

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Adsorption of CTAB and DOWFAX 8390 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. The maximum adsorption of CTAB on clinoptilolite was determined as the mean value at the plateau region of the surfactant adsorption isotherm which was approximately 80 μmol of CTAB/gram of clinoptilolite. In addition, the critical micelle concentration (CMC) of surfactant is the aqueous surfactant concentration in equilibrium with the maximum adsorption. The CMC of CTAB adsorbed on clinoptilolite was approximately 960 μM . The adsorption density gives a molecule per area of nearly 4.75 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 .

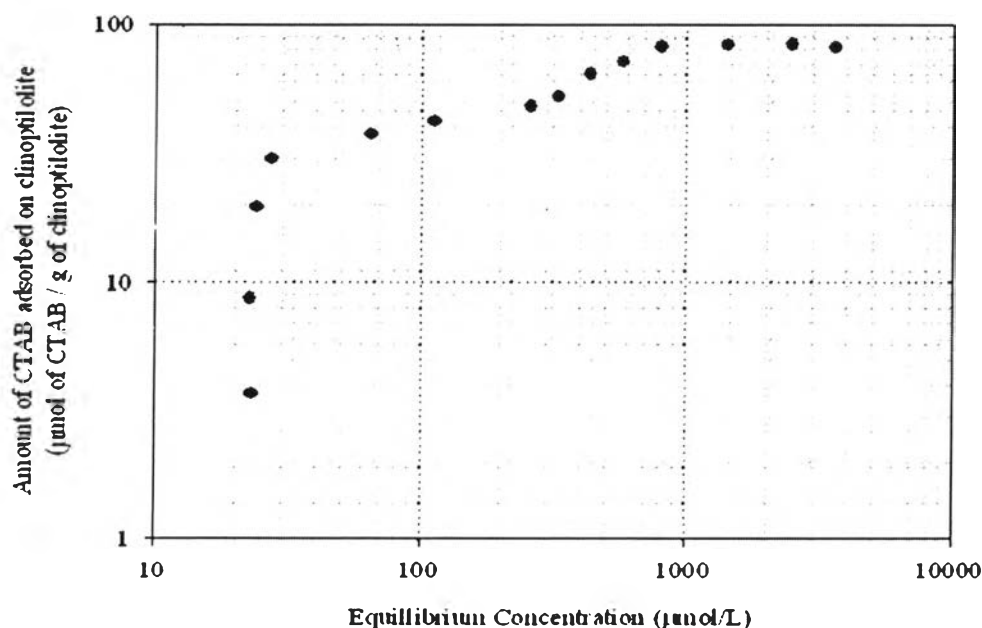


Figure 4.1 Adsorption isotherm of CTAB on clinoptilolite at 30 °C.

From the adsorption isotherm, it cannot clearly indicate the amount of CTAB adsorbed at monolayer on the surface of the zeolite. Consequently, the zeta potential of clinoptilolite surface was 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. Starting from negative charge of the original clinoptilolite surface, the zeta potential becomes less negative upon increasing CTAB loading and eventually became 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 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 40 μmol of CTAB/gram of clinoptilolite, indicates a completed monolayer surface coverage by CTAB.

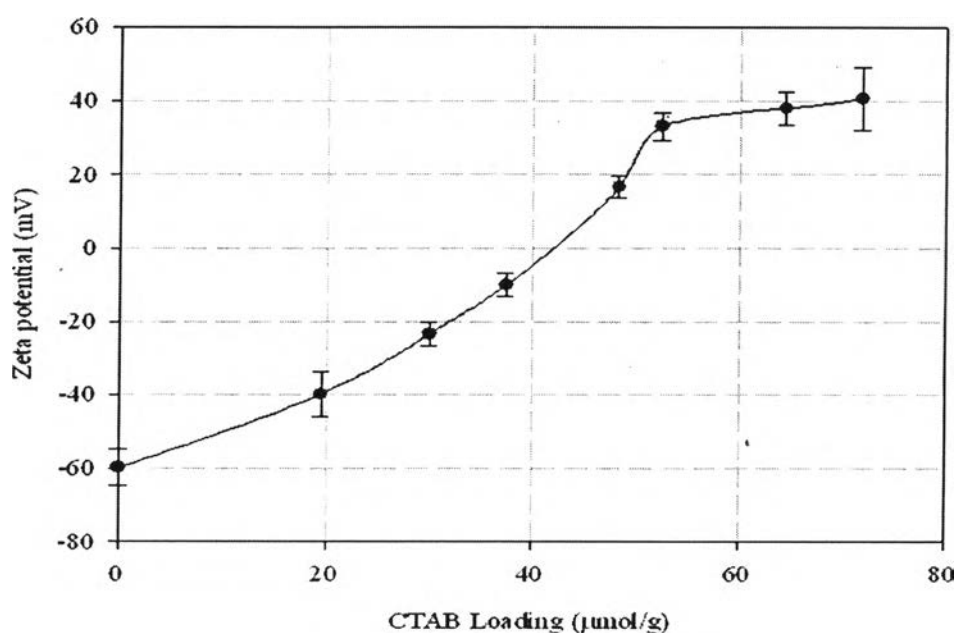


Figure 4.2 Zeta potential of clinoptilolite as a function of CTAB loading.

