

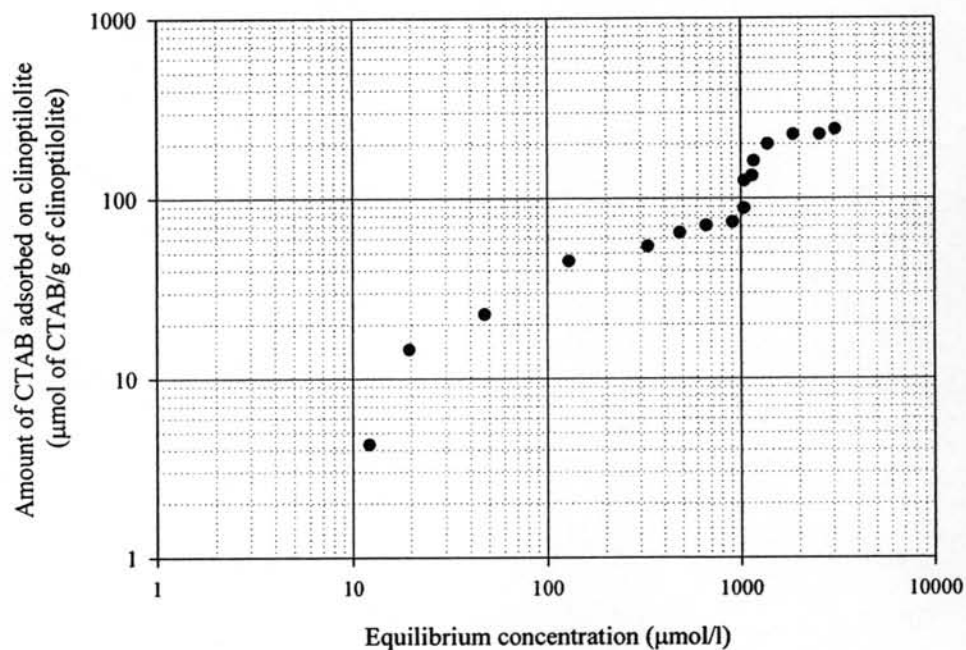
## CHAPTER IV

### RESULTS AND DISCUSSION

#### 4.1 Adsorption of Surfactants on Natural Zeolite

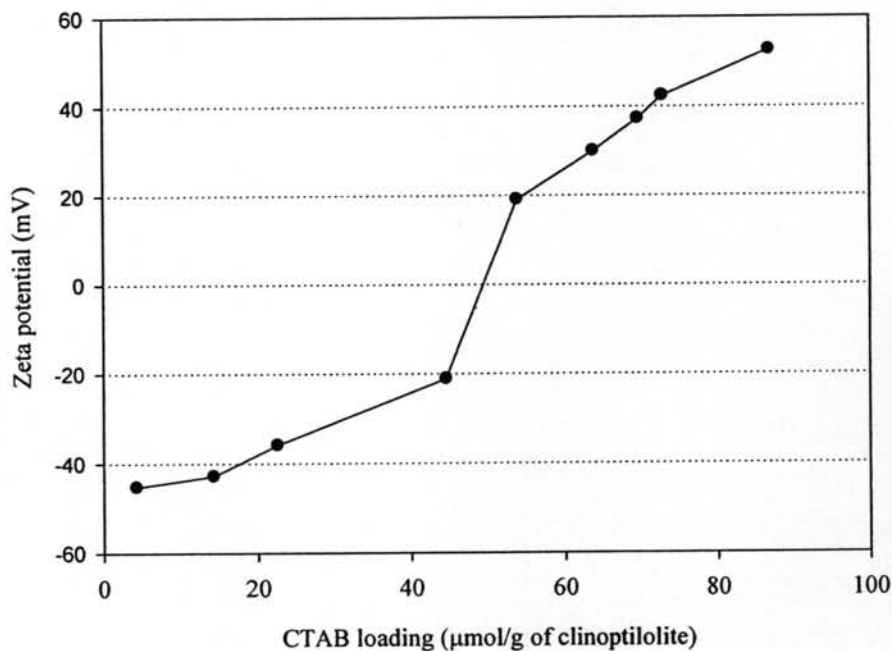
##### 4.1.1 Adsorption of Cetyl Trimethyl Ammonium Bromide (CTAB) on Clinoptilolite

The adsorption isotherm of cetyltrimethylammonium bromide (CTAB) on homoionic clinoptilolite at 30°C is shown in Figure 4.1.



**Figure 4.1** Adsorption isotherm of CTAB on clinoptilolite at 30°C.

The maximum adsorption of CTAB on clinoptilolite is approximately 200  $\mu\text{mol}$  of CTAB/gram of clinoptilolite owing to bilayer adsorption or approximately 2 times of external cationic exchange capacities of clinoptilolite (ECECs = 92  $\mu\text{mol/g}$  of clinoptilolite (Li *et al.*, 1998)). Figure 4.2 shows the plot between zeta potential and amount of CTAB loading on homoionic clinoptilolite.

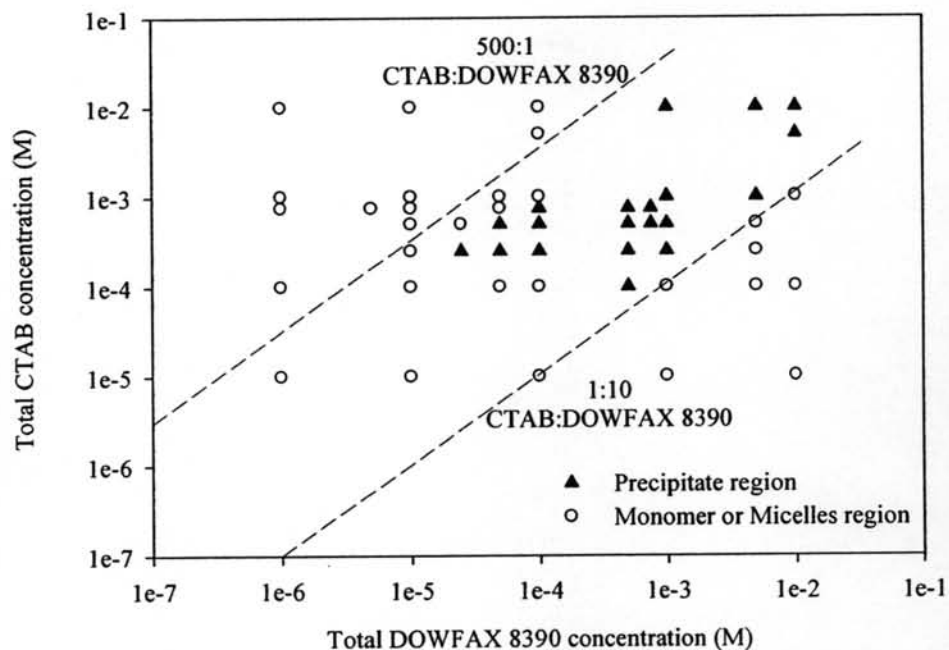


**Figure 4.2** Zeta potential of clinoptilolite as a function of CTAB loading.

The results demonstrate that as the amount of CTAB adsorbed on the surface increases, the charges become less negative and finally become positive due to bilayer adsorption. The point of zero charge which indicates the complete monolayer surface coverage by CTAB is around  $50 \mu\text{mol}$  of CTAB/gram of homoionic clinoptilolite. At this point, the surface is converted from a mixture of cations form to a homoionic state in the Na ion form which improved its exchangeability compared the untreated clinoptilolite. This is in good agreement with the previous study (Termkaew, 2005). The organic carbon content calculated from surfactant coverage of CTAB-modified clinoptilolite is 1.14 wt %.

#### 4.1.2 Adsorption of DOWFAX 8390 on CTAB-Modified Clinoptilolite

The concentration of DOWFAX 8390 used for mixed-bilayer DOWFAX 8390-CTAB-modified zeolite was firstly evaluated in order to prevent precipitation of the cationic and anionic surfactants used in this study (CTAB-DOWFAX 8390). The precipitation study of CTAB and DOWFAX 8390 is shown in Figure 4.3.



