

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Adsorption of CTAB on Clinoptilolite

The adsorption isotherm of cetyl trimethyl ammonium bromide (CTAB) was studied on clinoptilolite at 30°C. The adsorption isotherm was plotted on logarithm scale, as shown in Figure 4.1. This represents a system where the adsorbate is strongly attracted by the adsorbent, generally by ion-ion exchange interactions that reaches a saturation value represented by the 'plateau' of the isotherm, which was approximately 70 μmol of CTAB/gram of clinoptilolite. In addition, the critical micelle concentration (CMC) of surfactant could be determined from the isotherm. The CMC of CTAB adsorbed on clinoptilolite was found to be approximately 960 μM . The maximum adsorption density gives a molecule per area of nearly 4.15 molecules/ nm^2 which was calculated by assuming the surfactant molecule adsorbed onto the entire clinoptilolite surface with the specific area of clinoptilolite being 10.15 m^2/g .

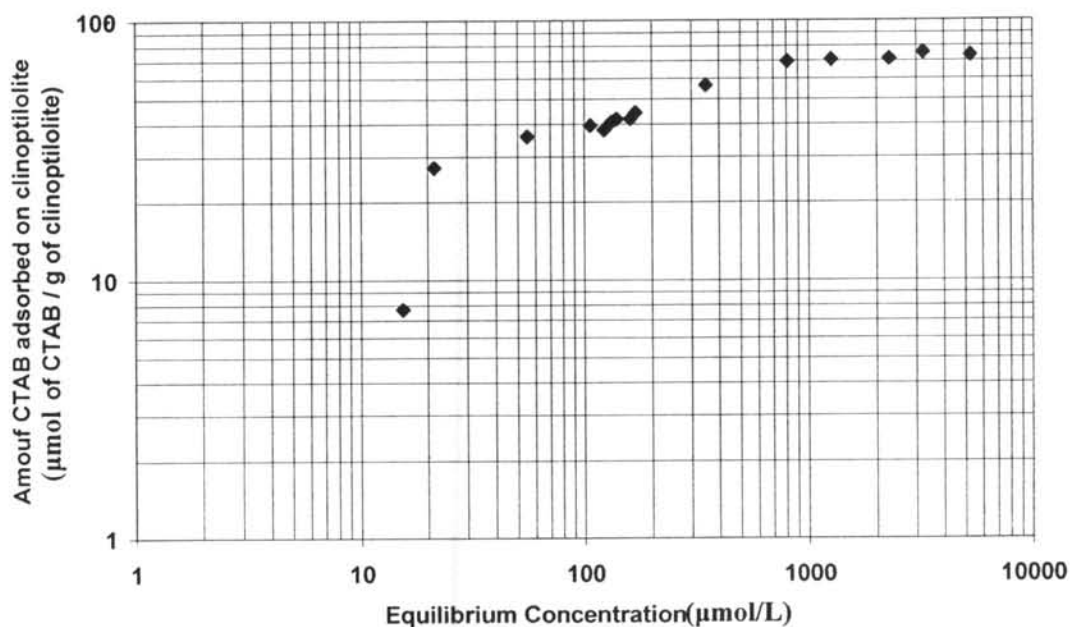


Figure 4.1 Adsorption isotherm of CTAB on clinoptilolite at 30 °C.

Apart from the adsorption isotherm, the zeta potential of clinoptilolite surface was also measured in order to find the amount of CTAB loading that provides a completed monolayer adsorption of CTAB on clinoptilolite. Figure 4.2 shows the zeta potential of clinoptilolite as a function of CTAB loading. It starts from negative charge of the original clinoptilolite surface and the surface becomes less negative, neutral, and then positive. This is due to the adsorption of CTAB molecules on the oppositely charged clinoptilolite surface, thus reducing the negative charges on the surface of the zeolite. Further increase in CTAB loading caused the surfactant molecules to orient outwards from the surface via a tail-tail interaction, the positive charge of head group of surfactant reverses the surface charge. The point where the net negative charge on zeolite surface was neutralized (point of zero charge, PZC), where CTAB loading was approximately 42 μmol of CTAB/gram of clinoptilolite, indicates a completed monolayer surface coverage by CTAB.

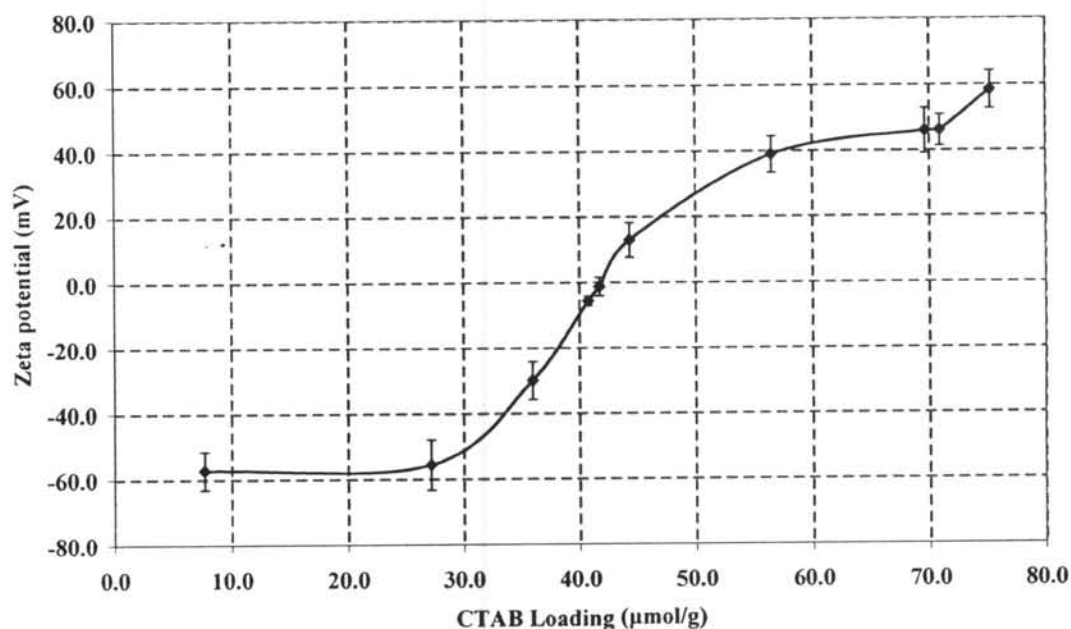


Figure 4.2 Zeta potential of clinoptilolite as a function of CTAB loading.

4.2 Adsorption of Anionic Surfactants

After the formation of a monolayer adsorption of CTAB on clinoptilolite could be determined from the adsorption isotherm and the zeta potential results (an initial CTAB concentration of 555 μM), SMZ was prepared by further adsorbing anionic surfactants (DOWFAX 8390, DOWFAX 2A1, or SDBS) to form a mixed layer of CTAB and anionic surfactants on clinoptilolite. Since CTAB and anionic surfactants could precipitate in the mixed surfactant system, precipitation experiments were first carried out. The anionic surfactant at various concentrations in the range of 1 to 10 times of the initial molar concentration of CTAB was mixed with CTAB to study the precipitation conditions. It was found that the systems having the anionic surfactant concentrations 6 and 10 times of CTAB did not show precipitation within 3 days. Consequently, the anionic surfactant concentration at 10 times of CTAB was chosen for the subsequent adsorption experiments. In addition, this ratio of anionic surfactant to CTAB (10:1 or 10 times of initial molar concentration of CTAB) yielded the highest adsorption of surfactant on SMZ. The amount of anionic surfactant adsorption as a function of equilibrium time was shown in Figure 4.3. The adsorbed anionic surfactant was found to be approximately 60 μmol of DOWFAX 8390 / g clinoptilolite, 56 μmol of SDBS / g clinoptilolite, and 49 μmol of DOWFAX 2A1 / g clinoptilolite. The zeta potential of the resulting SMZs having DOWFAX 8390, DOWFAX 2A1 and SDBS adsorbed on CTAB-modified clinoptilolite was found to be -73.19 mV, -70.81 mV, and -70.35 mV, respectively. It can also be seen that the ability to adsorb DOWFAX 8390 on modified clinoptilolite is higher than SDBS, because DOWFAX 8390 has twin head groups which contribute to a higher polarity than SDBS. Thus, it can adsorb to form a bilayer on CTAB-modified clinoptilolite at a higher amount than single head group surfactant. Among all the anionic surfactants used in this research, DOWFAX 2A1 adsorbed on clinoptilolite the lowest. Although it also has twin head group but its structure has branch at the alkyl chain which makes it bulky and difficult to form bilayer adsorption. The SMZ prepared by using anionic surfactants:CTAB ratio of 10:1 was

further used in the subsequent studies on the removal of heavy metal and organic contaminants.