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 550 μM), SMZ was prepared by further adsorbing DOWFAX to form a mixed layer of the CTAB and DOWFAX on clinoptilolite. Initially, DOWFAX concentration was varied in the range of 1 to 10 times of the initial molar concentration of CTAB. The results showed that the ratio of DOWFAX-to-CTAB of 10:1 yielded the highest adsorption of surfactant on SMZ which is approximately 20 μmol of DOWFAX/g clinoptilolite. The zeta potential of the resulting SMZ having DOWFAX adsorbed on CTAB-modified clinoptilolite was found to be -70.74 mV. The SMZ prepared at this DOWFAX:CTAB ratio of 10:1 was further used in the subsequent studies on the removal of heavy metal and organic contaminants.

4.2 Characterization of Surfactant-Modified Zeolite (SMZ)

In addition to the zeta potential measurement as seen in the previous section, SMZ was also analyzed for its organic carbon content using elemental analyzer (EA) to determine the amount of organic adsorbed on the surface. It was found that, through the surface modification using CTAB and DOWFAX, the organic carbon content of SMZ increased significantly from the original clinoptilolite (5%wt compared to 0.05%wt). SMZ was further characterized by using FTIR to examine the functional groups on the surface. Some fundamental IR absorption frequencies are showed 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} indicate 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} respectively were identified only in SMZ samples. Furthermore, the aliphatic C-O stretching frequency of phenyloxy group in DOWFAX 8390 at 1205 cm^{-1} was also observed only on the surface of SMZ.

Table 4.1 Some fundamental IR absorption frequencies of clinoptilolite and SMZ

Assignments	Band of IR (cm ⁻¹)	
	Clinoptilolite	SMZ
Si-O(Al) stretching	1066	1066
O-H stretching of aluminum hydroxide	3629	3629
C-H stretching of aliphatic group	-	2851
Quarternary amine salts	-	2922
C-O stretching of phenyloxy group	-	1205

4.3 Adsorption of Contaminants in Single-Solute System

4.3.1 Adsorption of Heavy Metal Ions in Single-Metal System

The adsorption of cadmium and lead by SMZ was carried out at ambient temperature of 30°C and at a fixed pH of 5 in order to ensure that the heavy metal ions were in their divalent cation form (Cd²⁺ and Pb²⁺) and to prevent an undesired precipitation of the metal ions. The chemical equilibrium of both heavy metal ions at various pH was calculated by using MEDUSA program (Cortes-Martinez *et al.*, 2004) as shown in Figures 4.3 and 4.4 for cadmium and lead, respectively. From the diagrams, it can be seen that the formation of Cd(OH)₂ occurs at pH above 8 whereas the formation of Pb(OH)₂ occurs at pH above 5.5. At pH 5, both metal ions are present mainly in Cd²⁺ and Pb²⁺ form, and thus, the pH of the adsorption medium was fixed at 5 throughout the study. The initial and final pH values after the adsorption were measured and were found to be nearly the same.

The adsorption isotherms for cadmium (Cd²⁺) and lead (Pb²⁺) by unmodified zeolite (clinoptilolite) and SMZ in single-metal system at 30°C are shown in Figures 4.5 and 4.6, respectively. The initial concentration of heavy metal ions was varied from 0.25 to 5 mM. After equilibrium, the amount of heavy metal ions adsorbed by clinoptilolite and SMZ was determined by AAS and then the adsorption isotherms were constructed. Both adsorption isotherms exhibit a Langmuir-type isotherm showing a sharp increase in the adsorption of both Cd²⁺ and Pb²⁺ in the range of heavy metal concentration between 0–0.5 mM and then the metal adsorption became relatively constant at higher concentrations.

