CHAPTER IV

RESULTS AND DISCUSSION

4.1 CTAB Adsorption on Clinoptilolite

The adsorption isotherm of cetyltrimethylammoniumbromide (CTAB) on clinoptilolite at 25°C is shown in Figure 4.1. The maximum adsorption of CTAB on clinoptilolite is approximately 80 μmol of CTAB/gram of clinoptilolite.
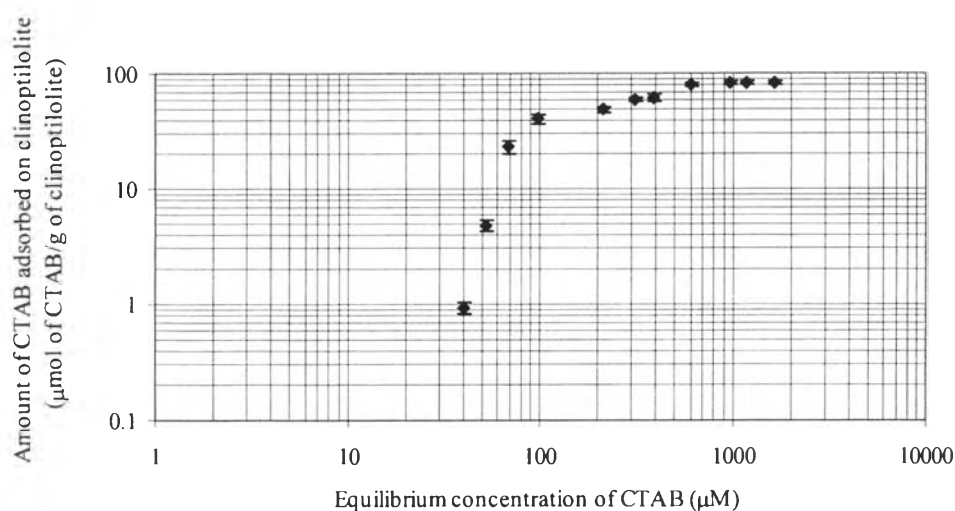

Figure 4.1 Adsorption isotherm of CTAB on clinoptilolite at 25°C.

After the adsorption isotherm of CTAB on clinoptilolite was constructed, the zeta potential of the surface was measured in order to find the amount of CTAB loading that provided a completed monolayer adsorption of CTAB on clinoptilolite. Figure 4.2 shows the zeta potential of clinoptilolite as a function of CTAB loading. The results show that zeta potential becomes less negative with increasing CTAB loading and eventually becomes positive. The point of zero charge (pzc) is approximately 38 to 40 μmol of CTAB/gram of clinoptilolite which indicates a completed monolayer surface coverage by CTAB. This can be explained by the fact that the negatively charged surface of clinoptilolite progressively loses its negative charge with increasing CTAB adsorption and becomes more hydrophobic as the pzc is approached. Beyond the neutral point, adsorbed CTAB molecules form a second

layer on the surface via tail-tail interaction with the positively charged head group oriented outwards from the surface, thus reversing the surface charge.
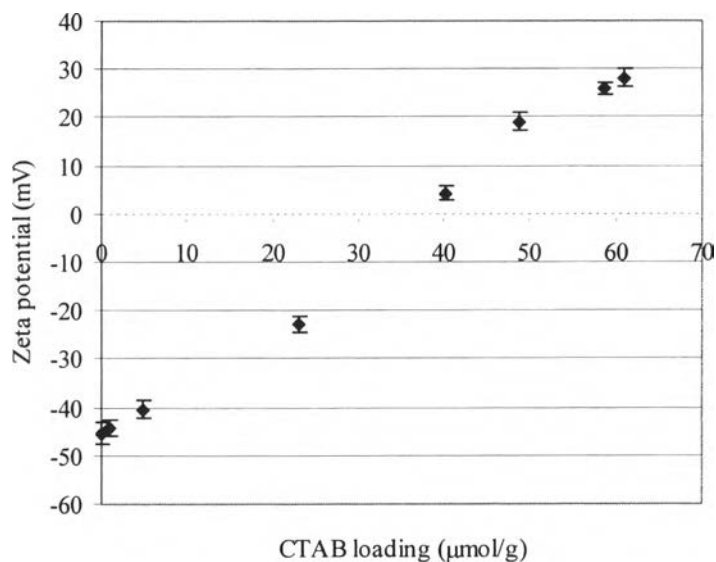

Figure 4.2 Zeta potential of clinoptilolite as a function of CTAB loading.

