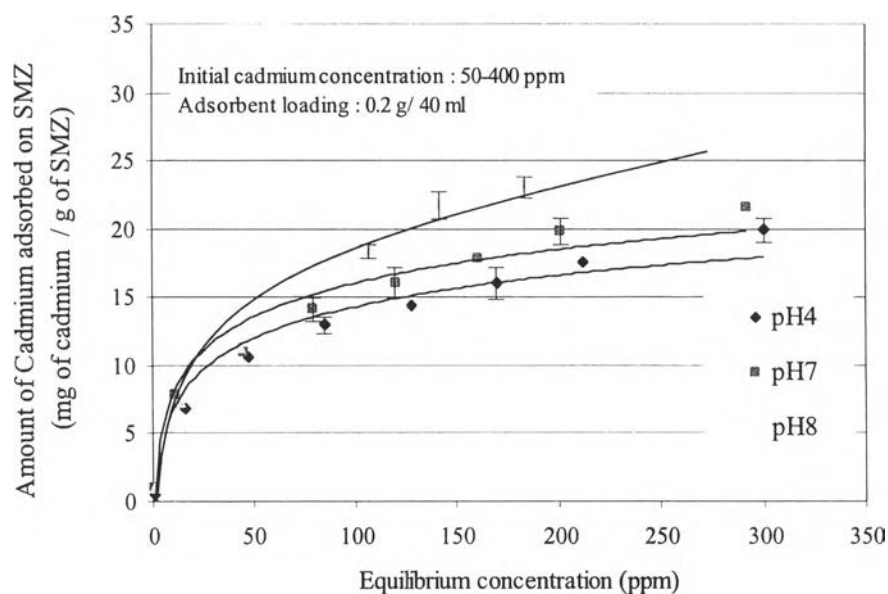

Figure 4.9 Adsorption isotherms of cadmium on SMZ at pH 4, 7 and 8.

At pH lower than pK_a of palmitic acid (pH<6.46), the carboxyl groups of palmitic acid on SMZ surface are protonated. Therefore, less uptake of cadmium was observed at pH 4. Increasing the pH from 4 to 7 caused deprotonation of some of the carboxyl groups, resulting in a slight increase in cadmium adsorption. At pH

values higher than pK_a of palmitic acid (pH>6.46), the carboxyl groups are deprotonated, thus providing the sorption sites for cadmium. The adsorption of cadmium ions on SMZ surface was also expected to be through metal complexation with carboxylic groups of palmitic acid on SMZ surface. This can be confirmed by the effect of ionic strength and FTIR study which will be discussed in the next section. Since pH 7 is quite close to the pK_a of palmitic acid, at this pH the carboxyl groups on SMZ surface may not be completely deprotonated. On the other hand, at pH 8 most of the carboxyl groups should be deprotonated and, consequently, a considerable increase in cadmium adsorption would be expected, as observed in Figure 4.9.

4.6 Effect of Ionic Strength on Cadmium Adsorption

The effect of ionic strength on the adsorption of cadmium with clinoptilolite and SMZ is shown in Figure 4.10. It should be noted that ionic strength was adjusted by using NaCl – no ionic strength means the system without the addition of NaCl.
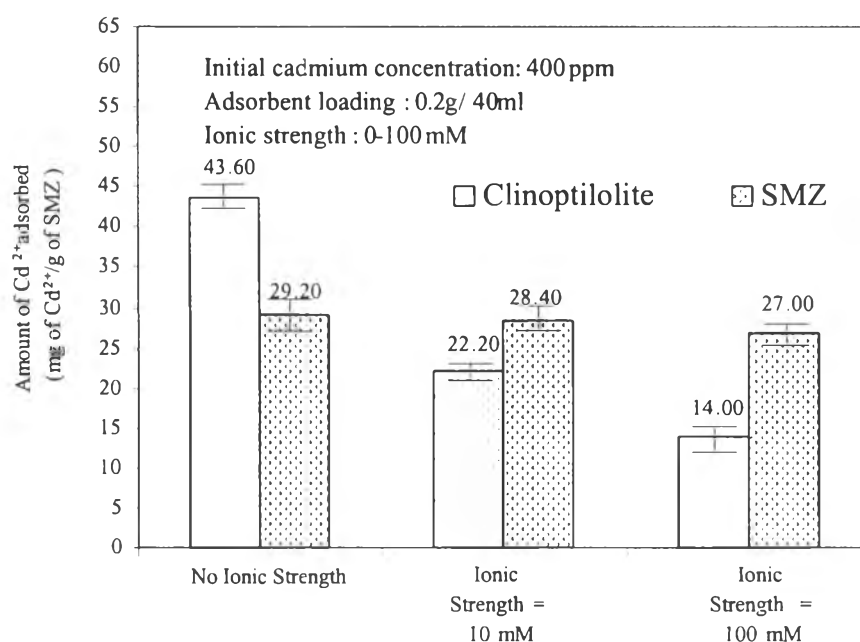