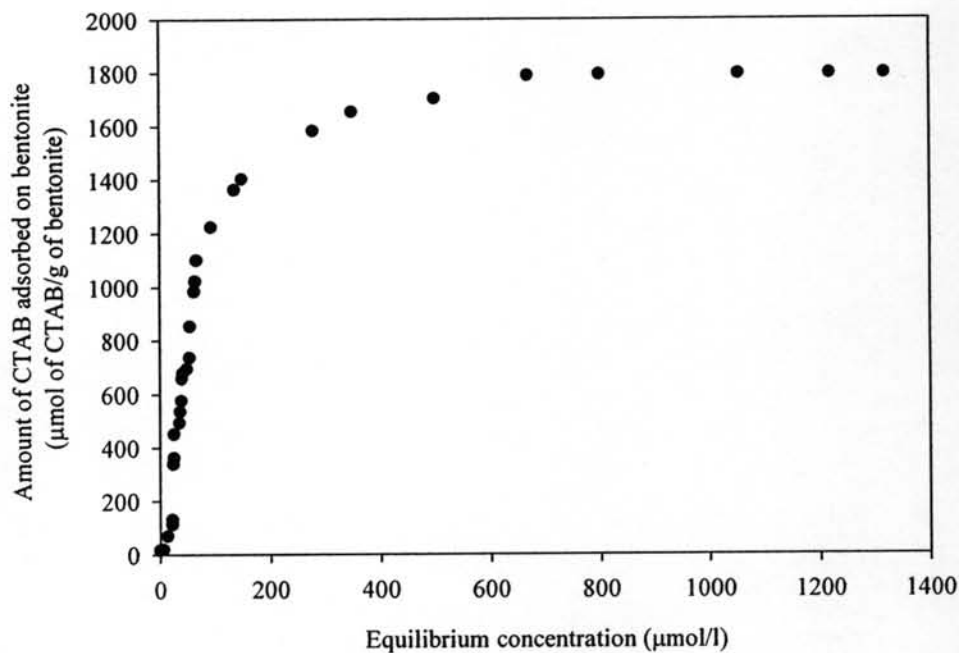
**Figure 4.3** Precipitation study of CTAB and DOWFAX 8390.

According to the precipitation diagram shown in Figure 4.3, the appropriate ratio of CTAB: DOWFAX 8390; 10:1 was chosen in order to avoid precipitation. The adsorption of DOWFAX 8390 on CTAB-modified homoionic clinoptilolite is about 77.325  $\mu\text{mol}$  or 0.154 mmol of DOWFAX 8390/gram of CTAB-modified homoionic clinoptilolite and the zeta potential of mixed-bilayer surfactant is approximately -78.88 mV which confirms the second layer adsorption of DOWFAX 8390 on complete monolayer of CTAB-modified homoionic clinoptilolite. The organic carbon content of SMZ is 3.738 wt %.

## 4.2 Adsorption of Surfactants on Clay Mineral

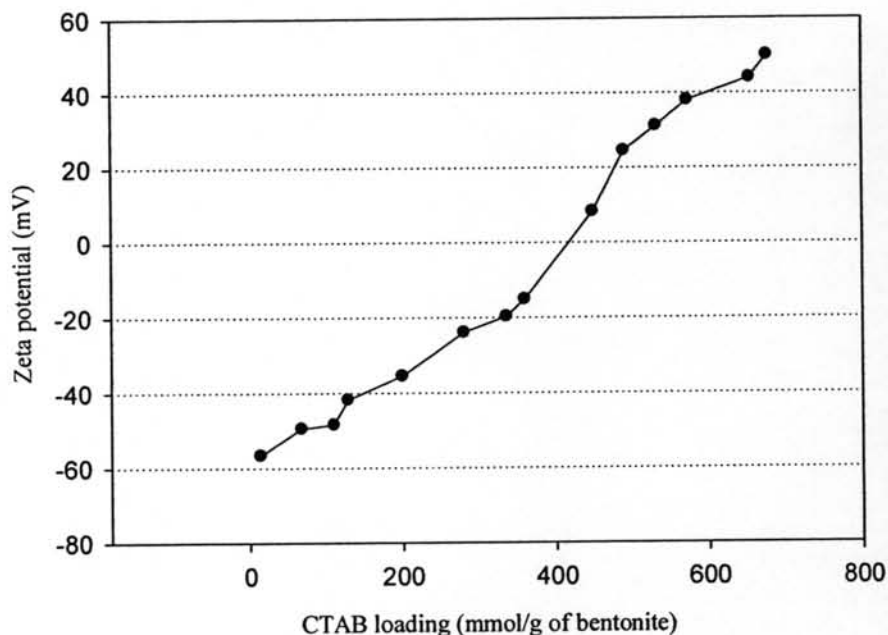
### 4.2.1 Adsorption of Cetyl Trimethyl Ammonium Bromide (CTAB) on Bentonite clay

The adsorption isotherm of cetyltrimethylammonium bromide (CTAB) on bentonite clay at 30°C is shown in Figure 4.4.



**Figure 4.4** Adsorption isotherm of CTAB on bentonite at 30°C.

The maximum adsorption of CTAB on bentonite clay is approximately 1,800  $\mu\text{mol}$  of CTAB/gram of bentonite or about 3.5 times of its cationic exchange capacity (CEC = 50 mmol/ 100gram clay). CTAB was able to adsorb by ion-exchange process and form monolayer coverage onto bentonite surface. The adsorption also went through interlayer spacing and developed an additional layer resulting in the adsorbed amount much higher than the CEC. According to Gitipour *et al.* (1998), the tendency of surfactant adsorption is probably attributed to molecular crowding by the longer chain in the interlamellar space, which tends to increase the uptake of surfactant. This makes increase the basal spacing of the modified bentonite. The point of zero charge which indicates the complete monolayer surface coverage was zero and subsequently continued to increase as more CTAB surfactant adsorbed. Monolayer CTAB coverage is 410  $\mu\text{mol}$ /gram of bentonite or approximately 82% CEC of bentonite. This results in an increase of organic content of the bentonite from 0 to 9.348 wt %. The plot between zeta potential and amount of CTAB loading on bentonite clay is shown in Figure 4.5.



**Figure 4.5** Zeta potential of bentonite as a function of CTAB loading.

#### 4.2.2 Adsorption of DOWFAX 8390 on CTAB-Modified Bentonite

Similar to the DOWFAX 8390 adsorption on CTAB-Modified Zeolite, DOWFAX 8390 concentration must be considered in order to avoid precipitate region. However, for the ratio of CTAB: DOWFAX 8390 more than 1:10, the modified bentonite structure was not stable. The appropriate ratio was consequently selected in the lower range in Figure 4.3 is CTAB: DOWFAX 8390 ratio; 500:1. At this ratio, the amount of DOWFAX 8390 on CTAB-modified bentonite is about 0.407  $\mu\text{mol}$  of DOWFAX 8390/gram of CTAB-modified bentonite and zeta potential is -25.66 mV which verifies the second layer adsorption of DOWFAX 8390 on a monolayer of CTAB-modified bentonite. The organic content of the resulting SMB increases to 9.361 wt %.

#### 4.2.3 FTIR Analysis

The infrared spectra of both the unmodified and modified adsorbents were investigated to identify the functional groups on the surface of SMZ

and SMB. The band assignments of both clinoptilolite and bentonite samples are presented in Tables 4.1 and 4.2, respectively.

**Table 4.1** Fundamental band assignments of homoionic clinoptilolite and SMZ

IR frequencies (cm <sup>-1</sup> )		Band assignments
Clinoptilolite	SMZ	
1066	1066	Si-O (Al) stretching
3635	3630	O-H stretching
-	2853	C-H stretching of aliphatic group
-	2925	Quaternary ammonium salts
-	1209	C-H stretching of phenoxide group

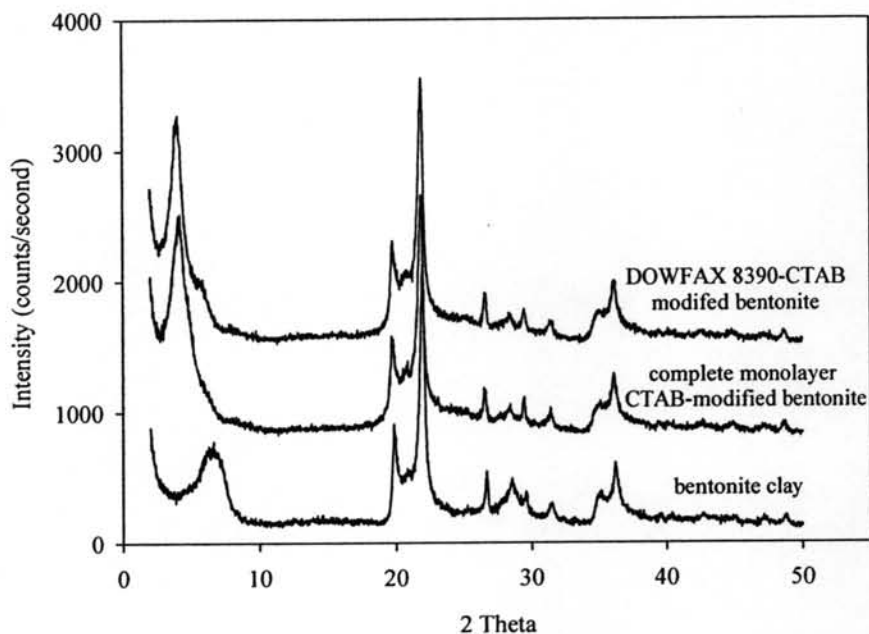
**Table 4.2** Fundamental band assignments of bentonite clay and SMB

IR frequencies (cm <sup>-1</sup> )		Band assignments
Bentonite clay	SMB	
1039	1039	Si-O (Al) bending
3629	3630	O-H stretching
-	2851	C-H stretching of aliphatic group
-	2922	Quaternary ammonium salts
-	1209	C-H stretching of phenoxide group

As shown in Table 4.1 and Table 4.2, the spectra obtained from both SMZ and SMB show similar IR sorption frequencies. The O-H stretching of aluminum hydroxide (1066 cm<sup>-1</sup> and 1039 cm<sup>-1</sup>) can be obviously seen in clinoptilolite samples and bentonite samples correspondingly. After the two-step surface modification, the spectra of quaternary ammonium stretching (2925 cm<sup>-1</sup> and 2922 cm<sup>-1</sup>) and C-H stretching (1929 cm<sup>-1</sup>) of phenoxide group are observable in SMZ and SMB which reflect the presence of the existing of CTAB and DOWFAX 8390 on clinoptilolite and bentonite.