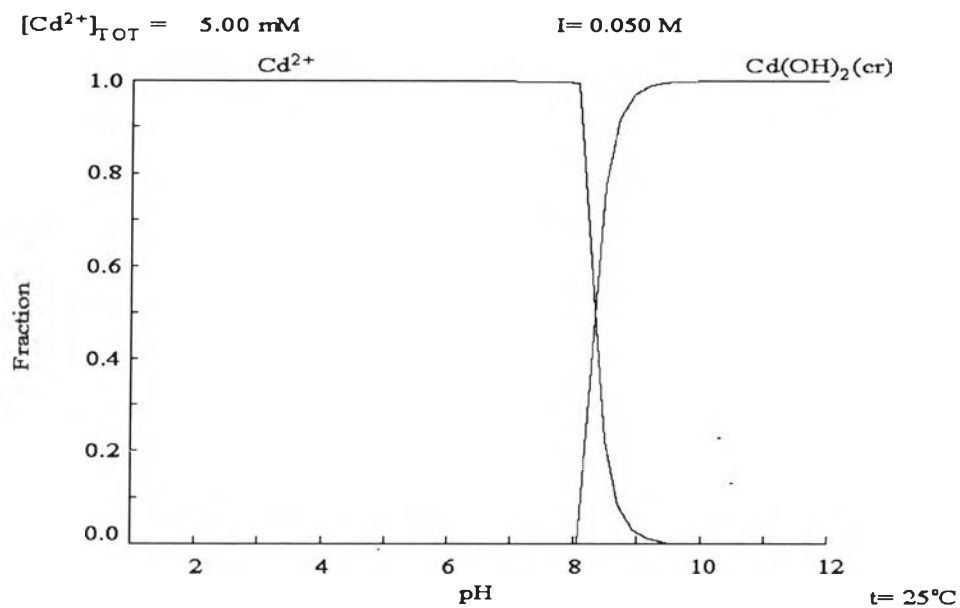


Figure 4.3 Chemical equilibrium diagram for cadmium at various pH.

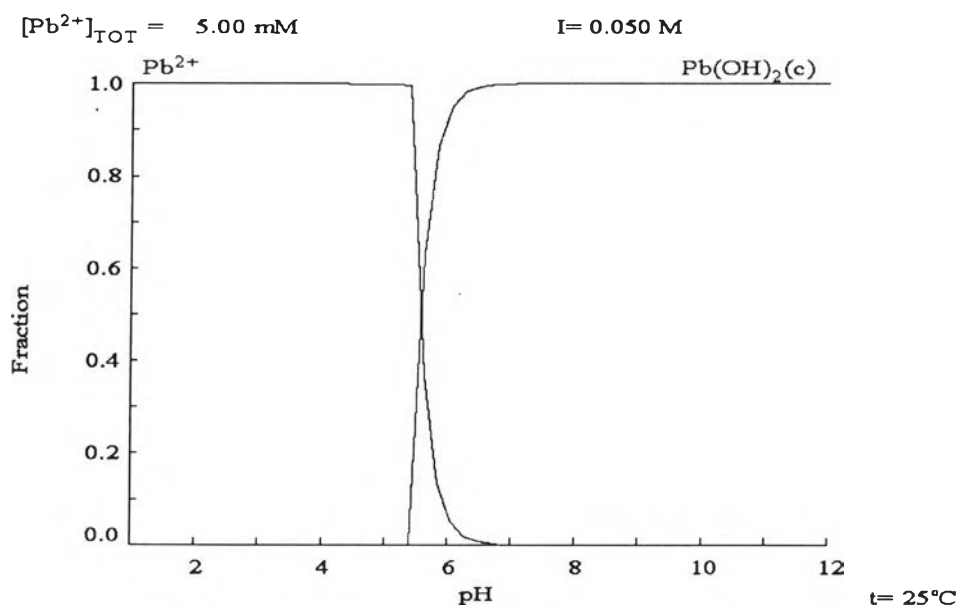


Figure 4.4 Chemical equilibrium diagram for lead at various pH.

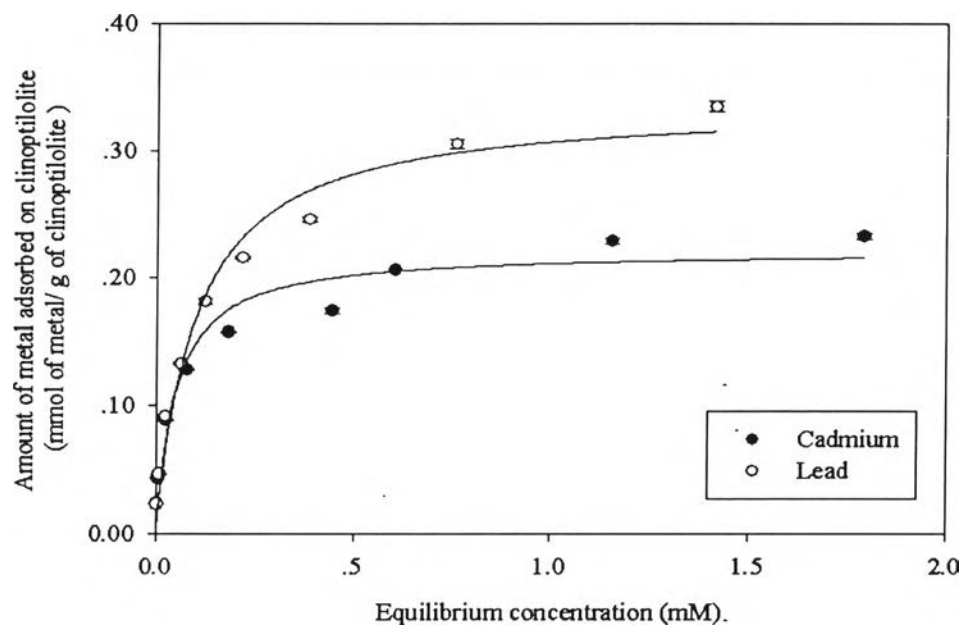


Figure 4.5 Adsorption isotherms of lead and cadmium on clinoptilolite in single-metal system at 30°C and pH 5.