4.2 Characterization of Surfactant-Modified Zeolite (SMZ)

The first step in preparing SMZ was achieved through the monolayer adsorption of CTAB on clinoptilolite surface, thus causing the surface to become highly hydrophobic. After CTAB adsorption, the surface was further modified by adsorbing palmitic acid with various initial molar ratios of palmitic acid to CTAB. The resulting SMZ with various PA:CTAB loading ratios was then subjected to surface characterization using FTIR and EA.

The FTIR studies were carried out to identify the functional groups on the surface of SMZ. Some fundamental IR absorption frequencies of clinoptilolite and SMZ with various metal ligand:surfactant loading ratios are shown in Table 4.1. The spectra obtained from both clinoptilolite and SMZ show IR absorption frequency at 3631 cm^{-1} representing the OH stretching of aluminum hydroxide of the base zeolite. The vibrational frequencies of the C-H stretching of aliphatic (2851 cm^{-1}) and the N-H stretching of quaternary amine salt (2919 cm^{-1}) were identified only in SMZ samples, which are characteristic frequencies of CTAB and palmitic acid. Moreover,

the C=O stretching of COO⁻ (1577 cm⁻¹) in palmitic acid was shown only in SMZ
(1:1), SMZ (2:1) and SMZ (4:1), but not in SMZ (0:1) where palmitic acid was not
added.

Table 4.1 Some fundamental IR absorption frequencies of clinoptilolite and various
SMZ with various PA:CTAB loading ratios

Clinoptilolite	SMZ (PA:CTAB)				Assignments
	(0:1)	(1:1)	(2:1)	(4:1)	
3631	3631	3631	3631	3631	O-H stretching of aluminum hydroxide
-	2851	2851	2851	2851	Aliphatic C-H stretching
-	2919	2919	2919	2919	Quarternary amine salts
-	-	1577	1577	1577	C=O stretching of COO⁻

All frequencies in cm⁻¹

Table 4.2 The organic carbon contents of SMZ with various PA:CTAB loading
ratios

SMZ	C content, wt %	μmol/g	mole ratio of PA:CTAB adsorbed
(0:1)	0.955	41.885[a]	-
(1:1)	1.481	41.885[a]/27.370[b]	0.653
(2:1)	1.869	41.885[a]/44.895[b]	1.072
(4:1)	2.473	41.885[a]/78.775[b]	1.881
(6:1)	2.479	41.885a/79.375[b]	1.895

[a] μmoles of CTAB/g of SMZ. [b] μmoles of PA/g of SMZ

The organic carbon contents of SMZ with various PA:CTAB loading ratios
are shown in Table 4.2. The results show that the organic carbon content increases
with increasing metal ligand/surfactant loading ratio. This confirms that palmitic
acid can bind to clinoptilolite-CTAB surface through a mixed bilayer formation. The
amount of CTAB in SMZ, as calculated from the organic carbon contents of SMZ
(0:1), is 41.885 μmol/g of SMZ (0:1) which corresponds to 40.282 μmol of CTAB/g
of clinoptilolite. The amount of metal ligands (PA) in SMZ can be calculated from