#### 4.2.4 XRD Analysis

After the two-step surface modification, the surfactant-modified bentonite was subjected to XRD analysis and compared with the unmodified bentonite as shown in Figure 4.6.



**Figure 4.6** X-ray diffraction patterns of bentonite clay, complete monolayer CTAB-modified bentonite and DOWFAX 8390-CTAB-modified bentonite.

For bentonite, a smectite clay having expandable interlayer, one could observe the change in the basal spacing of clay particles. When surfactant adsorbed into inter layer of bentonite, the basal spacing was increased from 14.11 Å to 21.22 Å as a result of interlayer interaction bentonite clay with CTAB. This is a clear evidence of the presence of the surfactant molecular in the structure of the bentonite. After being modified with DOWFAX 8390, the basal spacing of the modified bentonite shows a slight increase (to 22.0714 Å), suggesting that DOWFAX 8390 molecule penetrated into the adsorbed CTAB in the interlayer with sulfonate head group oriented towards the solution phase. These results are shown in Table 4.3.

**Table 4.3** X-ray diffraction analysis results for mineral bentonite sample

Sample	Basal spacing (Å)
Mineral bentonite clay	14.11
complete monolayer CTAB-modified bentonite	21.22
DOWFAX 8390-CTAB-modified bentonite.	22.07

### 4.3 Adsorption of Cadmium on Surfactant-Modified Adsorbents (SMADs) in Single-Solute System

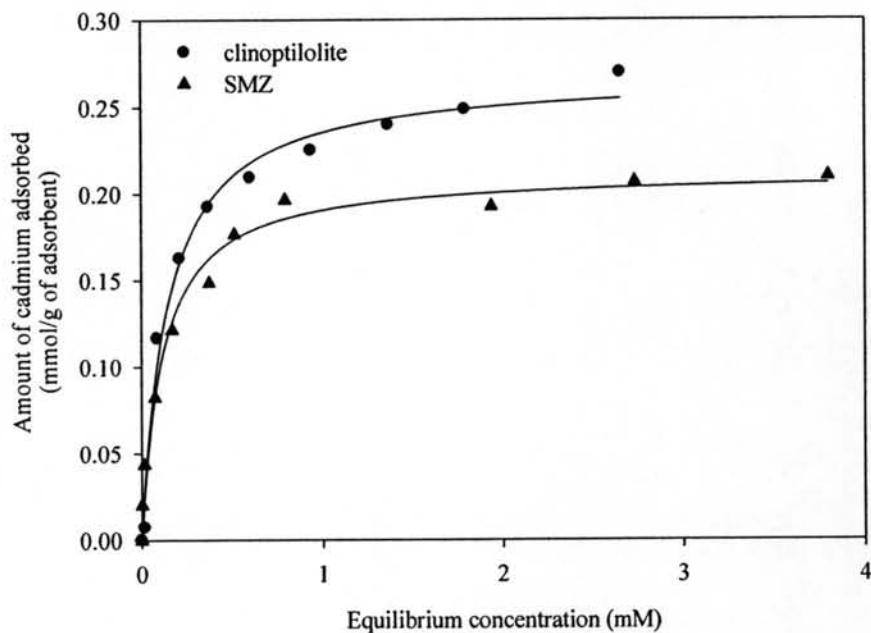
#### 4.3.1 Homoionic Clinoptilolite and Surfactant-Modified Zeolite (SMZ)

Adsorption isotherms of cadmium onto homoionic clinoptilolite and SMZ are shown in Figure 4.7. The results showed that the adsorption of cadmium in homoionic clinoptilolite is slightly higher than SMZ. The adsorption isotherms of cadmium can be fitted with a Langmuir adsorption model as shown below.

$$q = \frac{Q_{\max} \cdot C_e}{K + C_e} \quad (1)$$

Where  $q$  is the amount of metal adsorbed on adsorbent (mmol/g),  $C_e$  is an equilibrium concentration (mM),  $Q_{\max}$  is the maximum capacity of the adsorbent (mmol/g) and  $K$  is the affinity constant (mM). The Langmuir isotherm is based on a monolayer sorption on a surface containing a finite number of binding sites. All cadmium adsorption data were fitted to Langmuir model by a nonlinear regression analysis. The adsorptions parameters were determined as shown in Table 4.4.





**Figure 4.7** Adsorption isotherms of cadmium onto homoionic clinoptilolite and SMZ.

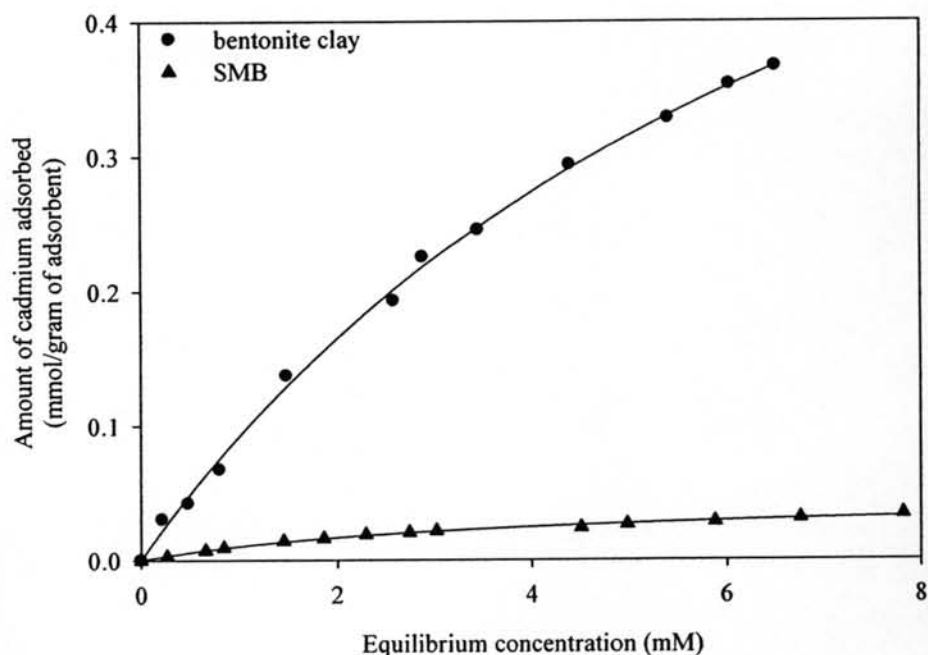
**Table 4.4** The Langmuir parameters for the adsorption of cadmium on homoionic clinoptilolite and SMZ

Adsorbents	Langmuir parameters		
	Q <sub>max</sub> (mmol/g)	K (mM)	R <sup>2</sup>
Homoionic clinoptilolite	0.2681	0.1397	0.99
SMZ	0.2119	0.1128	0.98

The parameters reveal a slightly lower affinity constant of SMZ than that of homoionic clinoptilolite. This indicates the literally lower cadmium adsorption of SMZ than homoionic clinoptilolite which may result from the different sites for metal adsorption. Cadmium can be adsorbed onto both internal and external site of homoionic clinoptilolite by means of ion-exchange process whereas SMZ can adsorb metal using head groups of DOWFAX 8390 exposing to the solution. However, the metal adsorption capability of SMZ is fairly comparable to homoionic clinoptilolite.

#### 4.3.2 Bentonite clay and Surfactant-modified Bentonite (SMB)

The adsorption isotherms of cadmium onto bentonite and SMB at pH 5 and 25 °C are illustrated in Figure 4.8.



**Figure 4.8** Adsorption isotherms of cadmium onto bentonite clay and SMB.

As can be seen from Figure 4.18, the adsorption of cadmium significantly decreased after surfactant modification. The equation parameters of the Langmuir model were calculated by curve-fitting and shown in Table 4.5.