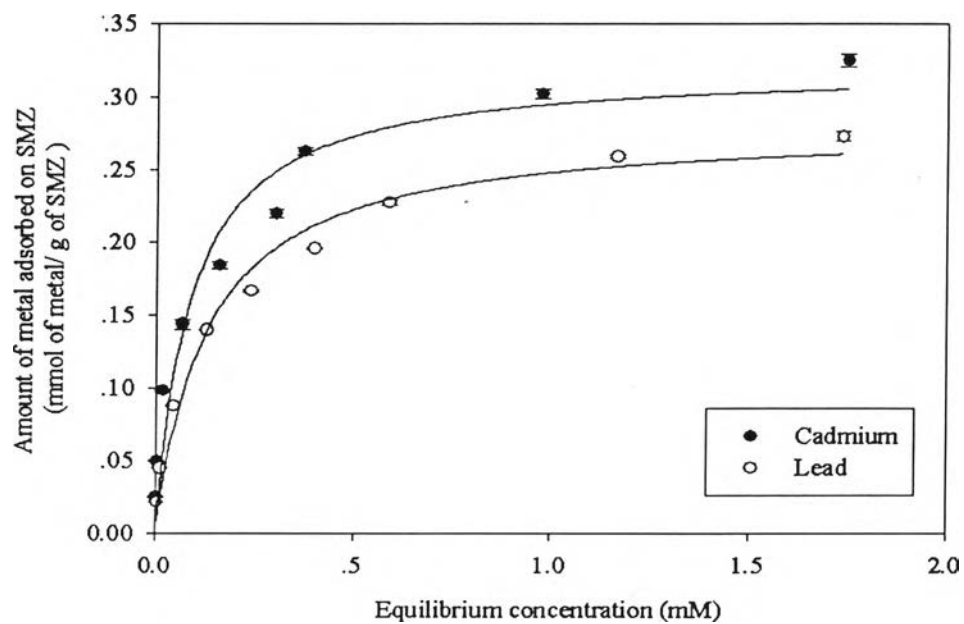


Figure 4.6 Adsorption isotherms of lead and cadmium on SMZ in single-metal system at 30°C and pH 5.

To quantify the adsorption characteristics of the adsorbents, the adsorption data were fitted with a Langmuir adsorption model by a nonlinear regression analysis using Sigma Plot 8.02, the model can be described by the following equation:

$$q = \frac{Q_{\max} C_e}{K + C_e}$$

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 its weight basis whereas K indicates the affinity of the adsorbent towards the adsorbate (e.g., metal ions).

The Langmuir adsorption parameters determined from the isotherms for cadmium and lead adsorption on clinoptilolite and SMZ in single-metal systems are listed in Tables 4.2 and 4.3, respectively.

Table 4.2 Langmuir parameters for the adsorption of lead and cadmium on clinoptilolite in single-metal system

Metal	Q_{\max} (mmol/g)	K (mM)	R^2
Lead	0.33	0.01	0.97
Cadmium	0.22	0.05	0.95

Table 4.3 Langmuir parameters for the adsorption of lead and cadmium on SMZ in single-metal system

Metal	Q_{\max} (mmol/g)	K (mM)	R^2
Lead	0.28	0.13	0.98
Cadmium	0.32	0.09	0.94

From the results, it can be seen that clinoptilolite tends to adsorb lead more than cadmium as shown by a much higher maximum adsorption capacity of lead adsorption than that of cadmium adsorption. Similar results have also been

reported by Ouki and Kavannagh (1999). In contrast, for SMZ, the results show that cadmium is preferentially adsorbed by SMZ than lead. The maximum capacity of cadmium adsorption on SMZ is much higher than that of lead. When comparing between the two adsorbents, clinoptilolite and SMZ, SMZ adsorbs cadmium to a greater extent than clinoptilolite does. The maximum capacity of cadmium adsorption by SMZ is approximately 1.45 times of clinoptilolite. On the other hand, SMZ adsorbs a lesser amount of lead than clinoptilolite does. This can be explained that SMZ and clinoptilolite have different sites for metal adsorption. For clinoptilolite, it possesses negative charges on the surface due to excess oxygen in the silica-alumina framework, and thus, the positively charged metal ions can be adsorbed on the clinoptilolite surface by ion-exchange mechanism. For SMZ, the sulfonate group of DOWFAX adsorbed on SMZ acts as adsorption site for metal ions. In general, the adsorption of transition metals can be explained by hard-soft acid base (HSAB) principle (Shawabkeh *et al.*, 2004). Reactions are more favorable for hard-hard and soft-soft interactions than for a mix of hard and soft in the reactions. 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. Lead has higher electronegativity (1.854) than cadmium (1.521), which yields a harder acid than cadmium. The excess oxygen of clinoptilolite surface is hard base and the sulfonate group of DOWFAX is 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.