Figure 4.10 Effect of ionic strength on the adsorption of cadmium by clinoptilolite and SMZ.

The results in Figure 4.10 show that ionic strength had a significant effect on the adsorption of cadmium by clinoptilolite. As the ionic strength of the system was increased to 10 mM, the amount of cadmium adsorbed by clinoptilolite was found to decrease by almost 50%. And when the ionic strength was further increased to 100 mM, the uptake of cadmium by clinoptilolite decreased by 70% of its original capacity. The results observed here clearly indicated that the adsorption of cadmium on clinoptilolite is purely through an ion-exchange mechanism since an increase in ionic strength would simply result in an increased amount of cations (Na^+) to compete with Cd^{2+} ions for adsorption (Ouki and Kavannagh, 1999). In contrast, it is obviously that increasing the ionic strength had a very little effect on the adsorption of cadmium by SMZ. At the ionic strength as high as 100 mM, the adsorption of cadmium by SMZ was reduced by only 8% of its original values. The slight decrease in adsorption capacity of SMZ upon increasing ionic strength clearly indicates that the adsorption of cadmium by SMZ is not through ion exchange, but rather through a metal complexation. As a result, increasing ionic strength had only little effect on the metal adsorption capacity SMZ. The results observed here are in good agreement with a previous study on cadmium adsorption by surfactant-modified clay complexes (Malakul *et al.*, 1998). In this study, FTIR was employed to investigate the adsorption mechanism and the shift in the vibrational frequency of the carbonyl band was observed and used to confirm the complexation mechanism.

4.7 Toluene Adsorption on Clinoptilolite and SMZ

The adsorption isotherms of toluene on clinoptilolite and SMZ at pH 8 are shown in Figure 4.11. The results demonstrate that SMZ adsorbed more toluene than clinoptilolite on equal weight basis.
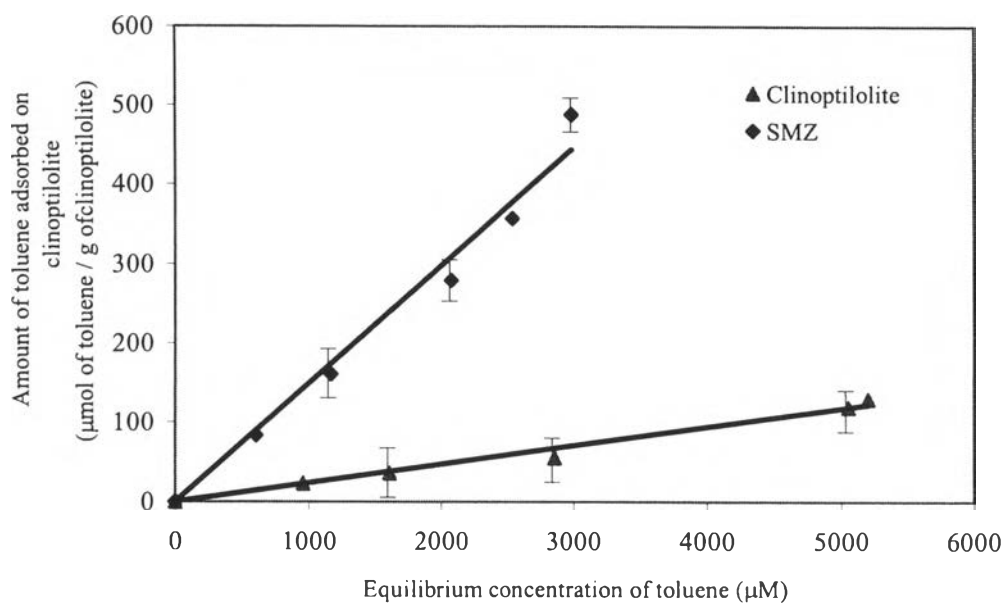
Figure 4.11 Adsorption isotherm of toluene on clinoptilolite and SMZ at pH 8.