**Table 4.5** The Langmuir parameters for the adsorption of cadmium on bentonite clay and SMB

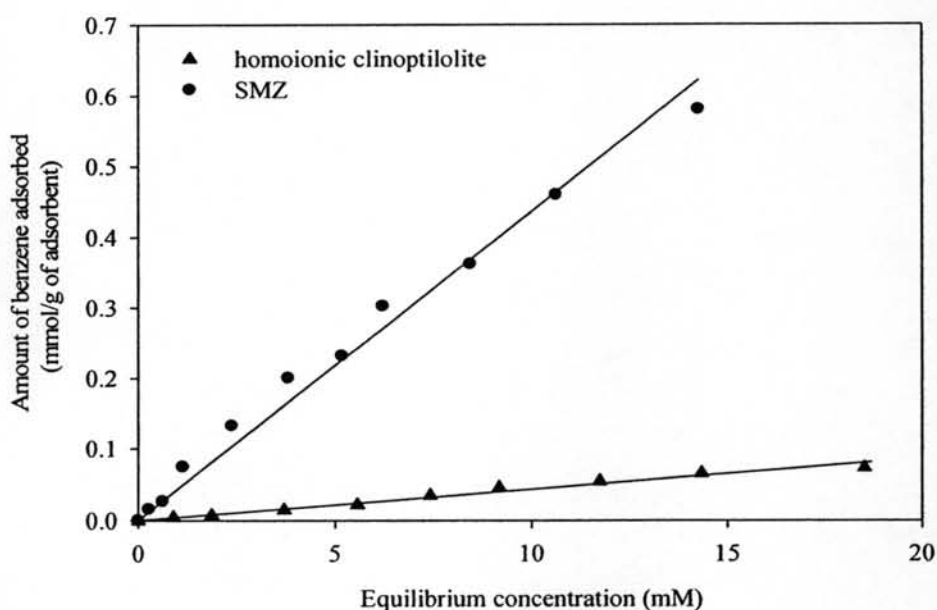
Adsorbents	Langmuir parameters		
	Q <sub>max</sub> (mmol/g)	K (mM)	R <sup>2</sup>
Bentonite clay	0.8026	7.7406	0.99
SMB	0.0464	3.5511	0.99

It can be seen that the affinity constant of SMB is smaller than that of bentonite clay. The reason for this may come from the stronger adsorption of HDTMA onto bentonite than  $\text{Na}^+$  ion (Sheng *et al.*, 1999). Consequently, ion-exchangeable sites are no longer available for cadmium adsorption. In addition, because of the limited adsorption of DOWFAX 8390 onto SMB as mentioned in the previous part, DOWFAX 8390 can only adsorb onto monolayer CTAB-modified bentonite 0.407  $\mu\text{mol}$  of DOWFAX 8390/gram of CTAB-modified bentonite. Furthermore, DOWFAX 8390 structure could fold into inter-lamellar region hiding its head group. This made cadmium poorly sorbed on SMB.

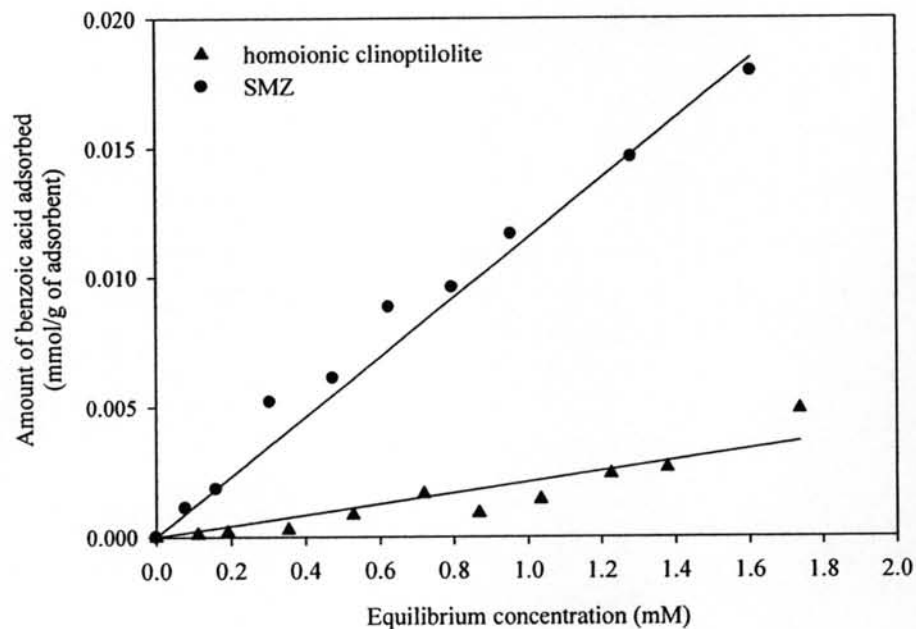
#### 4.4 Adsorption of Organic Compounds on Surfactant-Modified Adsorbents (SMADs) in Single-Solute System

##### 4.4.1 Homoionic Clinoptilolite and Surfactant-Modified Zeolite (SMZ)

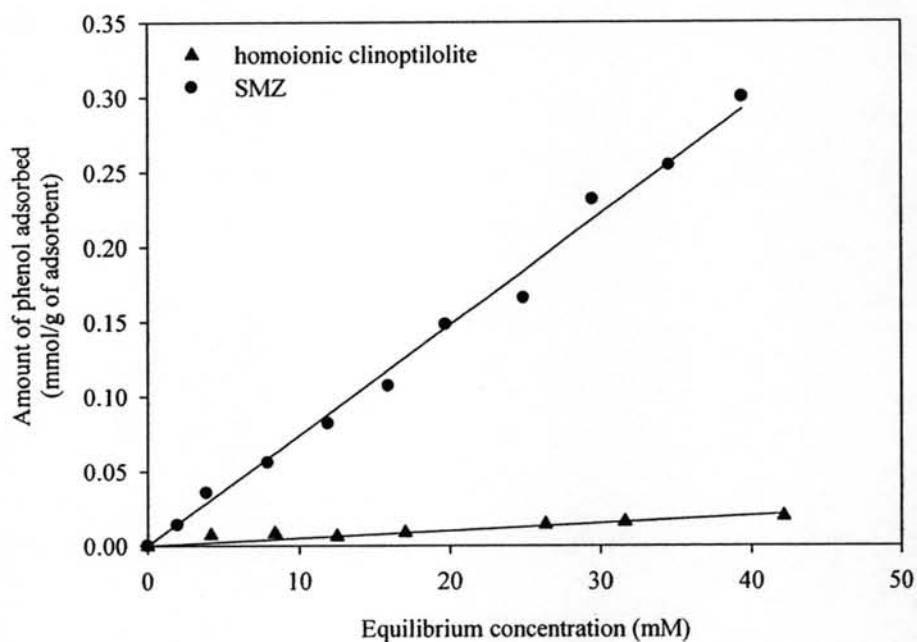
Adsorption of benzene, benzoic acid, phenol, chlorobenzene and naphthalene onto homoionic clinoptilolite and SMZ at pH 7 and 25 °C were investigated and the adsorption isotherms are shown in Figures 4.9-4.13.



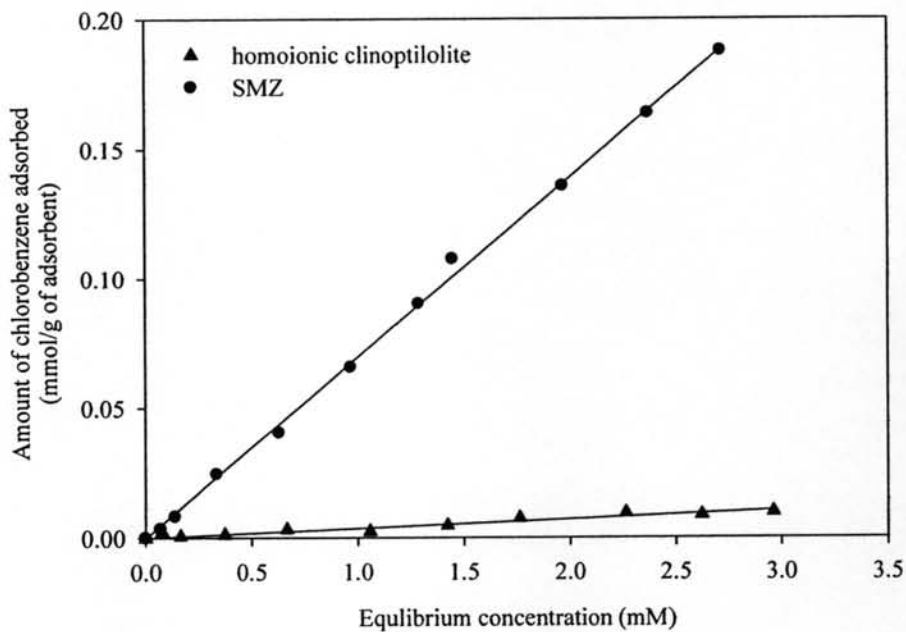
**Figure 4.9** Adsorption isotherms of benzene onto homoionic clinoptilolite and SMZ.