the excess organic carbon after subtracting the organic carbon content due to CTAB. It was found that SMZ (1:1), SMZ (2:1), SMZ (4:1) and SMZ (6:1) contain 27.370, 44.895, 78.775 and 79.375 μmol of PA/g of SMZ, respectively. The results shown in Table 4.2 also reveal the mole ratio of PA to CTAB in SMZ increases with increasing metal ligand loading. When PA:CTAB loading ratio is increased beyond 4 to 1 (i.e., 6:1), the amount of adsorbed PA and the mole ratio of PA to CTAB in SMZ are nearly the same as SMZ (4:1). This indicates that, at a loading ratio higher than 4:1, the binding of palmitic acid to CTAB modified surface of clinoptilolite, which occurs through hydrophobic interaction between tail of palmitic acid and tail of adsorbed CTAB, is not strong and thus allows the weakly adsorbed PA on SMZ was washed out with DI water during the washing step. Therefore, the maximum adsorption of PA on modified clinoptilolite surface occurs at PA:CTAB loading ratio of 4:1. The adsorbed CTAB and PA on SMZ at this ratio and lower has shown to be quite stable through several washing cycles with DI water as the adsorbed amounts remain relatively constant during the experimentation.

4.3 Contaminants Adsorption on SMZ in Single System

4.3.1 Cadmium Adsorption on SMZ

Figure 4.3 shows adsorption isotherms of cadmium on SMZ with various PA:CTAB loading ratios. The results obtained from the isotherms clearly reveal the significant effect of metal ligand/surfactant loading ratios on cadmium adsorption. The uptake of cadmium by SMZ increased significantly with increased loading of metal ligand on the SMZ surface. At the same equilibrium concentration, SMZ (4:1) adsorbed Cd^{2+} approximate 5 times higher than SMZ (0:1). When loaded with only surfactant, SMZ (0:1) adsorbed very little cadmium, as expected since the modified surface has become very hydrophobic. The amount adsorbed is probably due to the interaction of Cd^{2+} ions with some parts of clinoptilolite surface, which remain uncovered by CTAB.

The adsorption results exhibit a Langmuir-type isotherm which can be described by the following equation:

$$q = \frac{Q_{max}C_e}{K + C_e} \tag{4.1}$$

where q is the amount of cadmium adsorbed (mg/g of adsorbent), C_e is an equilibrium cadmium concentration (μM), Q_{max} is the maximum capacity of the adsorbent (mg/g), and K is the affinity constant (μM). The adsorption parameters of the adsorbents were determined and are summarized in Table 4.3. 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 adsorbent with good performance in adsorbing the adsorbate should have high adsorption capacity (Q_{max}) and low K value, indicating that high adsorbed amount can be achieved at low concentration.
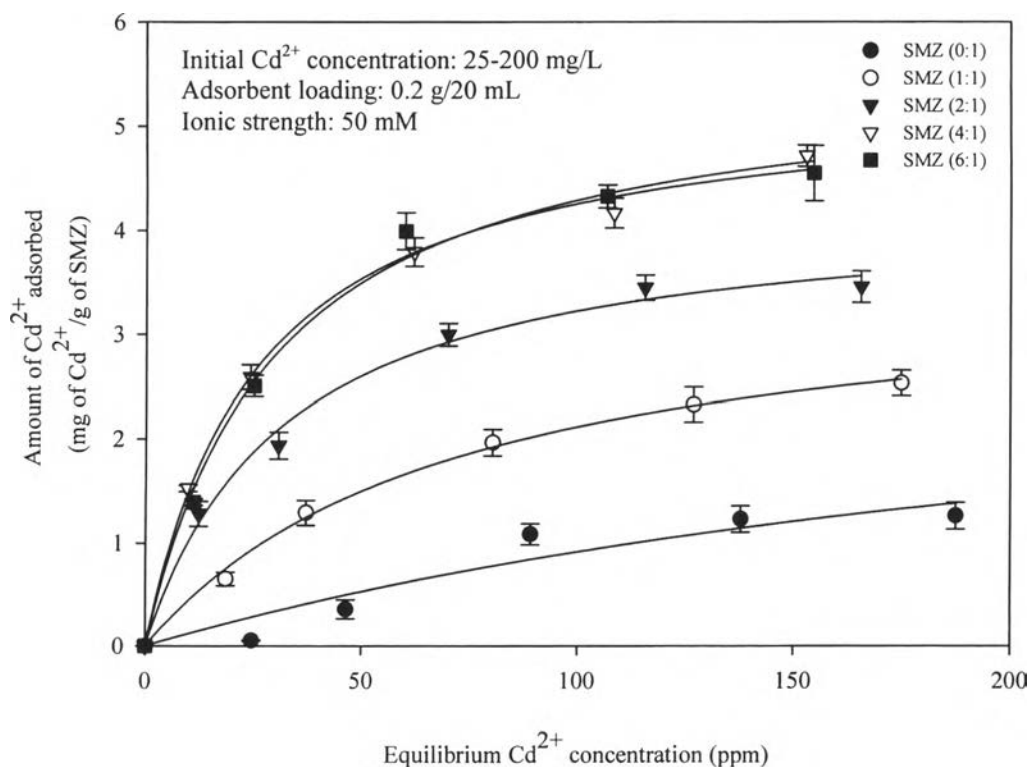