4.3.2 Adsorption of Heavy Metal in Mixed-Metal Ions System

Figure 4.7 shows the adsorption isotherms of cadmium and lead on SMZ in mixed-metal system containing both cadmium and lead at pH 5. The initial concentration of metal was varied from 0.25 to 3 mM using an equal normal concentration of cadmium and lead. Langmuir isotherm was also used to describe the adsorption data of mixed-metal system for SMZ and the parameters are shown in Table 4.4. The results from the adsorption in the mixed-metal system show a similar

trend as observed in the single-metal system. SMZ adsorbs cadmium more than lead as shown by the higher adsorption capacity of SMZ for cadmium than lead.

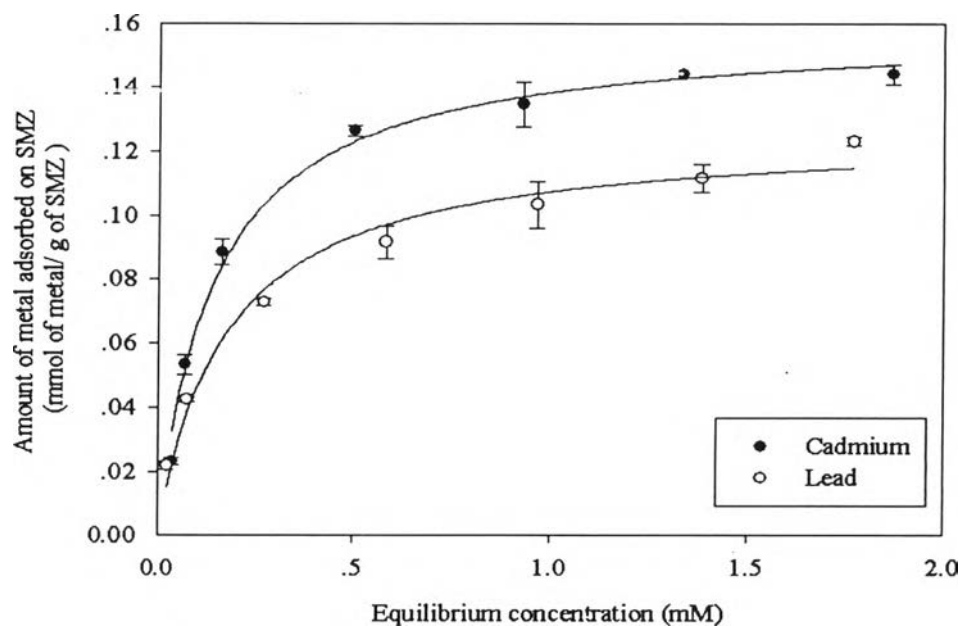


Figure 4.7 Adsorption isotherms of lead and cadmium on SMZ in mixed-metal system at 30°C and pH 5.

Table 4.4 Langmuir parameters for the adsorption of lead and cadmium on SMZ in mixed-metal system

Metal	Q_{\max} (mmol/g)	K (mM)	R^2
Lead	0.13	0.17	0.97
Cadmium	0.16	0.14	0.99

Figures 4.8 and 4.9 show the comparison of the adsorption of cadmium and lead by SMZ in single-metal and mixed-metal systems. The results clearly show that the amount of heavy metal adsorbed in mixed-metal system was lower than in single-metal system. Approximately 50-55% decrease in the adsorption was observed for both cadmium and lead in mixed-metal system when compared to the single-metal system which is possibly due to the competitive between cadmium and lead for the adsorption sites on SMZ in mixed-metal system.