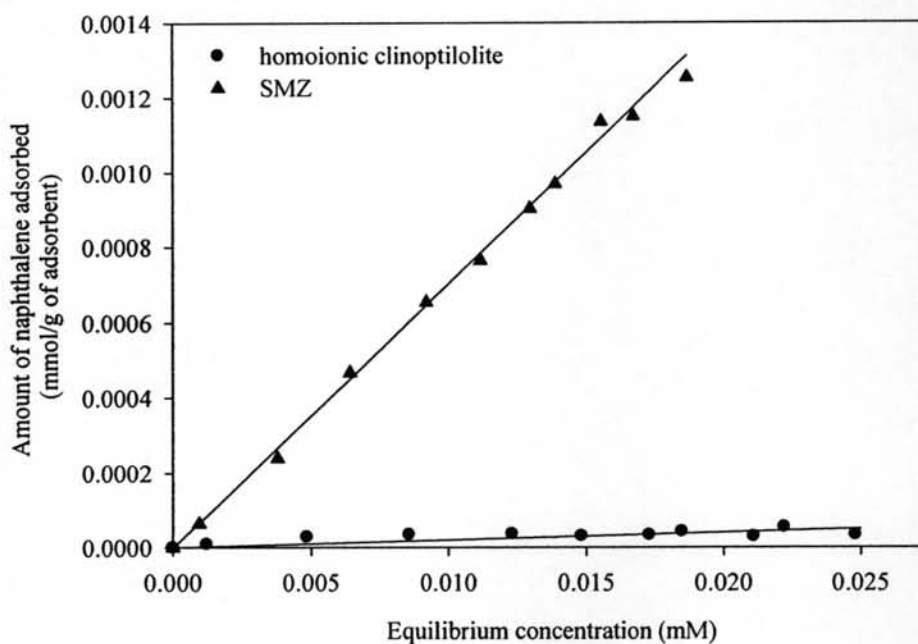
**Figure 4.10** Adsorption isotherms of benzoic acid onto homoionic clinoptilolite and SMZ.



**Figure 4.11** Adsorption isotherms of phenol onto homoionic clinoptilolite and SMZ.



**Figure 4.12** Adsorption isotherms of chlorobenzene onto homoionic clinoptilolite and SMZ.



**Figure 4.13** Adsorption isotherms of naphthalene onto homoionic clinoptilolite and SMZ.

In order to examine the sorption characteristics of benzene derivative compounds with different functional groups. Different concentration ranges of organic compounds were used according to their aqueous solubility and the detection range. General observation can be made from the figures that after modification, sorption ability of the SMZ increased significantly as compared to unmodified clinoptilolite (more than 3.5 times). The adsorption isotherms can be described by sorption model. The well-known sorption models of organic adsorption are

#### 1. Linear Isotherm

This isotherm presents linear sorption isotherm which can be described by

$$q = K_p \cdot C_e \quad (2)$$

Where  $q$  is the amount of solute adsorbed (mmol/gram of adsorbent),  $C_e$  is the concentration of solute in the solution at equilibrium (mM) and  $K_p$  is a constant related to the extent of sorption ( $\text{dm}^3/\text{g}$  of adsorbent). A basic assumption of the Langmuir theory is that sorption takes place at specific homogeneous sites on the surface of the sorbent. It is then assumed that once a sorbate molecule occupies a site, no further sorption can take place at that site. The rate of sorption to the surface should be proportional to a driving force and area. The driving force is the concentration in the solution, and the area is the amount of bare surface.

#### 2. Freundlich isotherm

Freundlich isotherm can be used to explain a nonlinear adsorption isotherm, the equation is offered by

$$q = K_F \cdot C_e^{\frac{1}{n}} \quad (3)$$

Where  $q$  is the amount of solute adsorbed (mmol/gram of adsorbent),  $C_e$  is the concentration of solute in the solution at equilibrium (mM),  $K_F$  is a constant related to the extent of sorption and  $N$  is a constant related to the intensity of sorption or the degree of dependence of sorption on concentration. Freundlich development was based on the assumption that the adsorbent had a heterogeneous surface

composed of different classes of adsorption sites, with adsorption on each class of sites following the Langmuir isotherm. Freundlich demonstrated that the ratio of the amount of solute adsorbed onto a given mass of an adsorbent to the concentration of the solute in the solution was not constant at different solution concentrations.

From Figures 4.9-4.13, the adsorption isotherms of benzene, benzoic acid, phenol, chlorobenzene and naphthalene exhibit linear characteristic suggesting a partitioning mechanism into SMZ organic phase. The linear isotherm was used to fit with the experimental data and the adsorption coefficient ( $K_P$ ) could be determined as shown in Table 4.6.

**Table 4.6** Parameters for adsorption isotherms of organic compounds onto homoionic clinoptilolite and SMZ

Organic compounds	Homoionic clinoptilolite		SMZ	
	Equation parameter $K_P$ (dm <sup>3</sup> /g)	$R^2$	Equation parameter $K_P$ (dm <sup>3</sup> /g)	$R^2$
Benzene	0.0046	0.98	0.0445	0.99
Benzoic acid	0.0021	0.93	0.0115	0.97
Phenol	0.0005	0.91	0.0074	0.99
Chlorobenzene	0.0035	0.99	0.0694	0.99
Naphthalene	0.0020	0.96	0.0702	0.99

From the regression equations of the adsorption isotherms of different organics. The adsorption parameters can be compared in term of partitioning constant ( $K_P$ ) of organic solute into the mixed bilayer of surfactants on zeolite surface. A greater value of  $K_P$  indicates a higher capacity for adsorption. Thus, the sorption amount of naphthalene is the largest and that of phenol is the least. The sorption magnitude appears to be inversely related to the aqueous solubility of the organic compounds as follows: naphthalene < chlorobenzene < benzene < benzoic acid < phenol (3,205, 390.7, 1,755, 3,390 and 80,190 mg/l, respectively). This is

reasonable as the organic sorption can also be viewed as solubilization into the surfactant-modified surface.

It can be obviously seen that the adsorption of organic compounds onto SMZ demonstrated superior capability than homoionic clinoptilolite. Due to the inorganic nature of homoionic clinoptilolite, it can uptake much less amount of organic compounds. After the surfactant modification, the adsorbent surface turned into organic form, and thus, provided better organic adsorption following the "like dissolves like" theory.

According to benzoic acid sorption in Figure 4.8, the benzoic acid adsorption isotherm is demonstrated a lower adsorbed amount as compared with other organics except phenol. This is due to its chemical nature and the pH value of solution as benzoic acid can exist as aromatic anion in aqueous phase. The pKa of benzoic acid is 4.2 so, ionic species are predominant at controlled pH 7 as a free ion or an ion pair in the solution. The less benzoic acid adsorption can be attributed to the repulsion of anionic benzoate from the negatively charged head groups of the DOWFAX 8390 layer system (Li *et al.*, 2000).

For chlorobenzene adsorption, the addition of chlorine to the benzene structure could reduce its energy of interaction with water (decrease water solubility), thereby allowing a more significant hydrophobic interaction with such surface. In the case of naphthalene, the larger the aromatic rings of the adsorbates, the less hydrophilic which was repelled from solution into surfactant core region. This made naphthalene can be the best adsorbate to SMZ.

#### 4.4.2 Bentonite clay and Surfactant-modified Bentonite (SMB)

In organic adsorption part: benzene, benzoic acid, phenol, chlorobenzene and naphthalene, the experiments were conducted at pH 7 and 25 °C in order to compare the different in functional groups of benzene and substrates. Adsorption isotherms are shown in Figures 4.14-4.18.



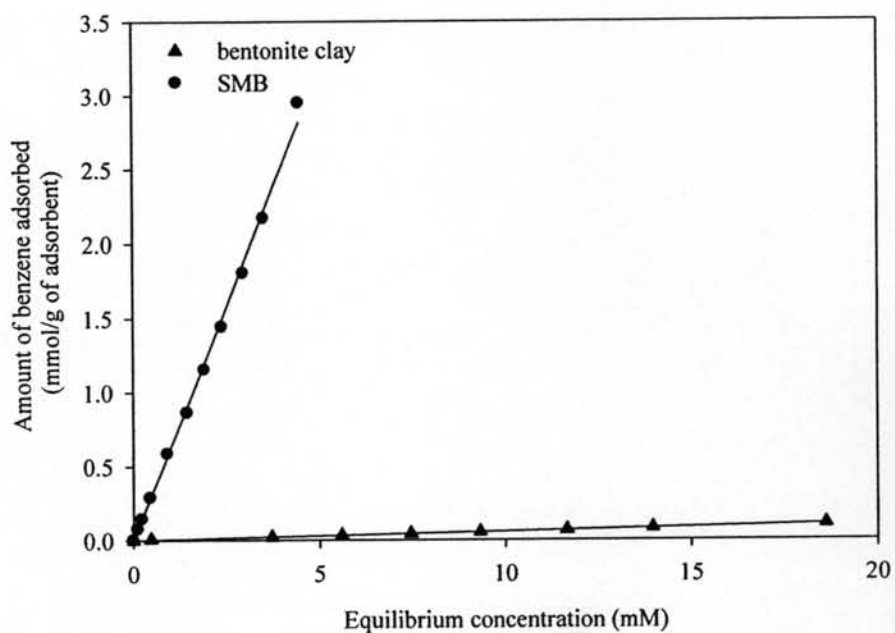


Figure 4.14 Adsorption isotherms of benzene onto bentonite clay and SMB.