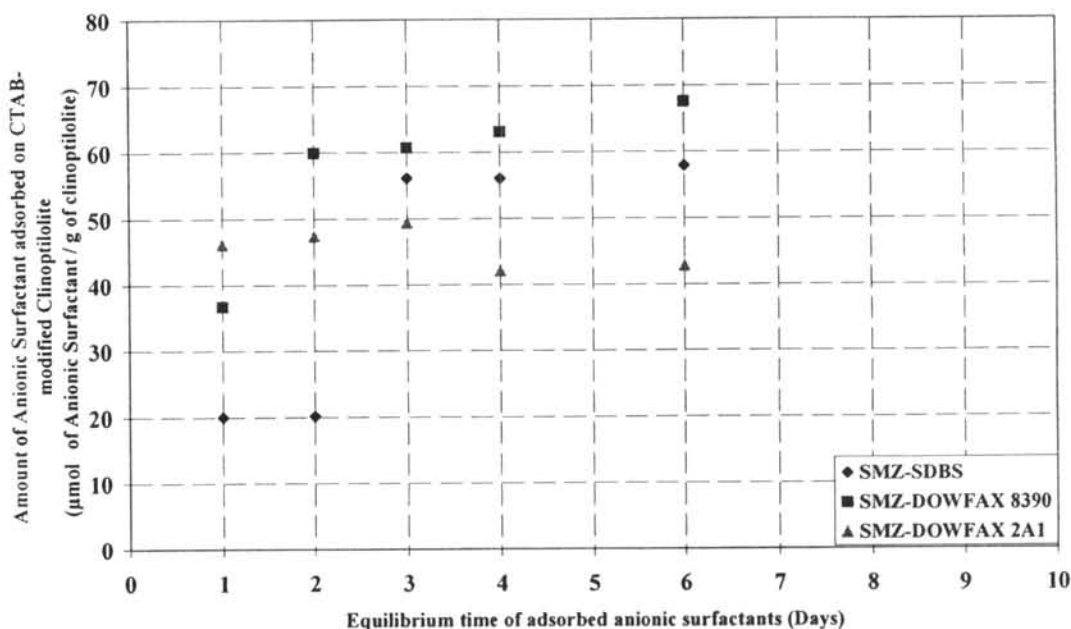


Figure 4.3 Dynamic adsorption of anionic surfactants on CTAB-modified clinoptilolite at 30 °C.

The results also reveal that the amount of anionic surfactant adsorbed on the CTAB-modified clinoptilolite (~ 40-65 µmol/g) is higher than the amount of the CTAB adsorbed in the upper layer of bilayer form. This may be due to the synergism between the cationic and the anionic surfactants as the model adsorption as shown in Figures 4.4-4.6. The anionic surfactant reduces the electrostatic repulsion forces between the molecules of cationic surfactant adsorbed on the monolayer, therefore one part of the anionic surfactant intercalates their molecules between molecules of cationic surfactant and another part adsorbed to form the bilayer (Lee *et al.*, 1996). The amount of anionic surfactant adsorbed for each type of anionic surfactant is different, depending on their structure such as branching and polarity. The amount of anionic surfactant adsorbed decreased in the order of DOWFAX 8390 > SDBS > DOWFAX 2A1.

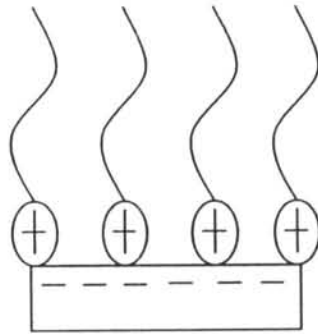


Figure 4.4 Schematic of CTAB binding onto clinoptilolite in monolayer form.

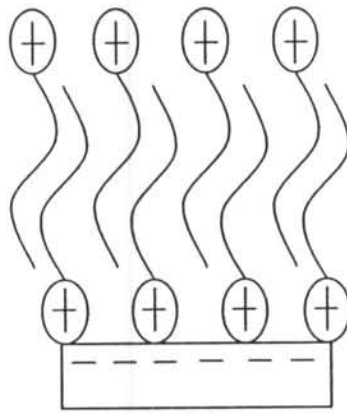


Figure 4.5 Schematic of CTAB binding onto clinoptilolite in monolayer and bilayer form.

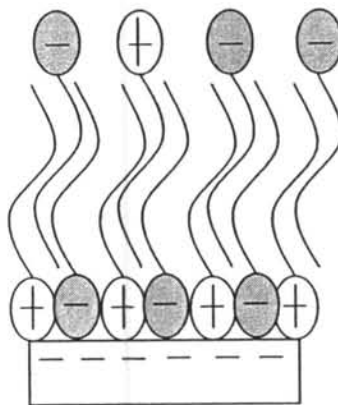


Figure 4.6 Schematic showing synergism between anionic surfactant and CTAB.

4.3 Characterization of Surfactant-Modified Zeolite (SMZ)

In addition to the zeta potential measurement as seen in the previous section, SMZ was also characterized by using FTIR to examine the functional groups on the surface. The spectra are shown in Figures 4.7-4.15. Some fundamental IR absorption frequencies of clinoptilolite and SMZ with various types of anionic surfactants are shown in Table 4.1. The spectra show the OH stretching of aluminum hydroxide of the base zeolite at 3629 cm^{-1} . The absorption band at 1066 cm^{-1} indicates that the vibration of Si-O (Al) and Al-O (Si) bonds in the aluminosilicate oxygen framework which is the most intense band. The C-H stretching of aliphatic and the N-H stretching of quaternary amine salt in CTAB at 2851 and 2922 cm^{-1} were identified only in SMZ samples. Furthermore, the aliphatic C-O stretching frequency of phenyloxy group in DOWFAX 8390 and DOWFAX 2A1 at 1205 cm^{-1} were also observed only on the surface of SMZ, not on unmodified clinoptilolite.

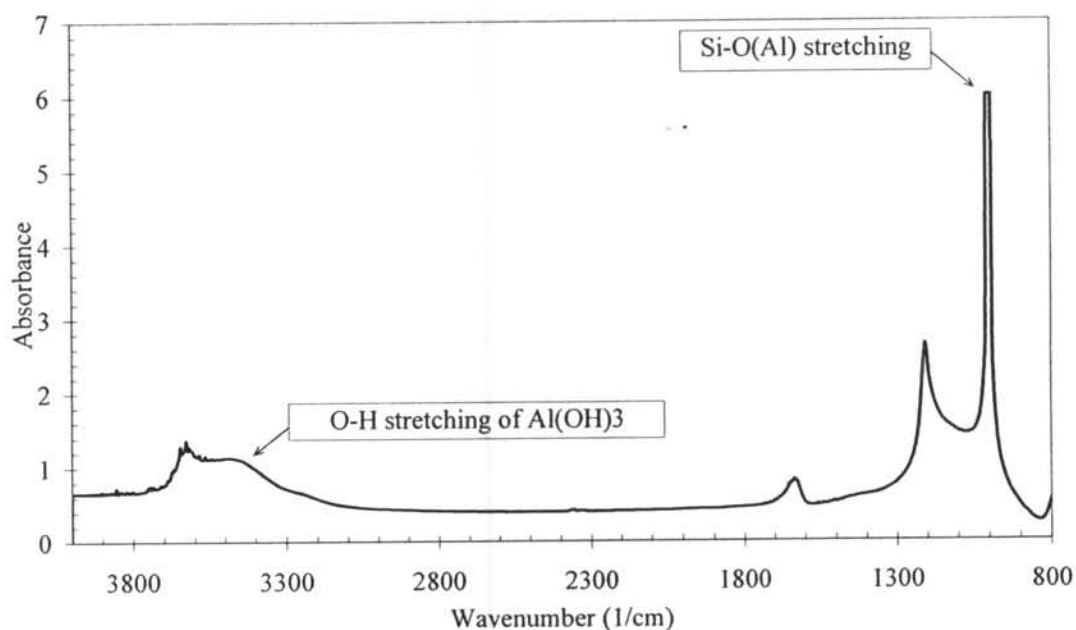


Figure 4.7 FTIR spectra of clinoptilolite.

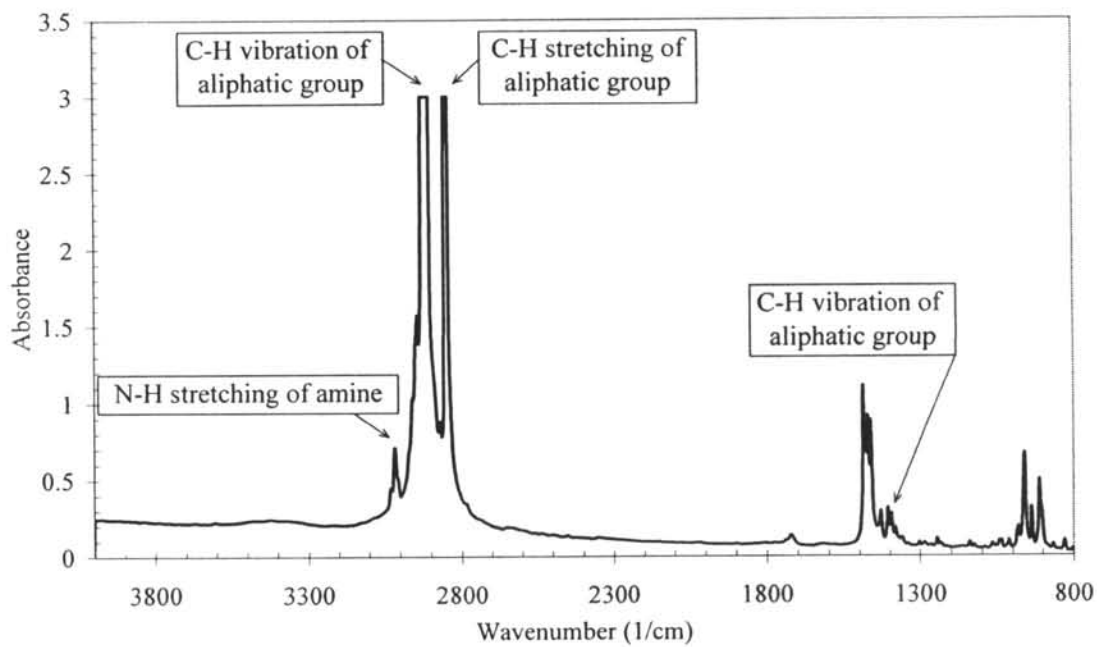


Figure 4.8 FTIR spectra of CTAB.