Figure 4.3 Adsorption isotherms of cadmium on SMZ with various PA:CTAB loading ratios at pH 7.

Table 4.3 Langmuir parameters for the adsorption of cadmium on SMZ with various PA:CTAB loading ratios

SMZ(PA:CTAB)	Q_{max} (mg/g)	K (μM)
SMZ(0:1)	3.34	2360.00
SMZ(1:1)	3.60	625.70
SMZ(2:1)	4.25	284.10
SMZ(4:1)	5.22	226.60
SMZ(6:1)	5.55	260.94

It can be seen from this table that SMZ with no metal ligand (SMZ (0:1)) shows the lowest performance in cadmium adsorption as indicated by lowest Q_{max} and largest K. SMZ with loading ratio of 4:1 (SMZ (4:1)) and 6:1 (SMZ (6:1)) are quite comparable in their adsorption performance. Although SMZ (6:1) shows slightly higher Q_{max} than SMZ (4:1) but its affinity (K) is not as good as that of SMZ (4:1). Therefore, SMZ with loading ratio of 4:1 in the initial mixture showed the highest adsorption among all SMZ studied as indicated by the high Q_{max} of 5.22 mg/g and the lowest K of 226.60 μM. The small K value indicates that this SMZ has both high adsorption capacity and affinity for heavy metal ions.

4.3.2 Toluene Adsorption on SMZ

The adsorption isotherms of toluene on SMZ with various PA:CTAB loading ratios are shown in Figure 4.4. From the results, it can be seen that the adsorption of toluene by SMZ with various loading ratios were quite similar and all exhibit a linear relationship between the amount of toluene adsorbed and toluene equilibrium concentration. This clearly reveals that the mechanism of toluene adsorption on SMZ is through partitioning of the organic solutes to the organic phase of SMZ. This has been observed in other studies on the adsorption of organic solutes on modified natural adsorbents (Stephen *et al.*, 1988, Li and Bowman, 1998).

A slight decrease in the adsorption of toluene was observed as the loading ratio was increased. This suggests that toluene adsorption depends not only on the organic carbon content of the adsorbent but also on the configuration of the bound organic phase. Apparently, toluene is more efficiently partitioned into the