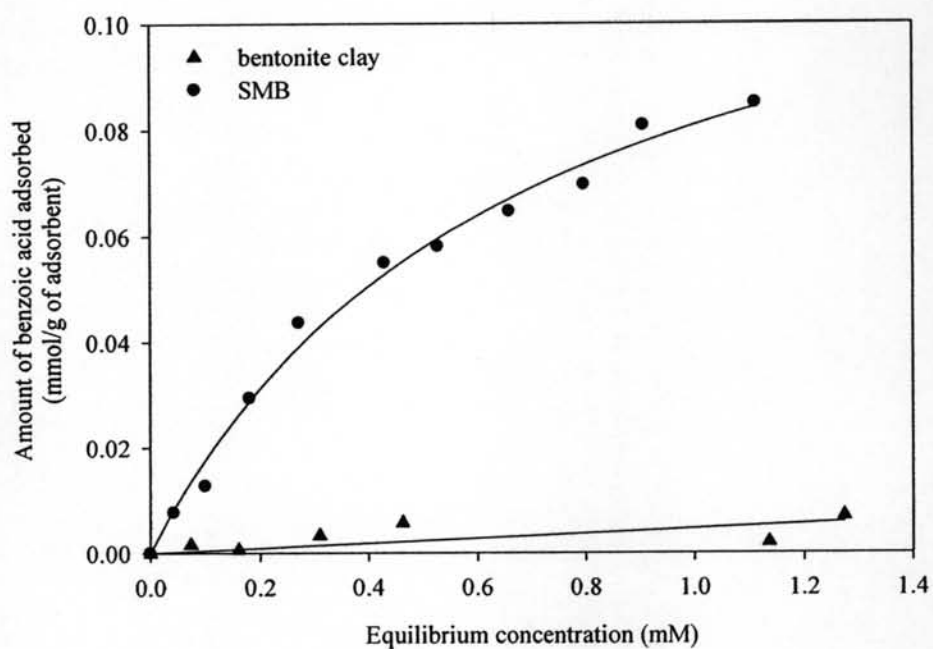


Figure 4.15 Adsorption isotherms of benzoic acid onto bentonite clay and SMB.

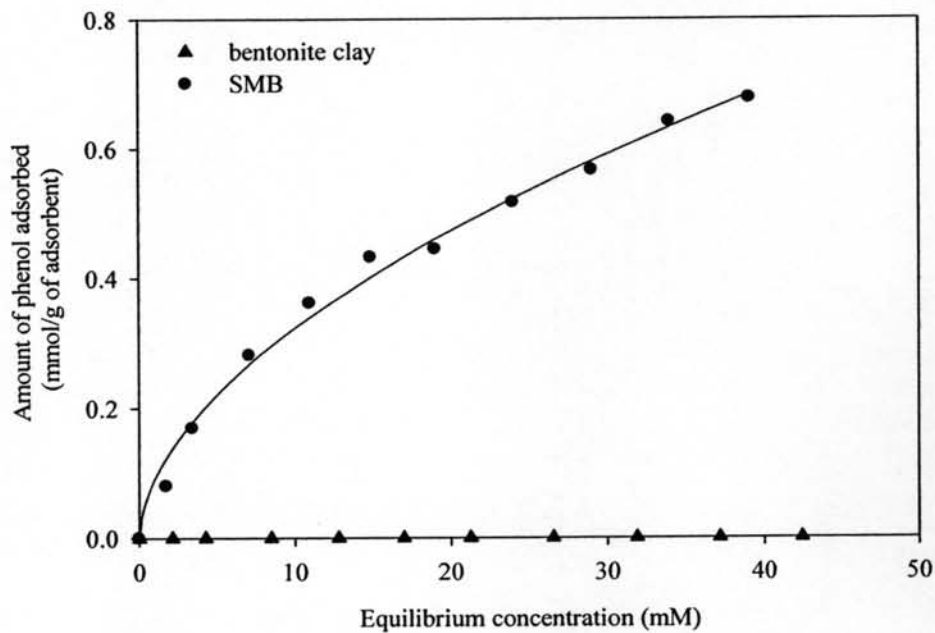


Figure 4.16 Adsorption isotherms of phenol onto bentonite clay and SMB.

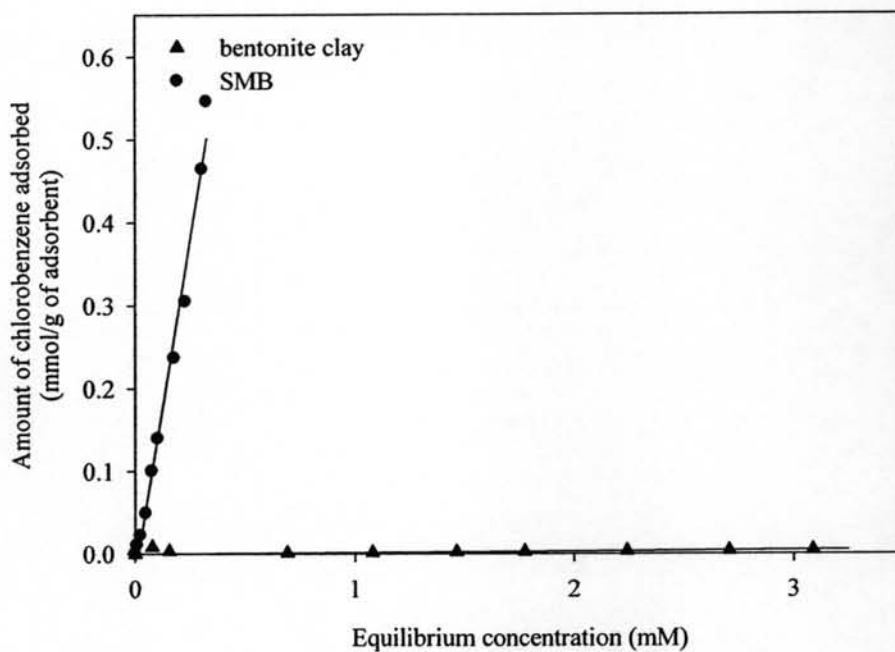
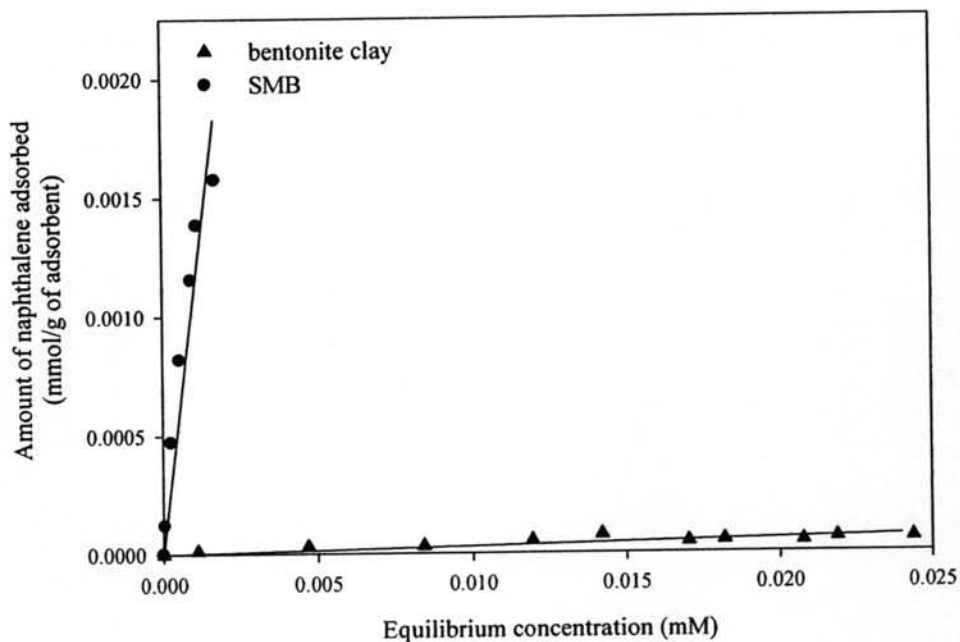


Figure 4.17 Adsorption isotherms of chlorobenzene onto bentonite clay and SMB.



**Figure 4.18** Adsorption isotherms of naphthalene onto bentonite clay and SMB.

From Figures 4.14-4.18, SMB showed superior adsorption of organic compounds than bentonite clay (over 13 times). All sorption isotherms were fitted to the sorption model and the parameters are shown in Table 4.7.

**Table 4.7** Parameters for adsorption isotherms of organic compounds onto bentonite and SMB

Organic compounds	bentonite		SMB	
	Equation parameter $K_p$ (dm <sup>3</sup> /g)	$R^2$	Equation parameter	$R^2$
Benzene	0.0056	0.99	$K_p=0.6284$	0.99
Benzoic acid	0.0218	0.97	$K_F=0.0851, n=1.8162$	0.98
Phenol	0.000004	0.95	$K_F=0.0907, n=1.6472$	0.99
Chlorobenzene	0.0015	0.99	$K_p=1.3649$	0.98
Naphthalene	0.0029	0.98	$K_p= 1.0765$	0.91

Adsorption of organic compounds onto bentonite clay demonstrates much poorer uptake than SMB. The extent of the organic sorption onto bentonite clay can be consequently compared from the maximum to the minimum, benzene, benzoic acid, naphthalene, chlorobenzene and phenol, correspondingly. Adsorption of organic compounds on clay particles can occur via physical adsorption, chemical adsorption, hydrogen bonding and/or coordination complexes. One or two may take place at the same time, depending on the nature of the organic functional group and the acidity of the system (Mortland, 1970). A lack of interaction between bentonite and aromatic compounds, which is also, supported by the results of the sorption isotherm tests.