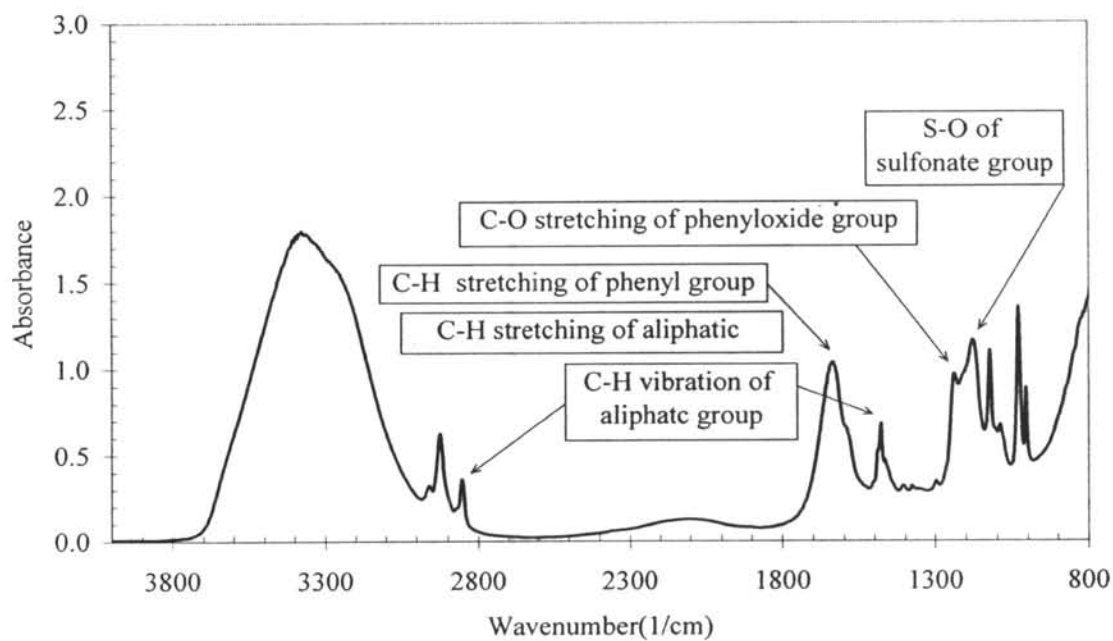


Figure 4.9 FTIR spectra of DOWFAX 8390.

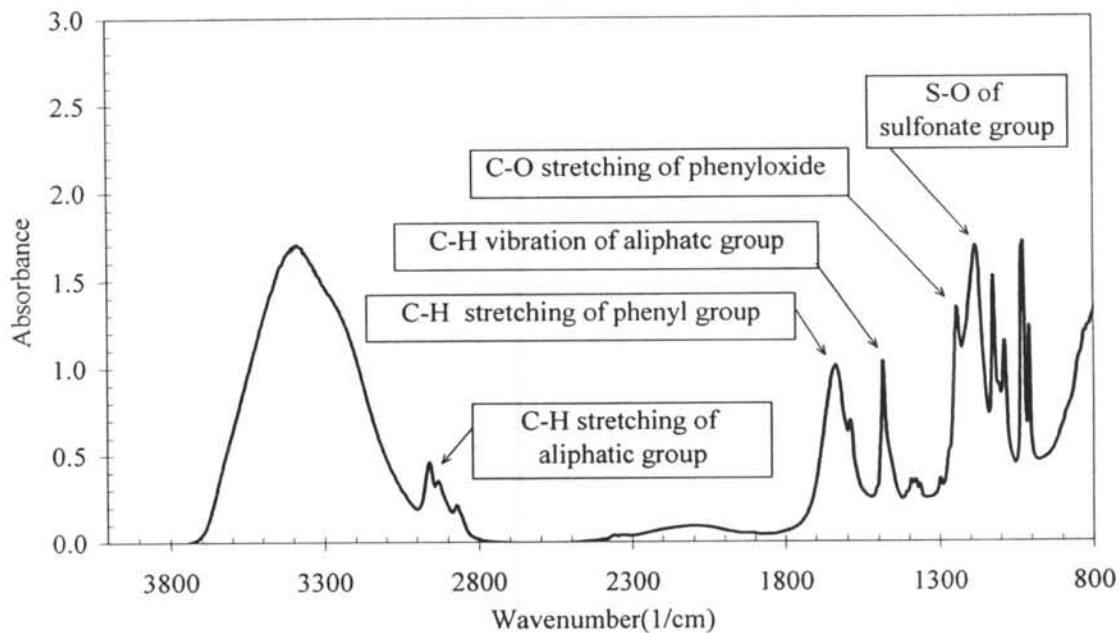


Figure 4.10 FTIR spectra of DOWFAX 2A1.

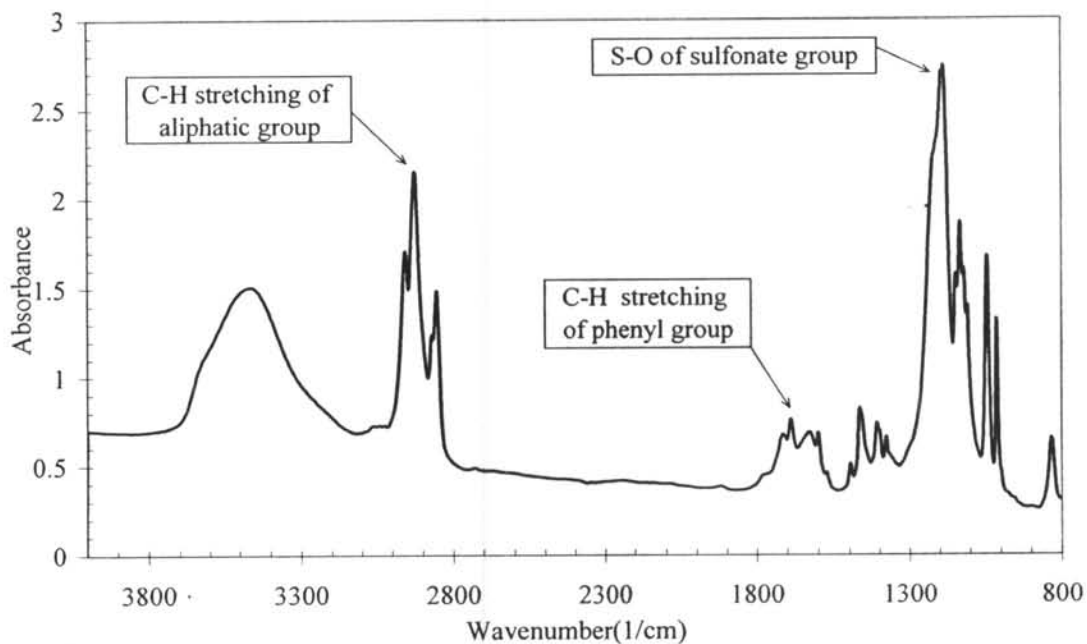


Figure 4.11 FTIR spectra of SDBS.

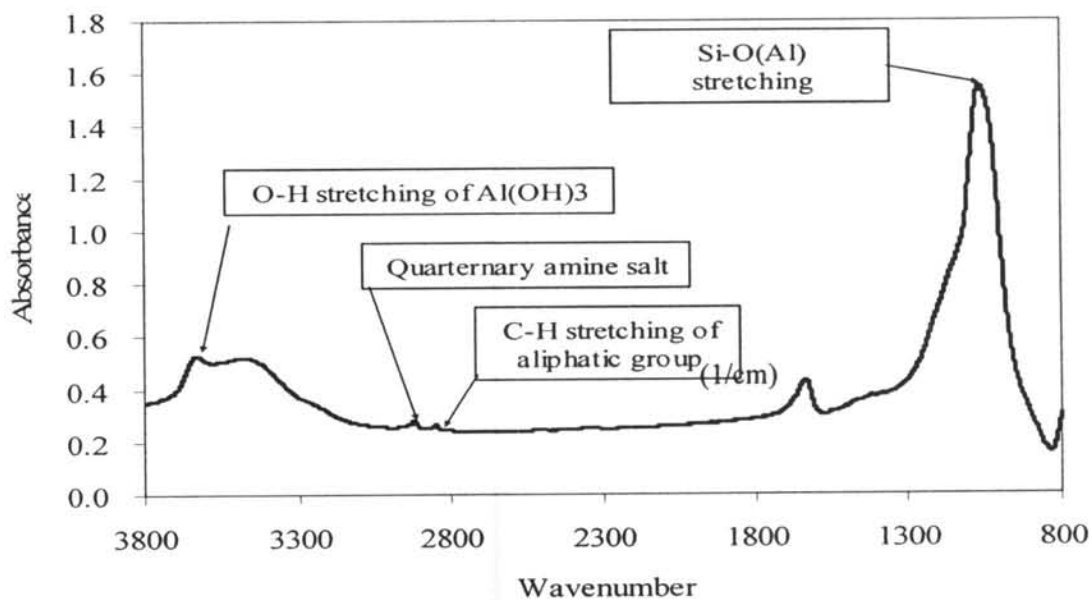


Figure 4.12 FTIR spectra of CTAB-modified clinoptililite.