Table 4.2 Partition coefficient of clinoptilolite and SMZ for toluene adsorption at pH 8.

Adsorbent	Partition coefficient (L/g)
Clinoptilolite	0.023
SMZ	0.149

In addition, the adsorption isotherm of SMZ exhibited a linear relationship between the amount of toluene adsorbed and toluene equilibrium concentration. Thus, the adsorption data can be model with simple linear isotherm $q=K_pC_e$. Where q is the amount of sorbed toluene (μmol/g adsorbent), K_p is partition coefficient (L/g) and C_e is the equilibrium toluene concentration in solution (μmol/L). The partition coefficients (K_p) of clinoptilolite and SMZ for toluene adsorption at pH 8 are shown in Table 4.2. The partition coefficient (K_p), which is independent of the solute concentration, of SMZ is approximately 6.5 times higher than that of the unmodified clinoptilolite and in the same range of the value previously reported for surfactant-

modified clay (Malakul *et al.*,1998). This clearly indicates that SMZ adsorbs more toluene than unmodified clinoptilolite at the same equilibrium concentration. This is due to the organic partitioning phase of SMZ, which greatly enhances the toluene adsorption. The adsorption of toluene on SMZ is believed to be through partitioning of the organic solutes to the organic phase of SMZ (Stephen *et.al*, 1988). In contrast, the adsorption isotherm of toluene on clinoptilolite showed much less amount of toluene adsorbed, yet exhibited similar linearity. This is probably due to the polarity and structure of the clinoptilolite which can lead to the interactions between the adsorbate and adsorbent. Therefore, only a limited amount of toluene was adsorbed by unmodified clinoptilolite.