It can be seen that the adsorption of benzene, chlorobenzene and naphthalene by SMB could be well fitted to a linear isotherm where as the adsorption of benzoic acid and phenol exhibit non-linear isotherm and can be fitted with Freundlich model. For Linear isotherm, the sorption amount of chlorobenzene is the largest followed by naphthalene and benzene, respectively.  $K_p$  values of linear isotherm remain constant as the mole fraction of the solubilize increase which indicates the solute partitions to both the core and the palisade.

For both sorption of phenol and benzoic acid can be satisfactorily described by an equation consisting of Freundlich equations. Freundlich fitting with  $n > 1$  would indicate conformity of the data to multilayer formation at the adsorbent surfaces. As the partition coefficients decrease as the mole fraction of the solubilize increases, the solute partitions primarily to the palisade region. This observation could also be attributed to adsorption/partition model associated with the interfacial behavior of organic compounds in the system organobentonite/water, and is related to the organic matter and mineral surface, respectively, of the medium. Mechanisms of sorption of phenol and benzoic acid onto SMB could be explained by Zhu *et al.* (2000) as well as the dual mode mechanism which was developed by Rawajfih and Nsour (2005). Because phenol and benzoic acid is ionic organic compound, surface adsorption may occur from coordination/ion-dipole reactions with clay surface and partition contribution is governed by the organic matter content. Accordingly, the

total sorption amount (mmol/gram of adsorbent) ( $Q_T$ ) for ionic organic compounds on SMB can be expressed as follow,

$$Q_T = Q_A + Q_P \quad (4)$$

Where  $Q_A$  is the sorption amount contributed by adsorption and  $Q_P$  is the sorption amount contributed by partition. In a mixed adsorption-partition system, the sorption at low concentration demonstrated adsorption mechanism whereas the sorption at high concentration verified partition mechanism. From this point of view, it is expected that adsorption isotherm at high concentration should approach linearity. As a result, the adsorption model for a linear equation is

$$Q_T = M \cdot C_e + N \quad (5)$$

Where  $M$  and  $N$  are constants.  $MC_e$  is the sorption contribution by partition at with  $M$  being the partition coefficient ( $K_p$ ) and  $N$  is the saturated adsorption capacity (mmol/g) estimated from the high concentration data. Therefore, the adsorption data at high concentration for benzoic acid and phenol were fitted with equation (5) in order to compare partition coefficient with other organics and investigate mechanism as presented in Table 4.8.

**Table 4.8** Linear regression data at high concentrations and partition coefficient ( $K_p$ ) for the sorption of phenol and benzoic acid on SMB

Organic compound	Regression equation at high concentration	$R^2$	Saturated capacity of adsorption (mmol/g)	$K_p$ ( $\text{dm}^3/\text{g}$ )
Benzoic acid	$Q_T=0.0546C_e+0.0271$	0.95	0.0271	0.0546
Phenol	$Q_T=0.0112C_e+0.2463$	0.99	0.2463	0.0112

From Table 4.8, it can be seen that phenol has higher saturated capacity of adsorption than that of benzoic acid (0.2463 and 0.0271 mmol/g) but has lower partition coefficient than benzoic acid (0.0112 and 0.0546 dm<sup>3</sup>/g).

As can be compared from the  $K_p$  value, the sorption magnitude of organic compound is chlorobenzene > naphthalene > benzene > phenol > benzoic acid which is not only related to solubility. There are two more factors involved in sorption of organic compounds in SMB. Since SMB sorption sites are interlamellar space where adsorbent-adsorbate interaction takes place. Molecular configuration may effects the organics uptake. The bigger kinetic diameter, naphthalene > benzoic acid > chlorobenzene > phenol > benzene (7.40, 7.02, 6.96, 6.09 and 5.85 Å respectively), the more difficult to enter the channel-like interlamellar region. In addition, the influence of functional groups can be interpreted on the basis of steric effect. The organics polarity identifies co-adsorption with quaternary ammonium ion at palisade region via dipole-dipole interaction. As can be explained in benzoic acid and phenol sorption, adsorption occurs related to polarity with dipole moment increasing, chlorobenzene > phenol > benzoic acid > naphthalene, benzene (1.69, 1.45, 1 and 0 respectively). Surfactant orientation also contributed the dominant co-adsorption site followed Jaynes and Boyd (1991). The results of HDTMA complexes with smectites yielded 2.0-2.3 nm basal spacing that are consistent with either pseudotrimolecular layer or interstratified mixtures of bilayer and paraffin complexes. Similar to SMB, basal spacing is approximately 2.2 nm. This made little more saturated capacity of phenol adsorption over benzoic acid adsorption and came into conclusion that chlorobenzene make obvious the best favorable adsorption behavior.

The adsorption of organic compounds may be attributed to the presence of a long alkyl chain of the tailoring agent used to modify the bentonite. According to Cadena (1989), the uptake of benzene by SMB such tendency is probably attributed to molecular crowding by the longer chains in the interlamellar spaces, which tends to reduce the space available for adsorption of benzene molecules, attenuating the removal by bentonite.

For organic adsorption capability of SMADs,  $K_p$  can be normalized by the sorbent's organic carbon content for comparison purposes and is defined as

$$K_{oc} = \frac{K_p}{f_{oc}} \quad (6)$$

Where  $K_{oc}$  is the organic carbon normalized coefficient and  $f_{oc}$  is fractional organic carbon content of the sorbent. For SMZ and SMB, organic carbon contents calculated from CTAB and DOWFAX 8390 amount adsorbed on each adsorbent are 3.738 and 9.361 wt%, respectively. The organic carbon normalized coefficients of organic compounds are demonstrated in Table 4.9.

**Table 4.9** Normalized partition coefficients for the sorption of organic compounds on SMZ and SMB

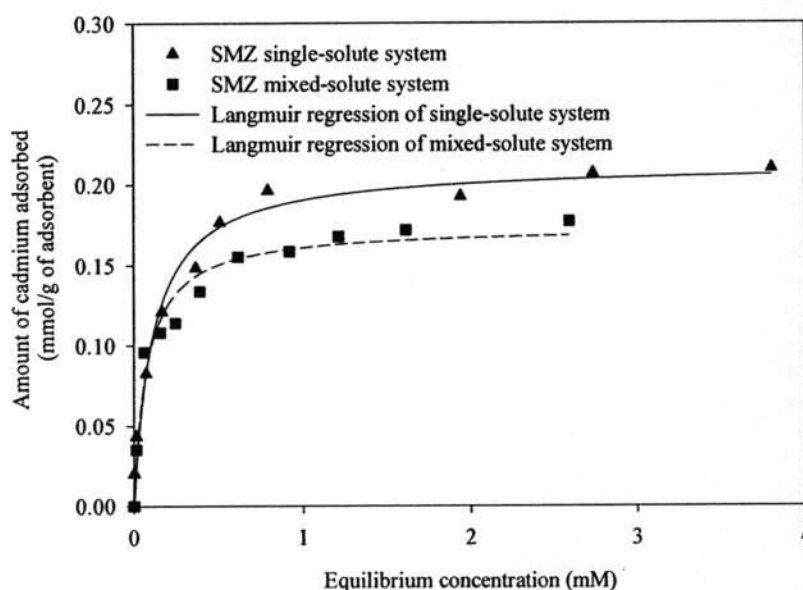
Organic compound	$K_{oc}$	
	SMZ	SMB
Benzene	1.1905	6.7129
Benzoic acid	0.3076	0.9742
Phenol	0.1980	0.1976
Chlorobenzene	1.8560	14.5807
Naphthalene	1.8780	11.4998

As shown in the table, once normalized, SMB demonstrates higher  $K_{oc}$  than SMZ for all organic compounds except phenol. It can be attributed to the difference in structure of the two adsorbents. Since SMB layers could be expandable, it can ease organic compounds to solubilize into the adsorbed organic region whereas the structure of SMZ is rather rigid. It is obviously concluded that SMB has higher organic adsorption capacity for organic adsorption than SMZ.

#### 4.5 Adsorption of Cadmium and Organic Compound (benzene) on Surfactant-Modified Adsorbent (SMADs) in Mixed-Solute System

#### 4.5.1 Surfactant-Modified Zeolite (SMZ)

To investigate the competitive sorption of heavy metal and organic contaminant in the mixed-solute systems, the adsorption experiments were conducted at pH 5 and 25 °C using cadmium and benzene. The adsorption isotherms are shown in Figures 4.19 and 4.20. A little lower adsorption of both cadmium and benzene can be observed in the mixed-solute systems when compared to the single-solute system. The adsorption parameters were calculated and shown in Tables 4.10 and 4.11 for benzene and cadmium, respectively.