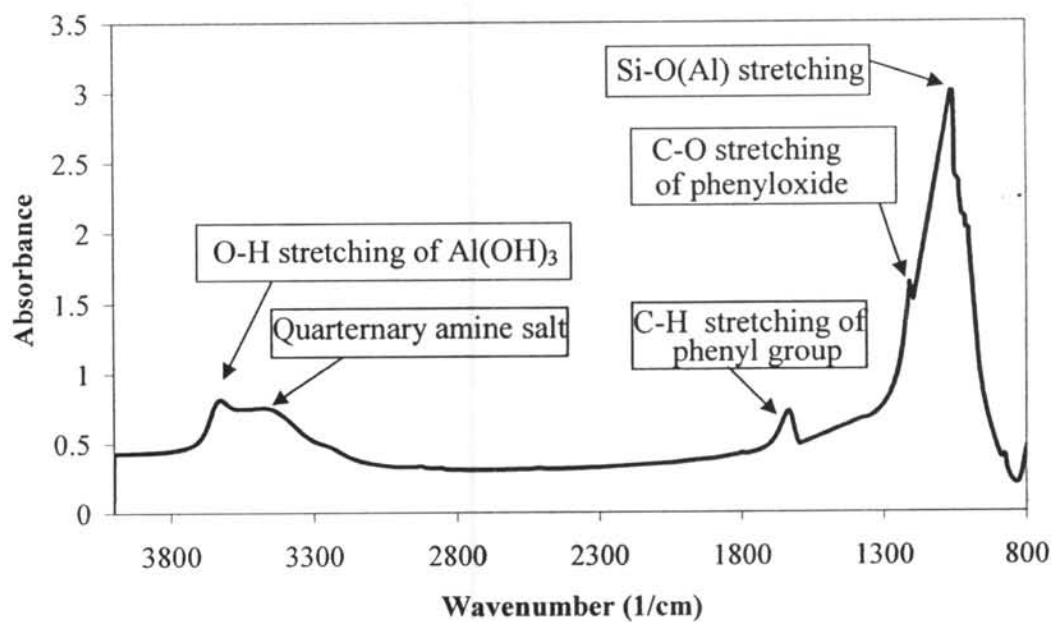


Figure 4.13 FTIR spectra of SMZ-DOWFAX 8390.

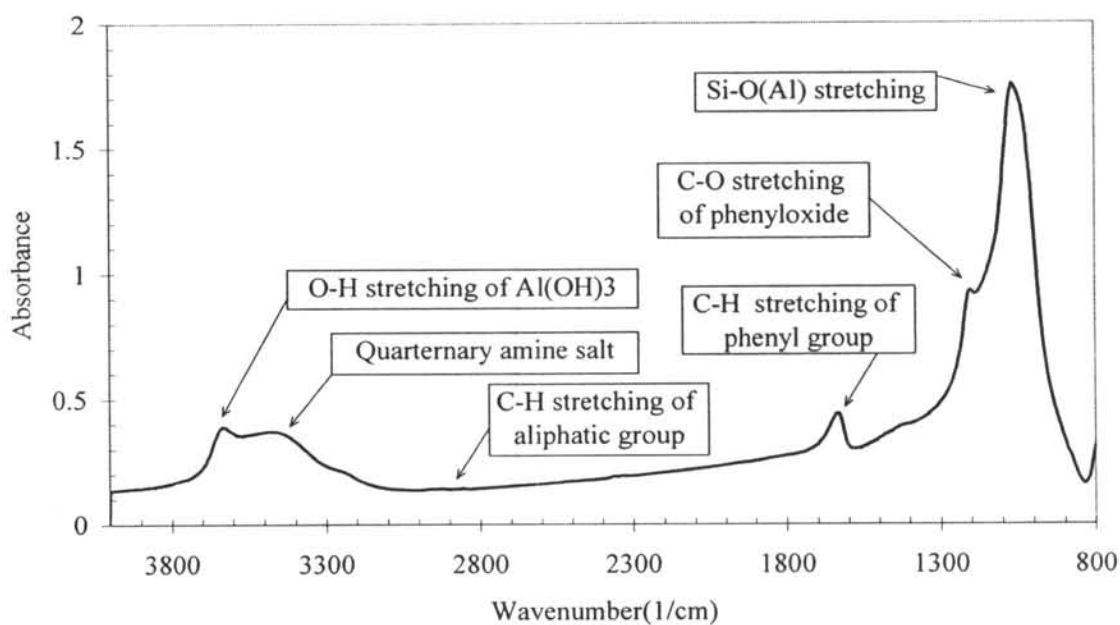


Figure 4.14 FTIR spectra of SMZ-DOWFAX 2A1.

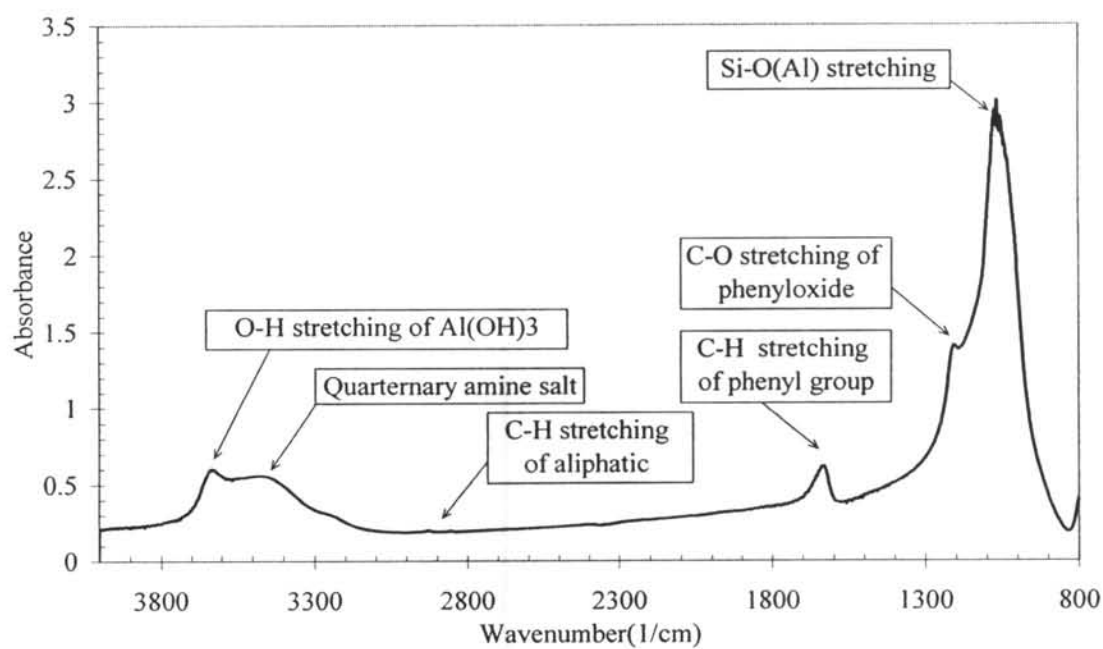


Figure 4.15 FTIR spectra of SMZ-SDBS.

Table 4.1 Some fundamental IR absorption frequencies of clinoptilolite and SMZ

Assignments	Clinoptilolite	SMZ varied anionic surfactants		
		DOWFAX 8390	DOWFAX 2A1	SDBS
Si-O(Al) stretching	1066	1064	1067	1066
O-H stretching of aluminum hydroxide	3629	3629	3632	3634
C-H stretching of aliphatic group	-	2851	2851	2851
Quarternary amine salts	-	2922	2922	2922
C-H stretching of phenyl group	-	1635	1633	1632
C-O stretching of phenyloxide	-	1210	1205	1206
S-O of sulfonate group	-	-	-	1059

4.4 Adsorption of Contaminants

4.4.1 Adsorption of Heavy Metal Ions in Single-Metal System

The speciation of metal ions in an aqueous solution significantly affects their interaction with a solid adsorbent and their species distributions are related to pH. The chemical equilibrium diagram for cadmium and lead in aqueous solution at various pH was calculated by using MEDUSA program (Cortes-Martinez *et al.*, 2004) as shown in Figures 4.16 and 4.17 for cadmium and lead, respectively.