bound organic phase when it is present in monolayer configuration of CTAB (SMZ (0:1)) than when it is present in bilayer comprising CTAB and PA. It is likely that increasing metal ligand/surfactant loading leads to tighter packing of the interlayer adsorbed on SMZ surface, thus the effective volume of the hydrophobic core of the mixed bilayer for toluene becomes smaller. Therefore, the toluene adsorption decreases as the effective volume of the hydrophobic core decreases or due to increasing amounts of metal ligand loading on SMZ surface as seen in this part of the study. Similar results were previously observed by Li and Bowman (1998) who studied the adsorption of perchloroethylene by surfactant-modified zeolite.
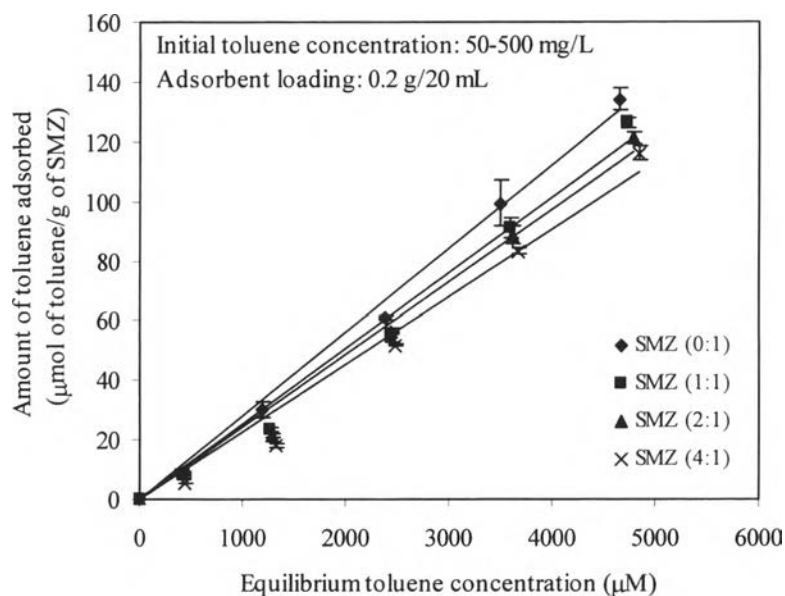

Figure 4.4 Adsorption isotherms of toluene on SMZ with various PA:CTAB loading ratios at pH 7.

4.4 Contaminants Adsorption on SMZ in Mixed System

From the cadmium and toluene adsorption in single-solute systems by SMZ with various PA:CTAB loading ratios seen in the previous sections, SMZ (4:1) adsorbent shows the best performance in the cadmium adsorption and gives similar adsorption capacity for toluene as compared to other SMZ adsorbents. Therefore, SMZ (4:1) was chosen to be further studied in mixed-solute systems. The

experiments were carefully designed to study the simultaneous adsorption of cadmium and toluene in mixed-solute systems with three different molar ratios of the two solutes of 3:1, 1:1 and 1:3.

Figures 4.5 and 4.6 show the comparison of the cadmium and toluene adsorption between single-solute and mixed-solute systems of toluene/cadmium at three different molar ratios of solutes, respectively. For cadmium adsorption shown in Figure 4.5, the results obtained from all three ratios clearly revealed that the presence of toluene in the mixed system does not affect the adsorption of cadmium; this can be seen from the fact that the amount of adsorbed cadmium is very similar to that obtained in the single-solute system. This is due to the difference in the sorption sites for cadmium and toluene on SMZ. Cadmium ions get adsorbed on the carboxylic sorption sites of the PA whereas toluene is partitioned to the bilayer organic phase of PA and CTAB on SMZ.
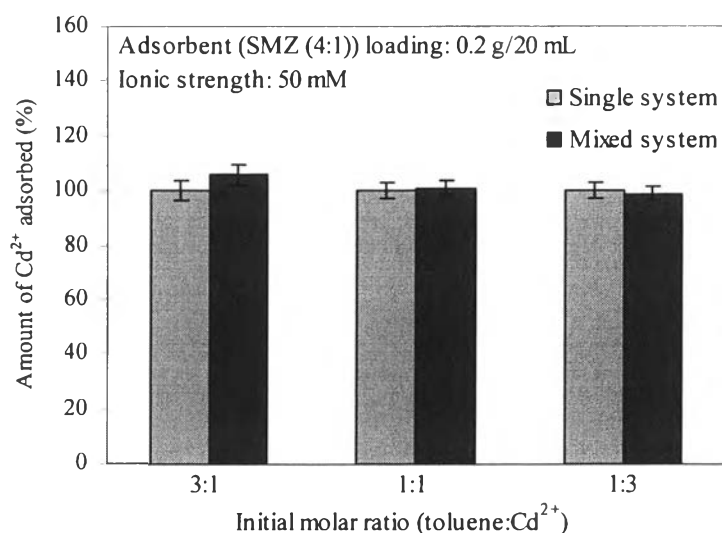

Figure 4.5 Comparison of the amount of Cd^{2+} adsorbed on SMZ in single-solute and mixed-solute systems.