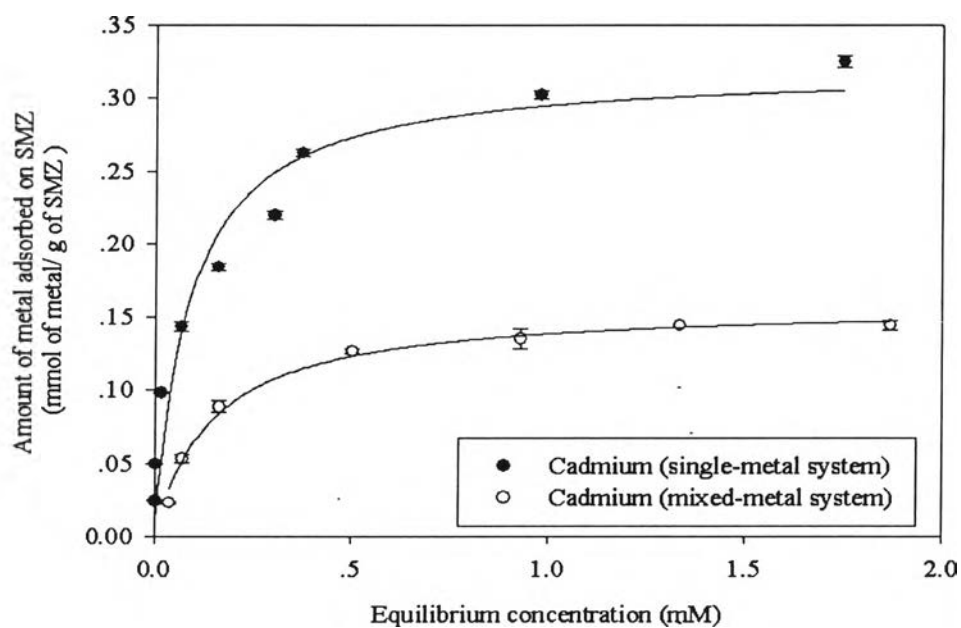


Figure 4.8 Comparison of the amount of cadmium adsorbed on SMZ in single-metal and mixed-metal systems.

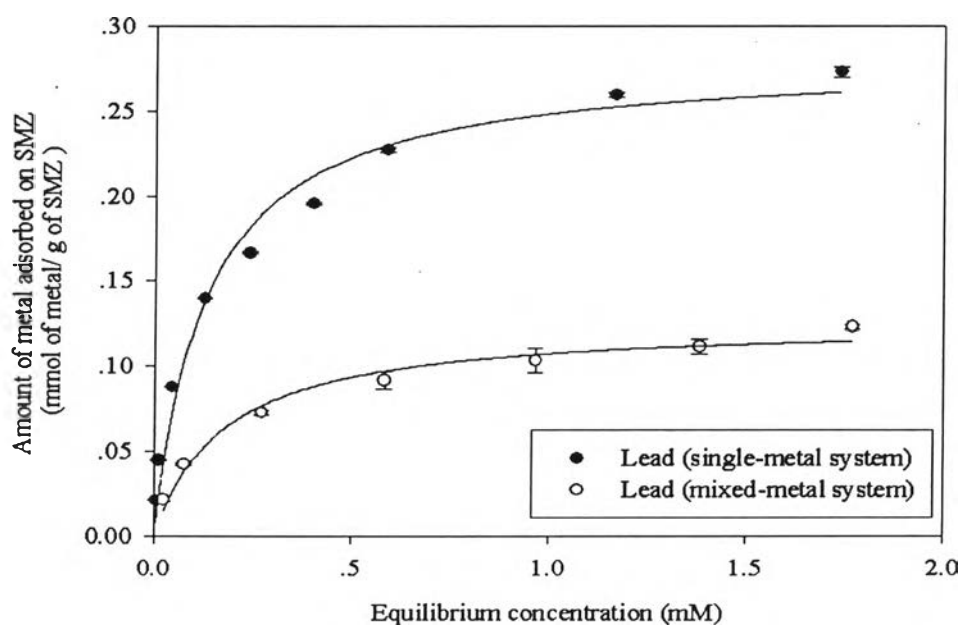


Figure 4.9 Comparison of the amount of lead adsorbed on SMZ in single-metal and mixed-metal systems.

4.3.3 Adsorption of Toluene on SMZ in Single-Solute System

The adsorption isotherms of toluene on SMZ and clinoptilolite are shown in Figure 4.10. It can be obviously seen that the adsorption of toluene on both adsorbents exhibits a linear-type isotherm which can be described by the following equation:

$$q = K_p C_e$$

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 data were fitted with the linear isotherms using linear regression method and the partitioning coefficients for toluene adsorption on both SMZ and clinoptilolite were determined as shown in Table 4.5.

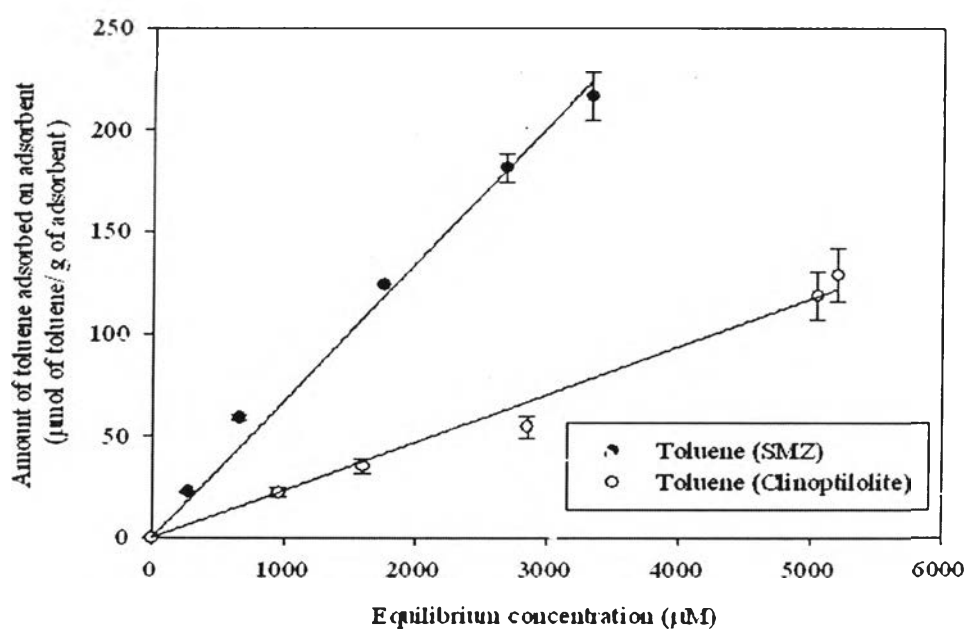


Figure 4.10 Adsorption isotherms of toluene on SMZ and clinoptilolite in single-solute system at 30°C.