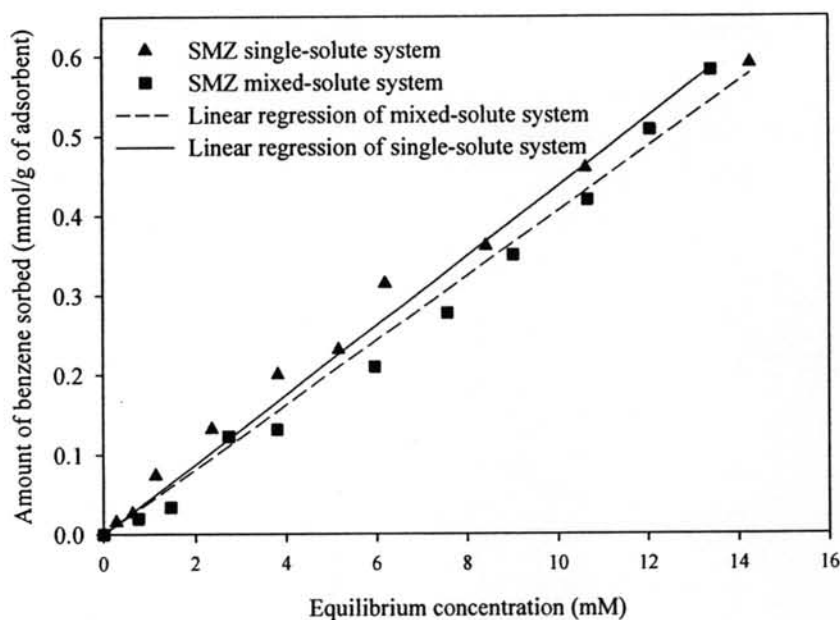


**Figure 4.19** Adsorption isotherms of cadmium onto SMZ in single-solute and mixed-solute systems.

**Table 4.10** The Langmuir parameters for the adsorption of cadmium on SMZ in single-solute and mixed solute systems

Adsorbents	Langmuir parameters		
	Q <sub>max</sub> (mmol/g)	K (mM)	R <sup>2</sup>
SMZ single-solute system	0.2119	0.1128	0.98
SMZ mixed-solute system	0.1734	0.0778	0.97





**Figure 4.20** Adsorption isotherms of benzene onto SMZ in single-solute and mixed-solute systems.

**Table 4.11** The parameters for the adsorption of benzene on SMZ in single-solute and mixed-solute systems

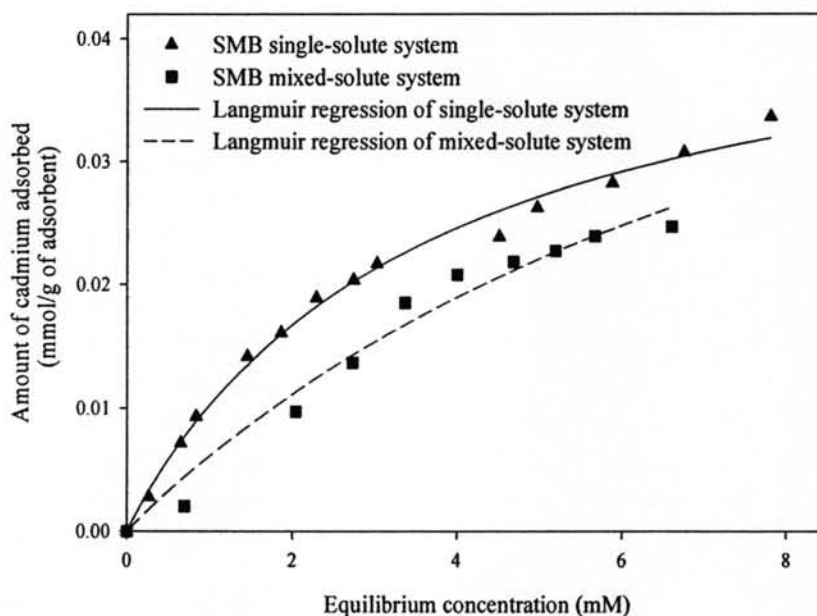
Adsorbents	Langmuir parameters	
	$K_P$ ( $\text{dm}^3/\text{g}$ )	$R^2$
SMZ single-solute system	0.0445	0.99
SMZ mixed-solute system	0.0405	0.987

The affinity constant of benzene in the mixed-solute system is slightly lower than that of the single-solute system which has also been observed by Vacamier *et al.* (2001) where they reported 3-5% decrease in the adsorption of cadmium and lead by clinoptilolite in the presence of phenol. This results from different sorption sites of SMZ; core region (hydrophobic) for organic solute and head region (hydrophilic) for metal ions. Cadmium can be adsorbed by sulfonate group at outer surface by means of ion exchange process. As a result, cadmium could shield the partition site of benzene, leading to a lower sorption site of benzene. On the other

hand, the cadmium adsorption in the mixed solute-system also shows a slight decrease when compared with the single-solute system. The possible reason is that not only the cadmium uptake on the SMZ was hindered by the presence of benzene in solution, but also the adsolubilized benzene in DOWFAX 8390 may block the cadmium sorption site.

#### 4.5.2 Surfactant-Modified Bentonite (SMB)

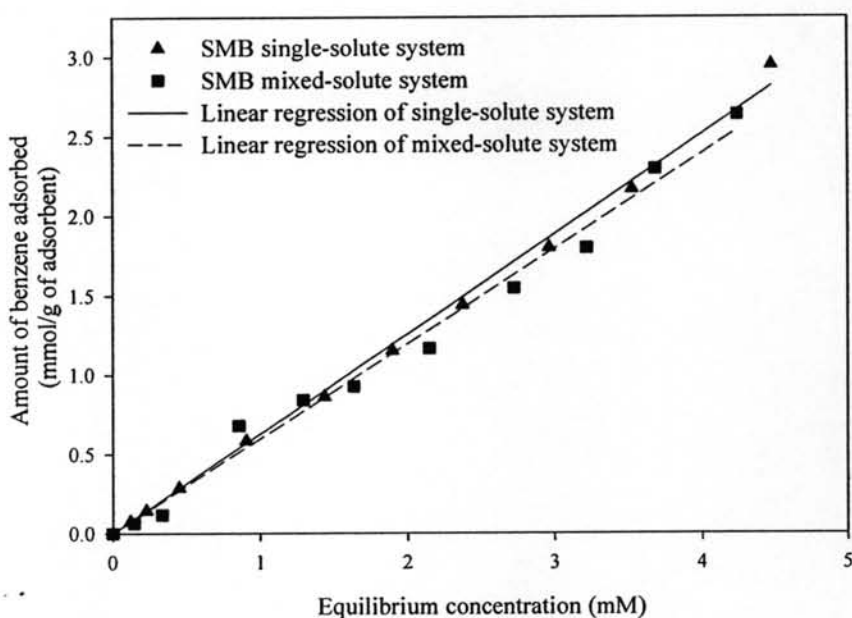
Similar to SMZ, the adsorption experiments in the mixed-solute systems were conducted with SMB at pH 5 and 25 °C. The adsorption isotherms are shown in Figures 4.21 and 4.22 and the adsorption parameters are presented in Tables 4.12 and 4.13 for cadmium and benzene, respectively.



**Figure 4.21** Adsorption isotherms of cadmium onto SMB in single-solute and mixed-solute systems.

**Table 4.12** The Langmuir parameters for the adsorption of cadmium on SMB in single-solute and mixed solute systems

Adsorbents	Langmuir parameters		
	Q <sub>max</sub> (mmol/g)	K (mM)	R <sup>2</sup>
SMB single-solute system	0.0464	3.5511	0.99
SMB mixed-solute system	0.0443	2.5567	0.97



**Figure 4.22** Adsorption isotherms of benzene onto SMB in single-solute and mixed-solute systems.

**Table 4.13** The parameters for the adsorption of benzene on SMB in single-solute and mixed-solute systems

Adsorbents	Langmuir parameters	
	K <sub>P</sub> (dm <sup>3</sup> /g)	R <sup>2</sup>
SMZ single-solute system	0.6284	0.99
SMZ mixed-solute system	0.598	0.99

The affinity constant of SMB for benzene in the mixed-solute systems is slightly lower than that of the single-solute system as previously seen in SMZ. The reason is similar to the mixed-solute systems of SMZ that cadmium could shield the partition site of benzene which slightly lower sorption yield of benzene. Cadmium adsorption in the mixed-solute system shows only a little decrease in adsorption when compared to the single-solute system. Lee *et al.* (2005) also observed no significant competition for sorption between benzene and lead on organobentonite. The reason for this may come from the different sorption sites of benzene and cadmium. While benzene was partitioned into the organic phase of interlayer space, which was modified by CTAB, cadmium would be mostly adsorbed on the cation-exchanged sites and bound to the edge site of bentonite (Sheng *et al.*, 1999).