In contrast to the cadmium adsorption, an approximately 20% increase in the amount of adsorbed toluene in the mixed-solute system was observed in all mixed-solute ratios (Figure 4.6). It is speculated that, due to the slightly polar nature of toluene, toluene can partition to both the hydrophobic core and the palisade layer of the adsorbed surfactant layer (Pradubmook *et al.*, 2003). In the cosorption of two

solutes, the adsorption of cadmium on the metal ligand may decrease the charged nature of the palisade layer, thus allowing more toluene molecules to solubilize into the bound organic phase on SMZ.
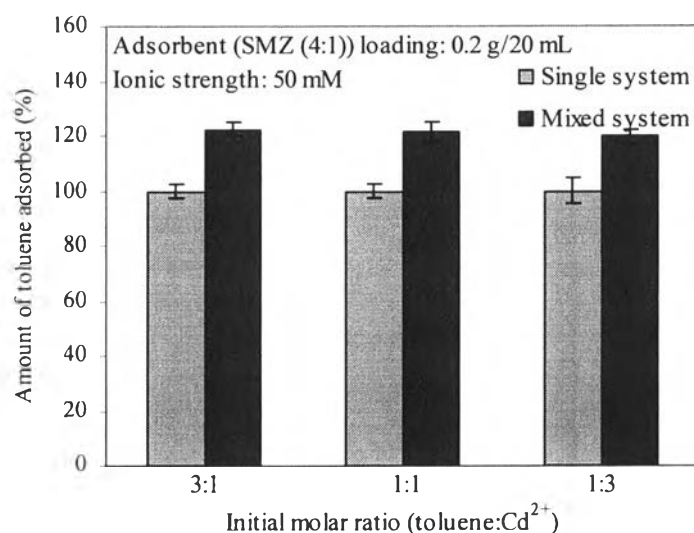

Figure 4.6 Comparison of the amount of toluene adsorbed on SMZ in single-solute and mixed-solute systems.

4.5 Regeneration and Reuse of SMZ

For the practical application of SMZ, it is important to study the ability to regenerate and reuse the SMZ. In this part of the study, attempts have been made to regenerate SMZ using techniques based on properties of the adsorbates and the adsorption mechanisms. Although there are several regeneration techniques available, two simple techniques were employed in this study since the main purpose was to see if the regenerated SMZ could be reused and to evaluate its performance with respect to the fresh SMZ.

For the regeneration of SMZ saturated with toluene, since toluene is a volatile organic compound, the regeneration of SMZ saturated with toluene could easily be done by using a simple air stripping technique. After toluene sorption for 48 hr, compressed air was purged into the adsorption solution overnight to promote air stripping of the volatile toluene. Figure 4.7 shows the adsorption and desorption of toluene using SMZ (4:1) as a model SMZ. The results indicated that most of the

adsorbed toluene was stripped off by air during regeneration step. Since all adsorbed toluene can be removed from SMZ, the adsorbent has been further evaluated for a reuse in toluene adsorption. The second and the third adsorption cycles reveal that SMZ can be reused with a small loss in efficiency. This may be due to lose of palmitic acid and CTAB molecules from the surface upon purging and rinsing. Approximately 91 and 86% of the initial adsorption capacity of SMZ could be obtained in the second and the third adsorption cycle, respectively. Parallel experiments showed that approximately 5% of the organic carbon content loses from the SMZ during the desorption cycle.
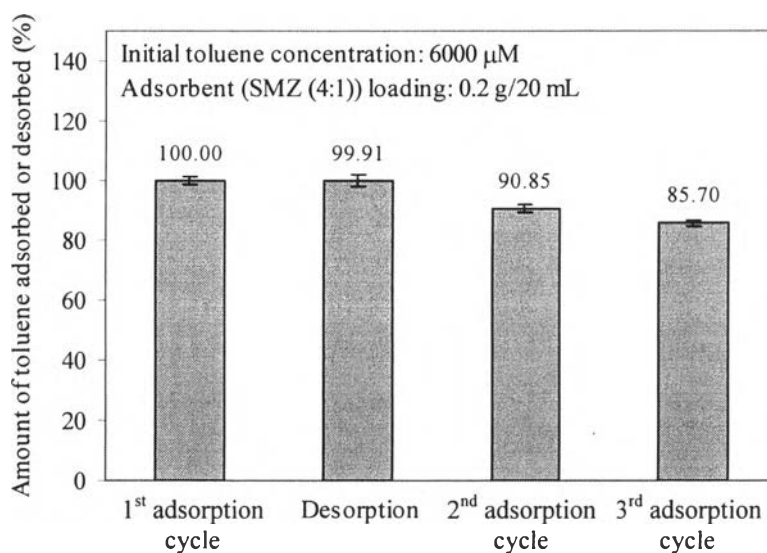