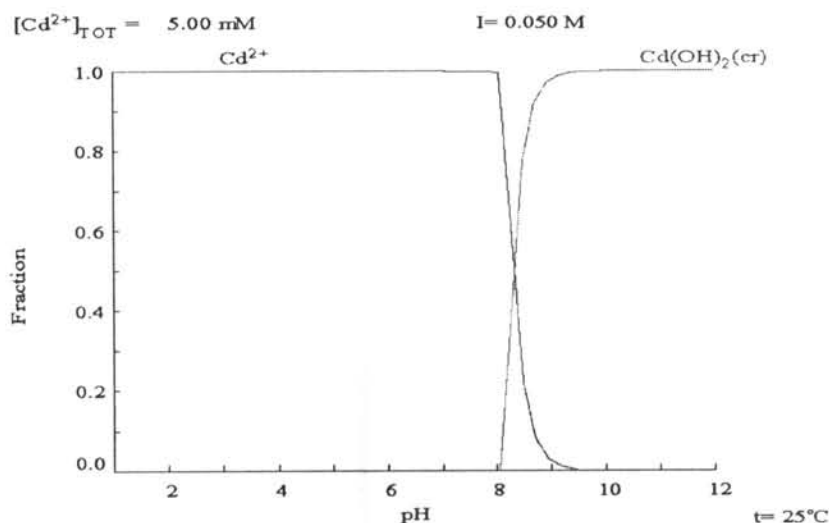


Figure 4.16 Chemical equilibrium diagram for cadmium at various pH.

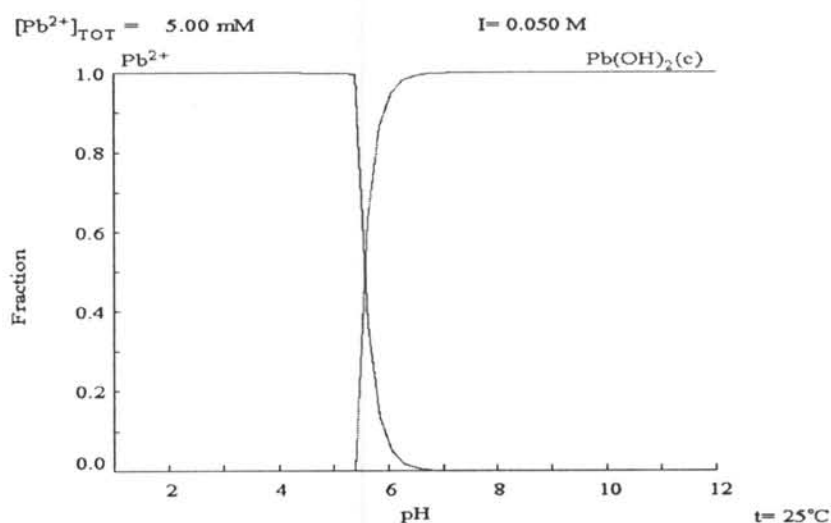


Figure 4.17 Chemical equilibrium diagram for lead at various pH.

From these figures, it can be seen that at $\text{pH} < 5$, Pb^{2+} and Cd^{2+} species are totally present in an ionic states (divalent form). With increasing pH, Pb^{2+} and Cd^{2+} species start to hydrolyze and entirely precipitate into Pb(OH)_2 and Cd(OH)_2 at $\text{pH} > 5.5$ and $\text{pH} > 8$, respectively. Therefore, the experimental conditions used in this study for the equilibrium adsorption was set at pH 5. The

initial and the final pH values after the adsorption were measured and were found to be nearly the same. The adsorption of heavy metal was conducted with the initial heavy metal concentrations in the range of 0.25 to 5 mM and at 30°C.

The adsorption isotherms of cadmium (Cd^{2+}) and lead (Pb^{2+}) on SMZs and unmodified clinoptilolite in single-metal system at 30°C are presented in Figures 4.18 and 4.19, respectively.

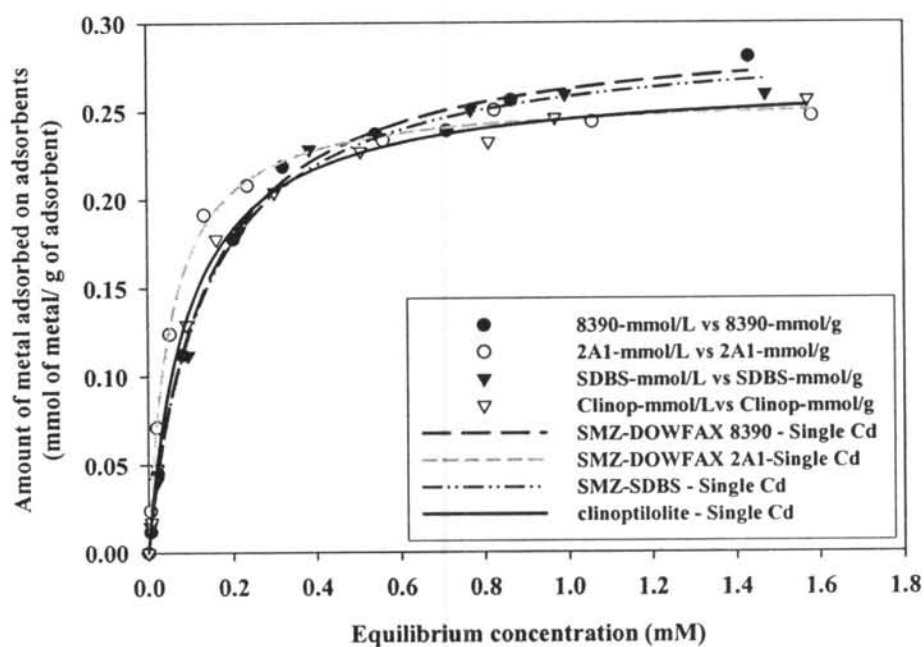


Figure 4.18 Adsorption isotherms of cadmium on SMZs and clinoptilolite in single-metal system at 30°C and pH 5.

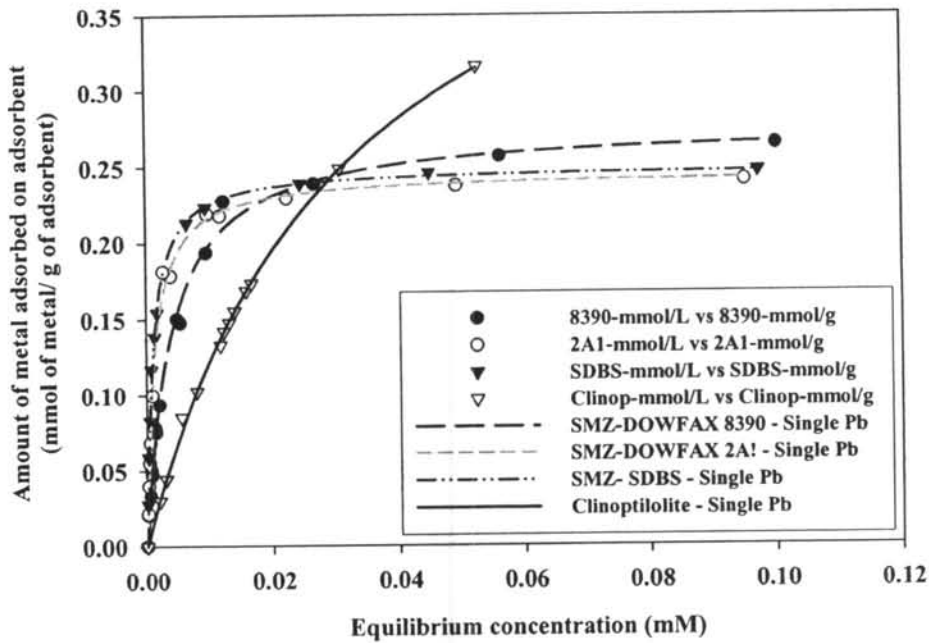


Figure 4.19 Adsorption isotherm of lead on SMZs and clinoptilolite in single-metal system at 30°C and pH 5.

These isotherms are presented as a plot of equilibrium concentration of the heavy metal (mM) versus the amount of the heavy metal adsorbed on the adsorbent ($\mu\text{mol/g}$) and the adsorption data were fitted to the Langmuir isotherm model by a nonlinear regression analysis by using the software Sigma Plot version 8.02. The model can be described by the following equation:

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

Where q is the amount of metal adsorbed on the 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). Q_{\max} is the parameter that reflects the ability of the adsorbent in adsorbing particular adsorbate on weight basis whereas K indicates the affinity of the adsorbent towards the adsorbate. The K values correspond to equilibrium metals concentrations at half of the maximum capacity. As the same maximum capacity of adsorbents, the very small K values of adsorbents indicate that these adsorbents have high affinity toward metals. The

adsorption parameters of the adsorbents for cadmium and lead adsorption on SMZs and clinoptilolite in single-metal system were determined as from Langmuir isotherm shown in Table 4.2 and Table 4.3, respectively.