4.8 Cadmium and Toluene Adsorpion on SMZ in Mixed Solute System

Figures 4.12 and 4.13 compare the results of cadmium and toluene adsorption for single-solute and mixed-solute systems at pH 8, respectively. The results showed that the presence of toluene may have caused a slight reduction in the cadmium adsorption. When compared to the cadmium adsorption in the single-solute system, approximately 10 % reduction in the cadmium adsorption capacity of SMZ was observed in the mixed-solute system. This may be due to the effect of toluene adsorption on the structure of the adsorbed surfactant and metal ligand comprising the organic phase of SMZ. The adsorption or solubilization of toluene into the organic phase of SMZ may cause changes in the structure of the adsorbed surfactant and metal ligand aggregates on the surface of SMZ, leading to the observed decrease in the adsorption of cadmium by SMZ.
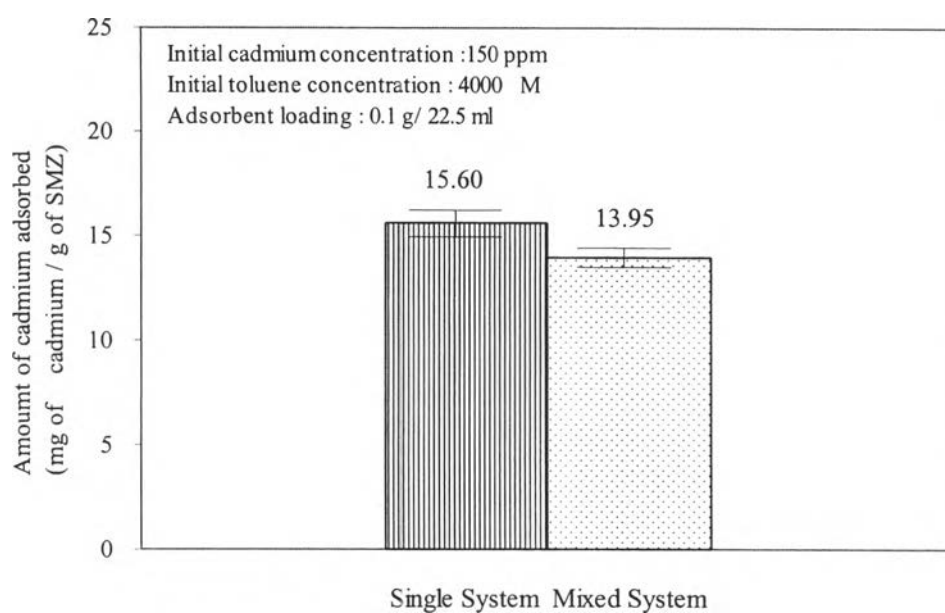
Figure 4.12 Comparison of the amounts of cadmium adsorbed on SMZ in single-solute and mixed-solute systems at pH 8.
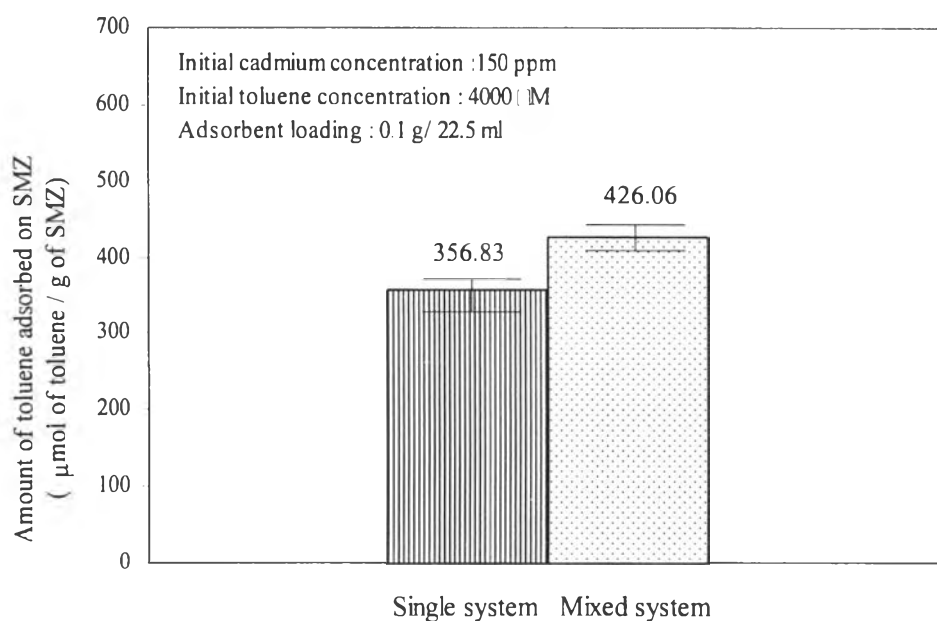

Figure 4.13 Comparison of the amounts of toluene adsorbed on SMZ in single-solute and mixed-solute systems at pH 8.

In contrast, it can be seen from Figure 4.13 that approximately 20 % increase in the adsorbed amount of toluene was observed in the presence of cadmium. This is an interesting result and not easy to explain. It may be due to the interaction between heavy metal complexes on SMZ surface and organic solute. Similar results were previously observed by (Shimizu et.al, 1999) who studied the adsorption of copper and organic dye and reported the increase in the adsorption of dye in the presence of copper ions.

4.9 Regeneration of SMZ

From the adsorption isotherms, it is clearly seen that the adsorption of cadmium by SMZ is pH dependent. Therefore changing pH of the adsorption medium was explored as a means to regenerate used SMZ. As previously discussed, at pH higher than pK_a of palmitic acid (pH>6.46), the carboxyl groups are deprotonated, and thus heavy metal ions can be adsorbed. In contrast, at pH lower than pK_a of palmitic acid (pH<6.46), the carboxyl groups of palmitic acid on SMZ surface are protonated, and thus sorbed metal ions can be released or desorbed. Consequently, pH alteration can be used to study the adsorption and desorption of cadmium by SMZ as shown in Figure 4.14. It can be seen that as much as 80% of the total adsorbed cadmium ions was released from SMZ at low pH (pH 3). The lowest pH studied was fixed at 3 since pH any lower than this may cause the desorption of surfactant aggregates on the surface of SMZ.