Figure 4.7 Adsorption and desorption of toluene by SMZ (4:1).

For the regeneration of cadmium saturated SMZ, since cadmium is adsorbed on the carboxylic functional group of palmitic acid which has pK_a ~6, the regeneration of SMZ saturated with cadmium could be achieved by lowering the pH. At a pH lower than pK_a of palmitic acid (pH<6), the carboxyl groups of palmitic acid are protonated, and thus sorbed metal ions can be released or desorbed. The adsorption and desorption of cadmium by SMZ are shown in Figure 4.8. It can be seen that only approximately 40% of the total adsorbed cadmium ions was released from SMZ when using pH 1.5. A parallel experiment using TOC reveals only 2% of the organic carbon content lost from the SMZ during the desorption. After adsorbed

cadmium ions can be removed from SMZ, the adsorbent has been further evaluated for a reuse in subsequent cadmium adsorption cycle. Approximately 3.893 and 3.336 mg of Cd^{2+}/g of SMZ or 83 and 71% of the initial adsorption capacity of SMZ are obtained in the second and the third adsorption cycle, respectively. The adsorbed amounts in the 2nd and 3rd cycles are higher than expected values based on the amount of cadmium released from SMZ upon regeneration/desorption. It is speculated that, after the first adsorption and desorption cycle, the modified surface of SMZ may have changed such that it affects the adsorption in the subsequent cycles. This speculation has been supported by the zeta potential study which reveals the change in zeta potential of the regenerated SMZ, suggesting that the rearrangement of the ligand on SMZ surface may have occurred. Further evaluation of this observation was beyond the scope of the current work, and should be further explored in future research.
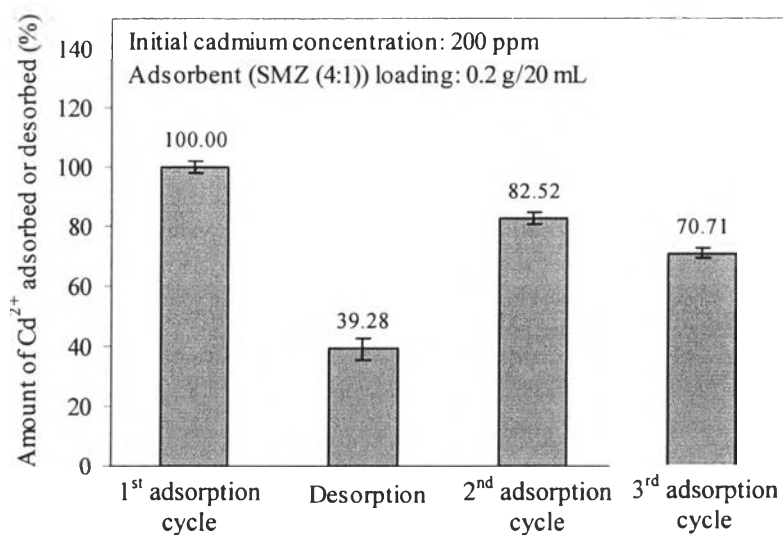

Figure 4.8 Adsorption and desorption of cadmium by SMZ (4:1).