Table 4.2 Langmuir parameters for the adsorption of cadmium on SMZs and clinoptilolite in single-metal system at 30°C and pH 5

Adsorbents	Single-metal system		
	Q_{\max} (mmol/g)	K (mM)	R^2
SMZ-DOWFAX 8390	0.2972	0.1324	0.9971
SMZ-DOWFAX 2A1	0.2590	0.0054	0.9982
SMZ-SDBS	0.2922	0.0132	0.9967
Clinoptilolite	0.2681	0.0093	0.9982

Table 4.3 Langmuir parameters for the adsorption of lead on SMZs and clinoptilolite in single-metal system at 30°C and pH 5

Adsorbents	single metal system		
	Q_{\max} (mmol/g)	K (mM)	R^2
SMZ-DOWFAX 8390	0.2765	0.0040	0.9942
SMZ-DOWFAX 2A1	0.2454	0.0014	0.9970
SMZ-SDBS	0.2493	0.0011	0.9986
Clinoptilolite	0.5072	0.0321	0.9986

It can be seen from the results that both the adsorbents, SMZs and unmodified clinoptilolite, have ability to adsorb Pb^{2+} and Cd^{2+} . SMZs have sulfonate groups which exhibit negatively charge whereas clinoptilolite has excess oxygen in the silica-alumina framework and thus it possesses negative charges on the surface. For SMZs, they have the same functional group (sulfonate of anionic surfactant) therefore they share similar abilities to adsorb metal ions. The slight difference in

metal adsorptions of the SMZs is probably due to the effect of modification clinoptilolite surface by each anionic surfactant.

The single system of Pb^{2+} , unmodified clinoptilolite has the ability to adsorb Pb^{2+} more than SMZs. The maximum capacity of lead adsorption of unmodified clinoptilolite is much higher than SMZs but its affinity (K) is not good. SMZ-DOWFAX 8390 is the most appropriate adsorbent for adsorbing Pb^{2+} among all adsorbents studied as indicated by highest Q_{max} (0.2765 mmol/g) and low K (0.0040 mM). When compare to the previous work, Q_{max} obtained in this study is similar to that of Sriplad (2005) but K is lower.

In contrast, the single system of Cd^{2+} is preferentially adsorbed on SMZs. SMZ-DOWFAX 2A1 has the lowest K of 0.0054 mM but Q_{max} is not as high as compare to others because the molecular structure of DOWFAX 2A1 has branch at the alkyl chain then it is more easily to desorbed. Thus, this reason has the effect on adsorption site for metal ions of SMZ-DOWFAX 2A1. Sriwongjanya (2004) studied on the adsorption of cadmium on SMZ by various loading ratio of metal ligand on SMZ (adsorption site of SMZ). The results observed that the cadmium uptake by SMZ increased significantly with increasing the amount of metal ligand (PA) loading on SMZ. It shows SMZ-DOWFAX 2A1 has ability to adsorb Cd^{2+} and high affinity at low Cd^{2+} concentration. SMZ-DOWFAX 8390 has the highest Q_{max} (0.2972 mmol/g) but K is highest (means lowest affinity toward Cd^{2+}). These values correspond reasonably well with the values reported in the previous work (Sriplad, 2005) (Q_{max} of 0.32 mmol/g and K of 0.09 mM). Therefore SMZ-DOWFAX 8390 has the highest ability in adsorbing cadmium at high concentration. This can be explained that SMZs and unmodified clinoptilolite have different sites for metal adsorption. Since SMZs were modified by anionic surfactants, the sulfonate group of anionic surfactants adsorbed on SMZ acts as adsorption site for metal ions. For unmodified clinoptilolite, the negative charges on the surface are due to excess oxygen in the silica-alumina framework, and thus, the positively charged metal ions can be adsorbed on the clinoptilolite surface through ion-exchange mechanism. In general, the adsorption of transition metals can be explained by hard-soft acid base (HSAB) principle (Shawabkeh *et al.*, 2004). That is reactions of hard-hard and soft-soft interactions are more favorable than the reaction of mixed hard and soft. In this

principle, the cation that has high electronegativity and small ionic size is classified as a strong acid or hard acid. Consequently, this cation prefers to react or form complexes with hard base. In this study, lead has higher electronegativity (1.854) than cadmium (1.521), which yields a harder acid than cadmium. The excess oxygen of clinoptilolite surface is a hard base and the sulfonate group of anionic surfactants is a borderline base as classified by Miessler and Tarr (2004). Thus, the excess oxygen is harder base than sulfonate. For this reason, it can be expected that the adsorption of clinoptilolite has a preference towards hard acid as lead whereas the adsorption of SMZ is directed towards soft acid such as cadmium. This explains the experimental results observed in this part of the study.

4.4.2 Adsorption of Heavy Metal Ions in Mixed-Metal System

The adsorption isotherms of cadmium and lead in mixed-metal ions system can be described by Langmuir isotherms as shown in Figures 4.20 and 4.21, respectively. The Langmuir adsorption parameters of cadmium and lead in mixed-metal system are shown in Table 4.4 and Table 4.5, respectively. The results from the adsorption in the mixed-metal systems show a similar trend as observed in the single-metal system.

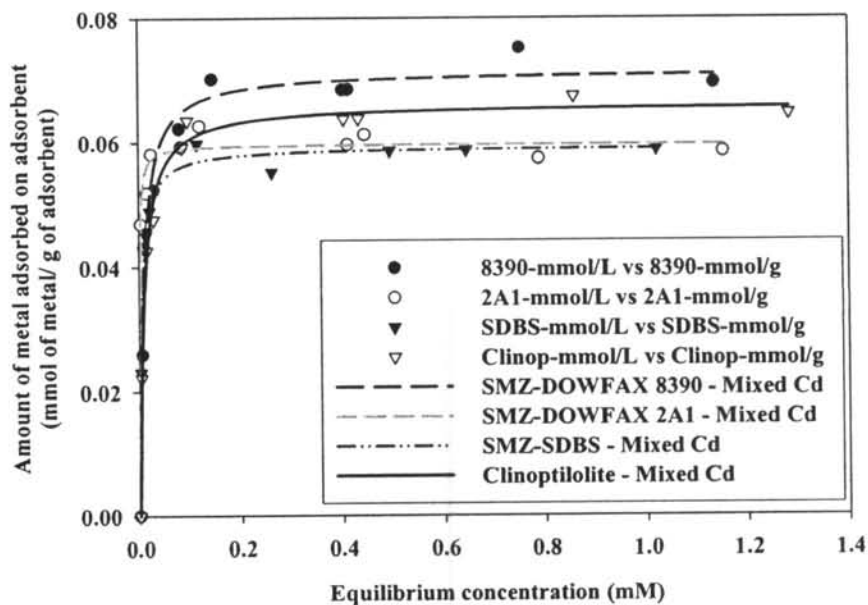


Figure 4.20 Adsorption isotherm of cadmium on SMZs and clinoptilolite in mixed-metal system at 30°C and pH 5.

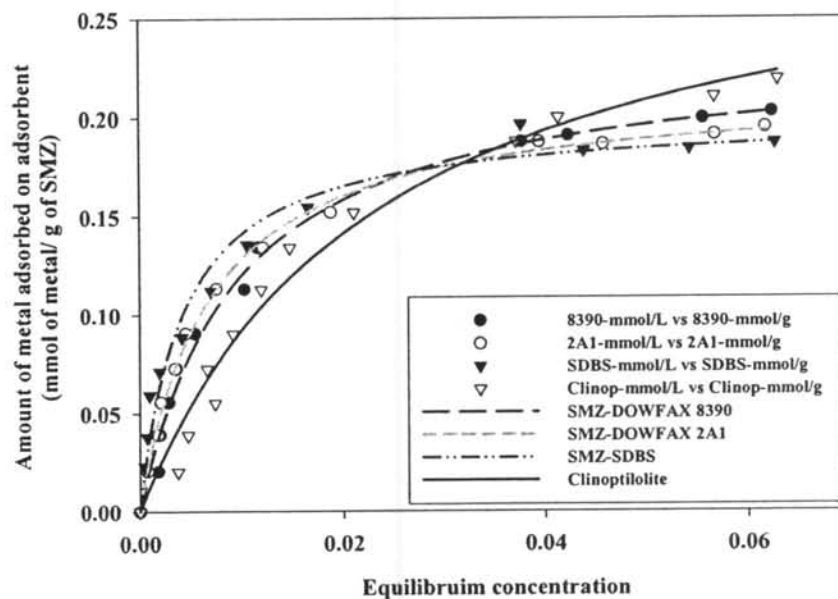


Figure 4.21 Adsorption isotherm of lead on SMZs and clinoptilolite in mixed-metal system at 30°C and pH 5.

