Simultaneous Removal of Heavy Metal and Organic Contaminants by Adsorption Using Surfactant-Modified Zeolite (SMZ)
On-line Number 959
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ABSTRACT

In this study, several surfactant-modified zeolite (SMZ) adsorbents were prepared from a naturally occurring zeolite, clinoptilolite, using a surface modification technique by forming a bilayer of a cationic surfactant (CTAB) and metal ligand such as palmitic acid (PA) on the zeolite surface. These SMZ adsorbents were further evaluated for their adsorption characteristics for heavy metal and organic contaminants as a function of metal ligand to surfactant loading ratio. The results showed that the adsorption of cadmium by SMZ was strongly affected by PA/CTAB loading on the SMZ. The cadmium uptake increased with increasing PA/CTAB loading ratio in the range of 1:1 to 4:1. In contrast, the adsorption of toluene slightly decreased with increasing PA/CTAB loading on the SMZ. In the mixed-solute systems where cadmium and toluene were adsorbed simultaneously, higher adsorption was observed in the case of toluene but not in cadmium adsorption. The regeneration of the SMZ was also demonstrated and the regenerated SMZ was shown to be reusable for several adsorption cycles with an acceptable loss in the adsorption capacity.

KEYWORDS
Surfactant-modified zeolite/ Wastewater treatment/ Separation process

INTRODUCTION

Wastewater generated from chemical and petrochemical industries is a major source of organic and heavy metal pollutants, which seriously affect all living elements in the environment because of their toxicity. For several years, various natural adsorbents such as clay minerals, activated carbon and zeolite have been used as economical adsorbents to remove heavy metals and hydrocarbons from contaminated wastewater (Ouki and Kavannagh, 1999; Sismanoglu and Pura, 2001). However, due to their inorganic nature, these natural adsorbents have limitations for the treatment of mixed wastes because of their poor capacity for organic adsorption. Now, there are two techniques to be used to modify the organic sorption property of natural adsorbents. For the first technique, the surface of natural adsorbent is modified by using cationic surfactant to form bilayer configuration of cationic surfactant on the natural adsorbent surface (Bowman et al., 1994). The formation of cationic surfactant bilayer provided the organic partitioning phase for sorption of toxic organic such as perchloroethylene and these adsorbent can be adsorbed only anion form of heavy metal such as chromate ($\text{CrO}_4^{2-}$) (Li and Bowman, 1998). Nevertheless, the metal sorption on these adsorbent is not selective because of the simple ion exchange mechanism, thus high ionic strength inhibits heavy metal sorption. Moreover, the second technique is called a two-step surface modification. In the first step, cationic surfactant is used to modify natural adsorbent surface by ion exchange mechanism to form monolayer, thus causing the natural adsorbent...
surface to become strongly hydrophobic. For the second step, the modified-zeolite surface from the first step can be further used to anchor metal ligand such as a long chain carboxylic acid through hydrophobic interactions to form a surfactant-modified zeolite (SMZ). The metal is expected to sorb onto SMZ through the formation of a metal complex. In addition, the organic region of the SMZ also provides an adsorption region for organic compounds (Saengchote, 2003). Thus, these SMZ can potentially be used to treat mixed wastes containing both heavy metals and toxic organic compounds (Malakul et al., 1998).

This research work focused on the preparation of surfactant-modified zeolite (SMZ) by using a simple two step surface modification technique and the adsorption characteristics of surfactant-modified zeolite (SMZ) for heavy metal and organic contaminants. The study investigated the adsorption capacity of SMZ for both contaminants as a function of metal ligand loading. SMZ were first prepared with various surfactant/metal ligand loadings. Batch liquid adsorption experiments were then carried out to examine the adsorption characteristics of SMZ for heavy metal and organic contaminants in single and mixed systems. In addition, SMZ saturated with heavy metal and organic contaminants was regenerated for reuse with the adsorption efficiency compared to its original capacity.