For the regeneration of SMZ saturated with toluene, a simple air sparging techniques was used in this preliminary study. After the adsorption of SMZ with toluene for 48 h, SMZ fully adsorbed with toluene was subject to air purging as a means to desorb sorbed toluene on SMZ. The compressed air was slowly purged or bubbled into the adsorption mixture overnight to promote air stripping of the volatile toluene. The comparison of adsorption and desorption of toluene by SMZ using this air-purging technique is shown in Figure 4.15. It can be seen that most of the adsorbed toluene was stripped off by air during the regeneration step. This technique was also used in a similar study by Li and Bowman (2001). The results shown in

this part of the study clearly demonstrated that SMZ saturated with toluene could easily be regenerated by a simple technique such as air sparging.
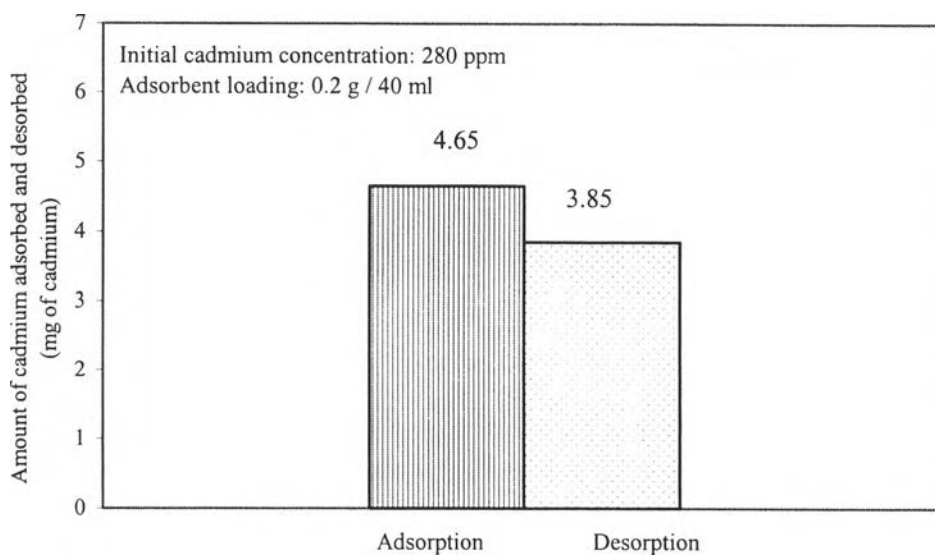

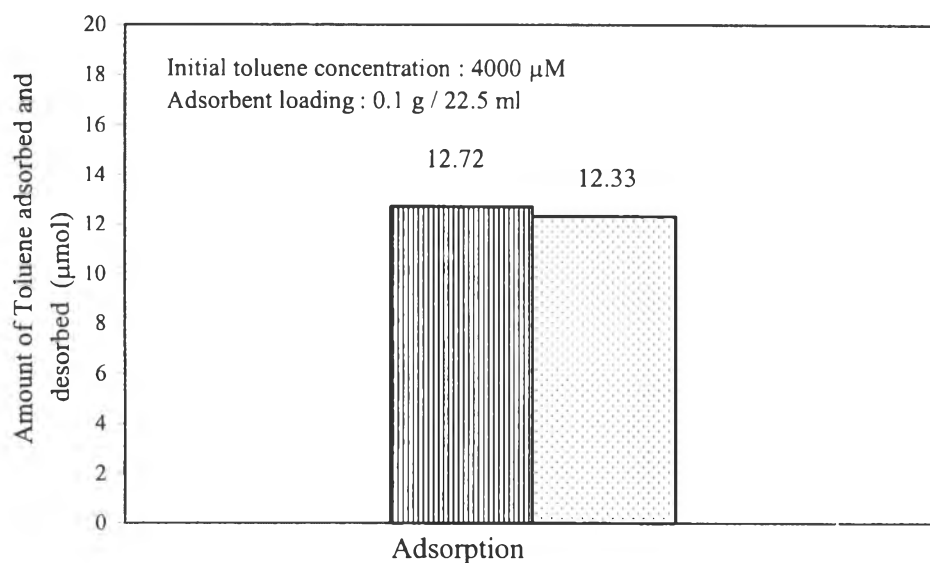**Figure 4.14** Adsorption and desorption of cadmium by SMZ.

Figure 4.15 Adsorption and desorption of toluene by SMZ.