Table 4.4 Langmuir parameters for the adsorption of cadmium on SMZs and clinoptilolite in mixed-metal systems at 30°C and pH 5

Adsorbents	mixed metal system		
	Q_{\max} (mmol/g)	K (mM)	R^2
SMZ-DOWFAX 8390	0.0714	0.0086	0.9817
SMZ-DOWFAX2A1	0.0597	0.0011	0.9875
SDBS	0.0592	0.0047	0.9944
Clinoptilolite	0.0661	0.0092	0.9941

Table 4.5 Langmuir parameters for the adsorption of lead on SMZs and clinoptilolite in mixed-metal systems at 30°C and pH 5

Adsorbents	mixed metal system		
	Q_{\max} (mmol/g)	K (mM)	R^2
SMZ-DOWFAX 8390	0.2331	0.0094	0.9915
SMZ-DOWFAX 2A1	0.2143	0.0067	0.9973
SDBS	0.1996	0.0042	0.9780
Clinoptilolite	0.3045	0.0231	0.9789

The results clearly show that the amount of heavy metal adsorbed in mixed-metal system was lower than in single-metal systems for both metal ions. Figures 4.22 and 4.24 show the comparison of the cadmium and lead adsorption isotherms in single- and mixed-metal systems. When compared to the single-metal system, the adsorption of cadmium in mixed-metal system decreases approximately 75-80% and adsorption of lead decreases approximately 13-33%. This is possibly due to the competitive adsorption between cadmium ion and lead ion for the adsorption sites of adsorbents in the mixed-metal system as show in Figure 4.24. This behavior is in accordance with the selectivity order, since both selectivity order and dependence of total uptake on solution components (e.g, metal ions) are the result of physicochemical and stereo chemical factors, such as the hydrated radii and

the hydration energy of cations (Helfferich, 1995). Lead ion species has lower hydration energy (1481 kJ/mol) than cadmium ion (1807 kJ/mol) (Ricordel *et al.*, 2001). Thus this may facilitate the hydrated lead ion more easily adsorbing on adsorbents than cadmium ion. In addition, adsorption of lead ions is higher than cadmium ion in the mixed-metal system because lead ion has higher adsorption kinetics than cadmium ion (Lu Lv *et al.*, 2005). They studied the competitive adsorption kinetics of binary system $\text{Cd}^{2+}/\text{Pb}^{2+}$, it can be seen that the uptake of Pb^{2+} ions was faster than uptake of Cd^{2+} ion, behaved strangely reaching a maximum at the early stage and then decreasing as the contact time was prolonged. Such an adsorption behavior indicates the possible underlying adsorption mechanism.

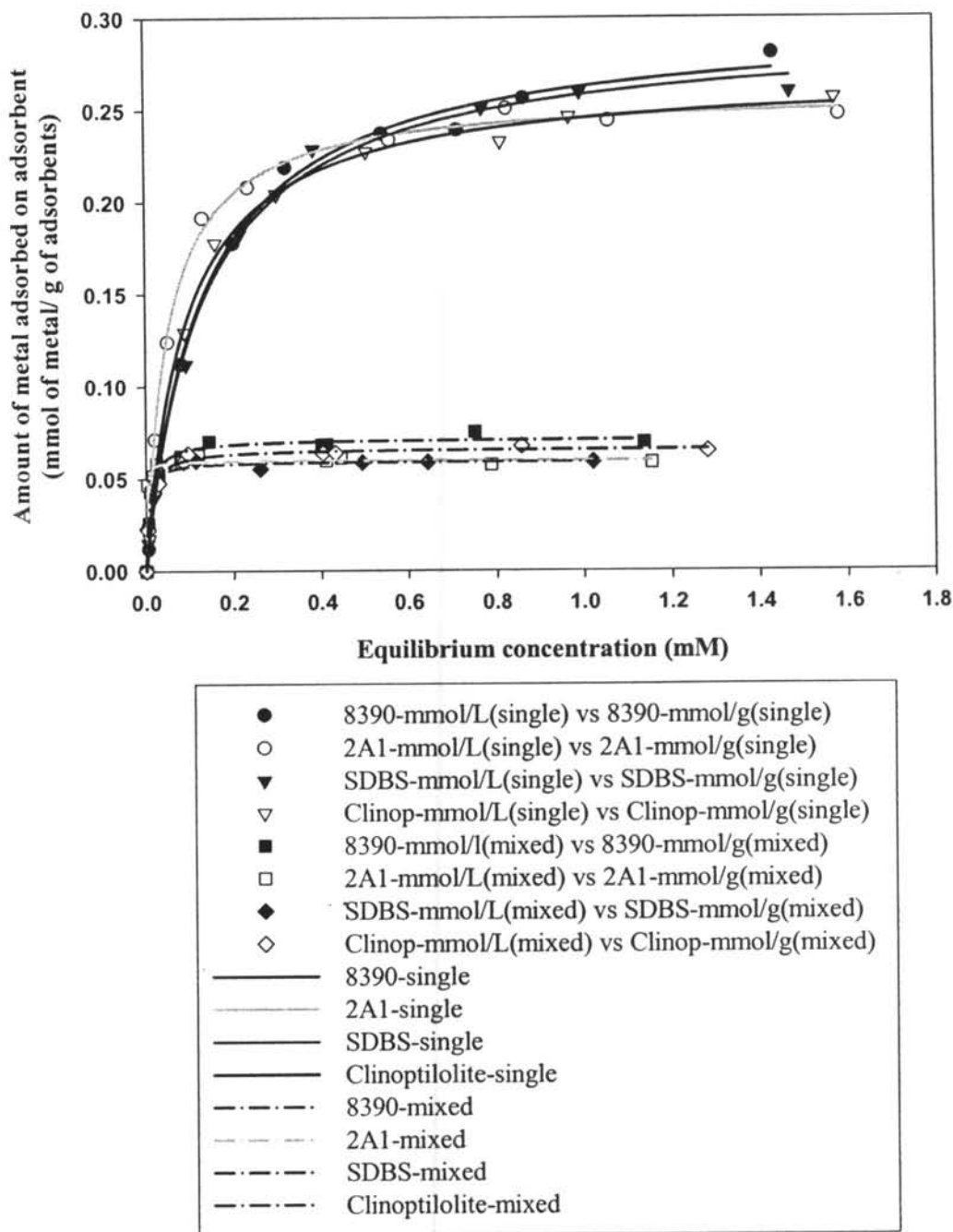


Figure 4.22 Adsorption isotherm of cadmium on SMZs and clinoptilolite in mixed and single-metal systems at 30°C and pH 5.

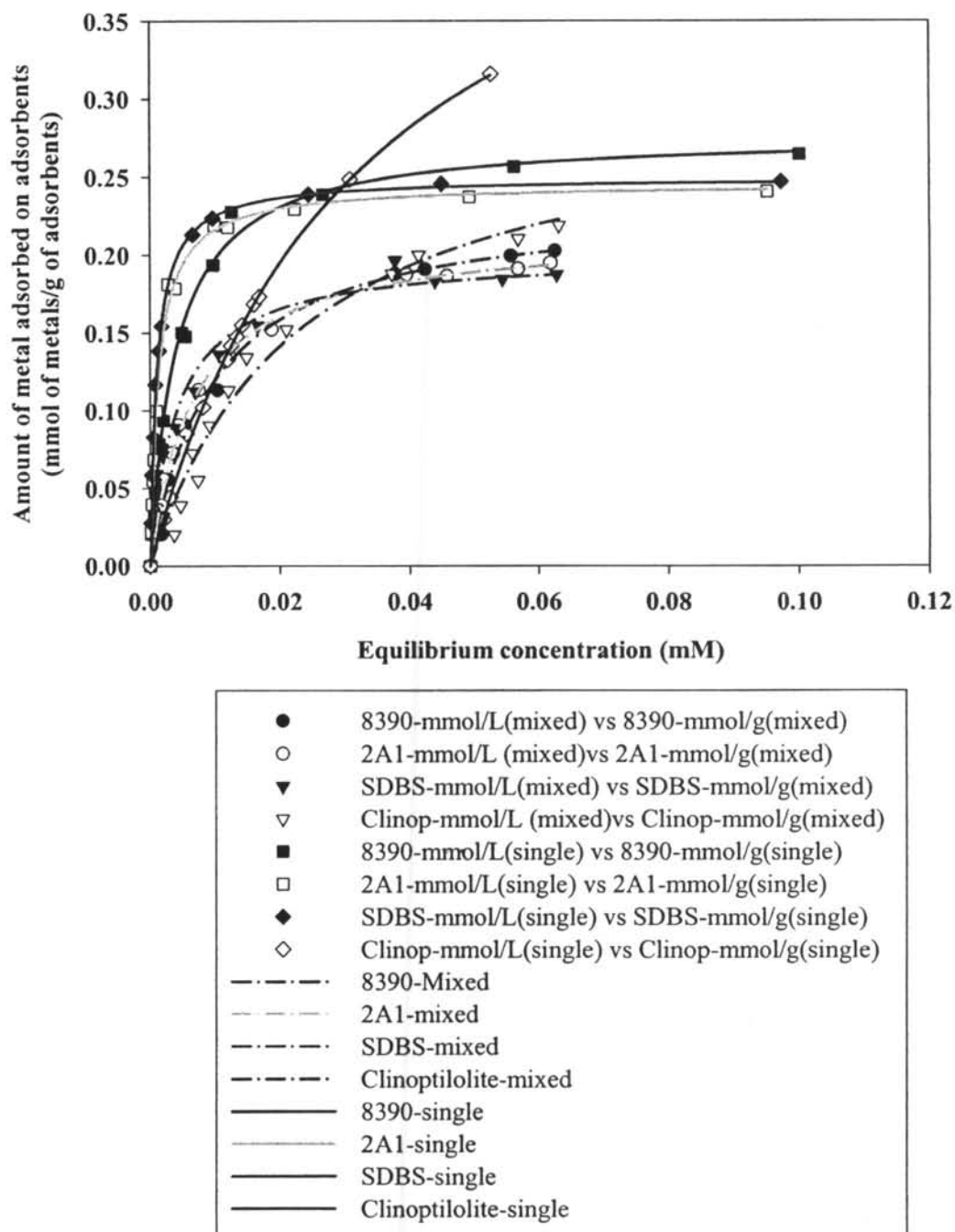


Figure 4.23 Adsorption isotherm of lead on SMZs and clinoptilolite in mixed and single-metal systems at 30°C and pH 5.