Table 4.5 The partitioning coefficients of clinoptilolite and SMZ for toluene adsorption

Adsorbent	Partitioning coefficient	R ²
clinoptilolite	0.023	0.985
SMZ	0.067	0.991

It can be seen that from the adsorption isotherms that SMZ adsorbs organic compound such as toluene at a much higher amount than unmodified clinoptilolite does. The partitioning coefficient of SMZ is approximately 2.87 times higher than that of clinoptilolite. At the same equilibrium concentration, SMZ can adsorb more toluene than clinoptilolite which can be attributed to the surface modification using surfactant. Due to its inorganic nature, the unmodified clinoptilolite has much lower organic content than SMZ which has been organically modified to become hydrophobic through surfactant adsorption. The linear adsorption characteristic reveals that the adsorption of toluene on SMZ is through partitioning of the organic solute to the organic phase of SMZ. This has been observed in other studies on the adsorption of organic solutes on organically-modified natural adsorbents such as clay minerals (Li and Bowman, 1998; Malakul *et al.*, 1998). The results observed in this study clearly show that SMZ is a potential adsorbent for the effective adsorption of organic compound such as toluene.

4.4 Adsorption of Heavy Metal and Organic Contaminants in Mixed-Solute System

In this part of the study, the adsorption of heavy metal (cadmium or lead) and toluene in mixed-solute systems in which both types of contaminants were adsorbed simultaneously by SMZ. Figures 4.11 and 4.12 show the adsorption isotherms of lead and cadmium in the presence of toluene at the concentration of 4000 μM , respectively. The initial metal concentrations used in this experiment was varied from 0.25 mM to 5 mM. The adsorption isotherms were constructed as previously described.

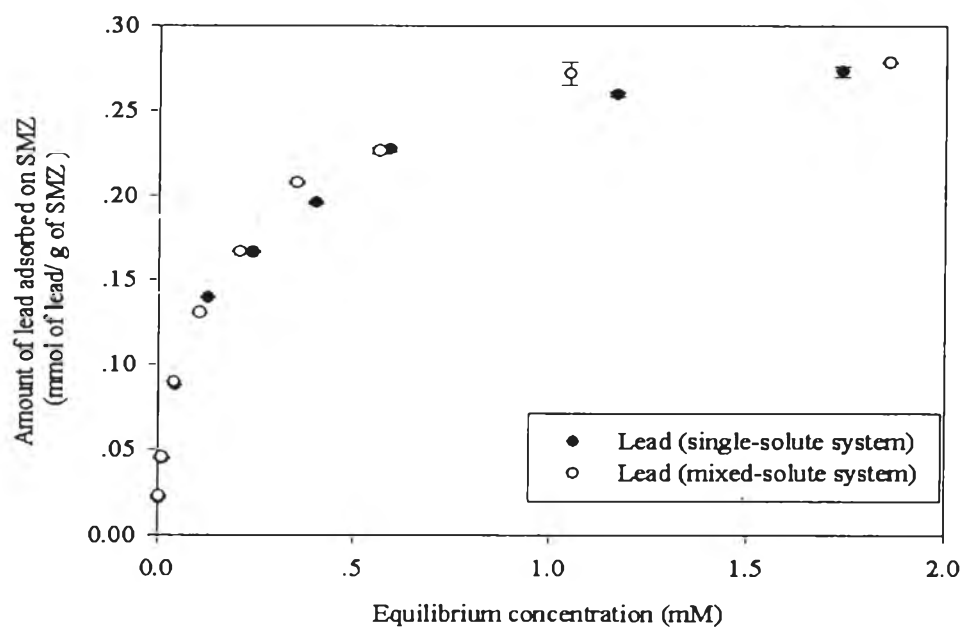


Figure 4.11 Adsorption isotherms of lead on SMZ in mixed-solute system at 30°C and pH 5.