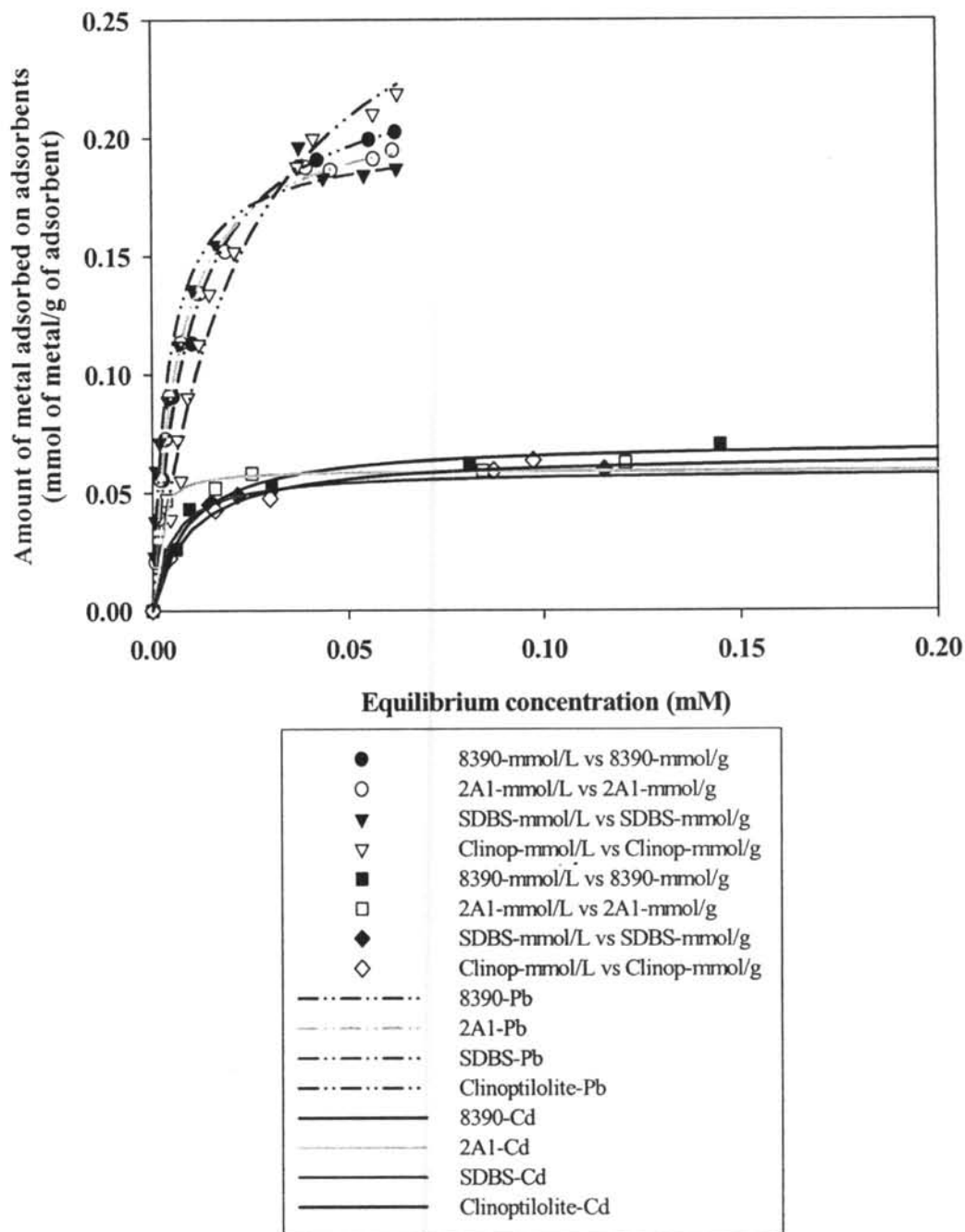


Figure 4.24 Adsorption isotherm of lead and cadmium on adsorbents in mixed-metal systems at 30°C and pH 5.

4.4.3 Adsorption of Toluene on SMZ in Single-Solute System

The potential of surfactant-modified zeolites to remove organic solute from the solution were studied by using toluene initial toluene concentrations used were in the range of 500 to 5500 μM and temperature of 30°C . The adsorption isotherms of toluene on SMZs and clinoptilolite were generated by plotting equilibrium concentration of toluene (μM) versus the amount of toluene adsorbed on the adsorbent ($\mu\text{mol/g}$), as presented in Figure 4.25.

It can be seen that the adsorption of toluene on almost all of the adsorbents demonstrate a linear-type isotherm. This can be described by the following equation:

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

Where q is the amount of toluene adsorbed on the adsorbent (μmol of toluene/g of SMZ), C_e is an equilibrium concentration ($\mu\text{mol/l}$) and K_p is partition coefficient (L/g). From this correlation, the partitioning coefficient is independent of the solute concentration. The adsorption of toluene to adsorbed hydrophobic phase is a partitioning-dominated process and linear regression lines were fitted through the origin for all the data points at each toluene concentration.

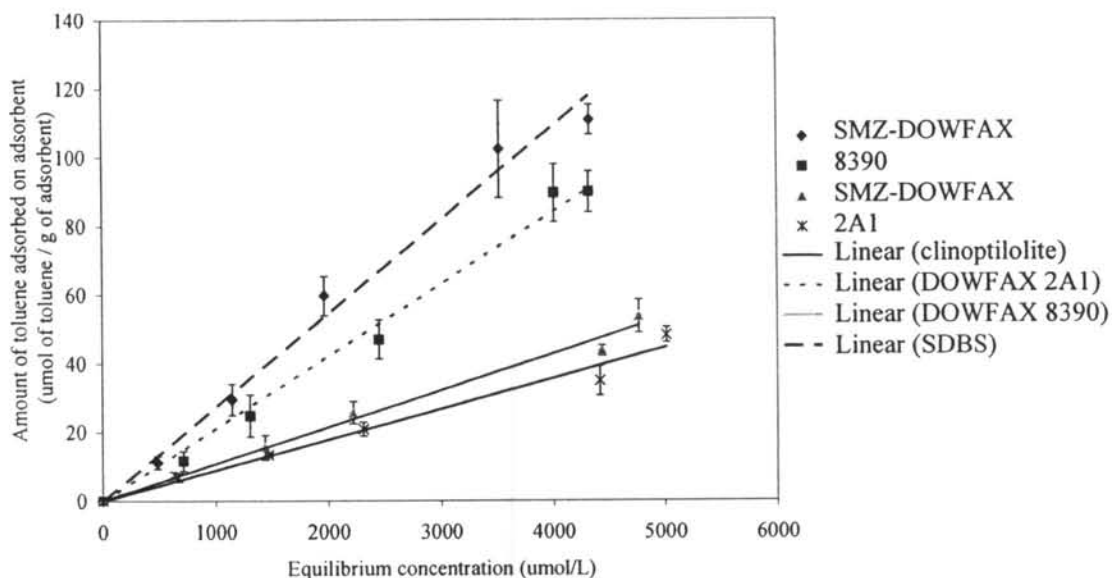


Figure 4.25 Adsorption isotherms of toluene on SMZs and clinoptilolite at 30°C.

The partition coefficients for toluene adsorption on SMZs and clinoptilolite were determined from the linear adsorption isotherms as shown in Table 4.6.

Table 4.6 The partitioning coefficients of SMZs and clinoptilolite for toluene adsorption

Adsorbent	Partitioning coefficient (L/g)	R ²
clinoptilolite	0.0089	0.9793
SMZ-DOWFAX 8390	0.0272	0.9877
SMZ-DOWFAX 2A1	0.0210	0.9911
SMZ-SDBS	0.0107	0.9886

The results from the adsorption isotherms show that SMZs adsorb an organic solute such as toluene at a much higher amount than unmodified clinoptilolite does. Due to its inorganic nature, the unmodified clinoptilolite has much lower organic content than SMZs which have been organically modified to

become hydrophobic through surfactant adsorption. The hydrophobic region provides a efficient partitioning phase for organic solute. The partitioning coefficients increase has as anionic surfactant adsorbed onto CTAB-modified zeolite more alkyl chain. The uptake of toluene by DOWFAX 8390-CTAB-modified zeolite is higher than by DOWFAX 2A1-CTAB-modified zeolite and by SDBS-CTAB-modified zeolite. This is believed to be caused by the fact that DOWFAX 8390 has one more alkyl chain in a single molecule than the other two surfactants. DOWFAX 2A1 is more disordered than SDBS because DOWFAX 2A1 has branch chain in molecule that DOWFAX 2A1 has higher hydrophobic phase. The result in adsorbing toluene of DOWFAX 2A1 is higher than SDBS. This has been observed in other studies on the adsorption of organic solutes on organically-modified nature adsorbents such as alumina (Deepak Neupane and Jae-woo Park., 1999), clay minerals (Li and Bowman, 1998; Malakul *et al.*, 1998). The results observed in this study clearly show that the highest alkyl chain of surfactant-modified zeolite is the most potential adsorbent for the effective adsorption of organic compound such as toluene.