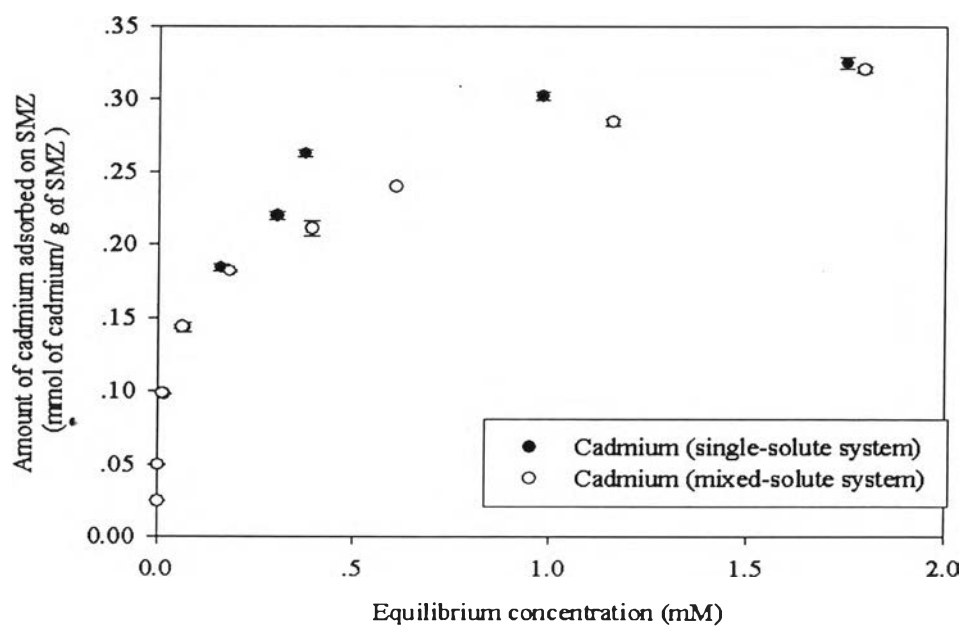


Figure 4.12 Adsorption isotherms of cadmium on SMZ in mixed-solute system at 30°C and pH 5.

The results showed that the adsorption of both metals in mixed-solute system was quite similar to those observed in single-solute system where only metal ions were present. Only slight decrease in the adsorption of cadmium was observed which has also been observed by Vaca-Mier *et al.* (2001) where they reported 3-5% decrease in the adsorption of cadmium and lead by clinoptilolite in the presence of phenol. This can be explained that metal ions and toluene adsorb onto different sorption sites of SMZ: hydrophilic and hydrophobic sites. The hydrophilic sulfonate group of DOWFAX on SMZ provides an adsorption site for metal ions whereas the hydrophobic part of SMZ, the adsorbed organic phase of CTAB and DOWFAX, provides adsorption site for toluene partitioning. For toluene adsorption, Figure 4.13 shows the comparison of the adsorbed amount of toluene between the single-solute and mixed-solute systems. The results showed that in the presence of heavy metal, the amount of toluene adsorbed by SMZ was approximately 20% higher than that observed in the absence of metal ions. It can be explained that, due to its slightly polar nature, toluene can adsorb into both core and palisade regions of the organic phase of SMZ (Pradubmook *et al.*, 2003), the adsorption of heavy metal onto the hydrophilic (polar) part of SMZ may reduce the polarity of the palisade region, thus allowing more toluene molecules to solubilize into the organic phase of SMZ.

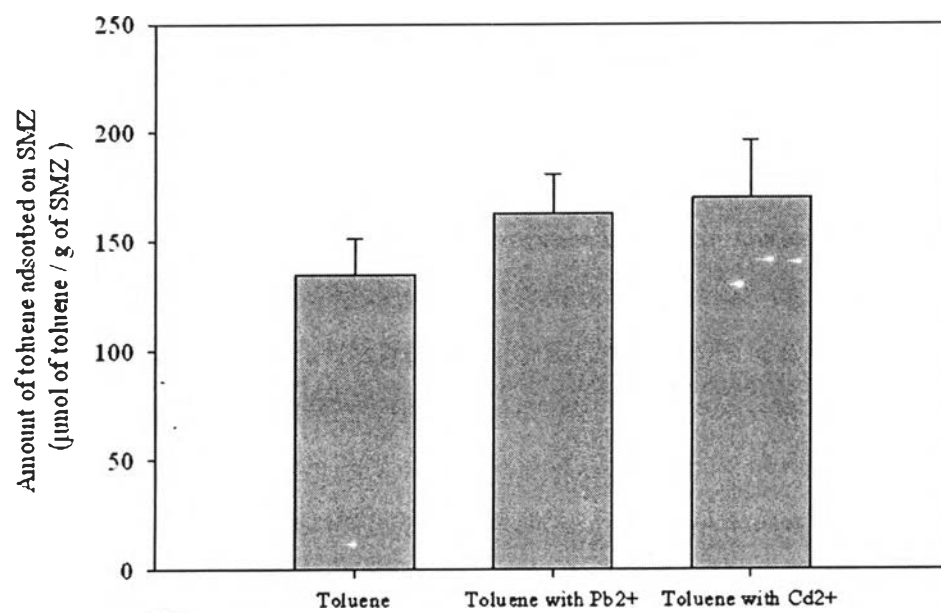


Figure 4.13 Comparison of the amount of toluene adsorbed on SMZ in single-solute and mixed-solute systems.