MATERIALS AND METHODS

The natural zeolite (clinoptilolite) used in this study was purchased from Marineland (Moorpark, CA). To obtain a particle size of 0.42-0.83 mm, the clinoptilolite was ground and sieved by using 20 and 40 mesh. Cetyltrimethylammonium-bromide or CTAB (C_{16}H_{32}BrN) and palmitic acid (C_{16}H_{32}O_{2}) were used as the surface modifying agents to modify clinoptilolite surface. CTAB with a purity of 98%, was purchased from Aldrich (Milwaukee, WI) and palmitic acid with a purity of 90%, was purchased from ACROS (New Jersey, NJ). Both chemicals were used without further purification. To study adsorption characteristic of SMZ for heavy metal and toxic organic, cadmium chloride and toluene were used as model compounds, respectively. Cadmium chloride (CdCl_{2} \cdot 2\frac{1}{2}H_{2}O) and toluene (C_{6}H_{5}CH_{3}) with a purity of 99.5%, were purchased from Carlo Erba (Milan, Italy).

Adsorption isotherm of cetyltrimethylammoniumbromide (CTAB) on clinoptilolite

An adsorption isotherm was constructed from batch adsorption data to determine the CTAB sorption on clinoptilolite at various CTAB concentrations. 0.2 g of clinoptilolite was mixed with 20 ml of CTAB aqueous solution in 24-ml screw-cap glass vial. The initial CTAB concentration was in the range of 50-6000 µM. Vials were equilibrated on a shaker at 150 rpm at 25°C for 8 hours, which was found to be sufficient to achieve equilibrium (Li and Bowman, 1997). After equilibration, the supernatant was separated from the mixture by syringe filter. The adsorption of CTAB onto clinoptilolite was quantified by measuring the surfactant concentration before and after equilibration using a total organic carbon (TOC) analyzer (Shimadzu, model 5000 A). A simple mass balance was performed to determine the amount of CTAB adsorbed onto the clinoptilolite. The adsorption isotherm was then constructed by plotting the amount of CTAB adsorbed on clinoptilolite (µmol/g) versus the equilibrium concentration of CTAB in the solution (µM).
Preparation of surfactant-modified zeolite (SMZ)

The first step of surface modification is surfactant adsorption. CTAB was used to replace the counterion on the exchange sites of the clinoptilolite, thus converting the clinoptilolite surface to become strongly hydrophobic. Clinoptilolite was initially treated with CTAB solution at an equilibrium CTAB concentration sufficient to provide a complete monolayer adsorption of CTAB on clinoptilolite. The mixture of clinoptilolite and CTAB solution was agitated at 25°C and 150 rpm for 8 hours and then the mixture was centrifuged for phase separation. The second step is ligand adsorption. Modified-clinoptilolite obtained from the first step was reacted with palmitic acid, which can be anchored onto the modified clinoptilolite surface through hydrophobic interaction. Palmitic acid loadings were varied from 0 to 6-fold excess of palmitic acid (moles of palmitic acid/moles of CTAB) and the pH of the reaction medium was maintained at pH 8.5 so that the acid was essentially in its carboxylate form, and thus the only mode of binding of palmitic acid to modified-clinoptilolite surface would be through a “mixed bilayer” formation. The mixtures of modified-clinoptilolite and palmitic solution were agitated at 25°C and 150 rpm for 8 hours and then centrifuged. The modified-clinoptilolite complex (SMZ) was washed with deionized water before being air-dried at 60°C.

The amount of surfactant and palmitic acid adsorbed on clinoptilolite was analyzed by Elemental Analyzer (EA)(PERKIN ELMER, PE 2400). Identification of surfactant and palmitic acid bound on the clinoptilolite surface was done by Fourier Transform Infrared Spectrophotometer (BRUKER EQUINOX, model 55/S).

Batch adsorption experiments for contaminants

0.2 g of SMZ and 20 ml of cadmium solution were placed into 50-ml polypropylene centrifuge tube. Initial cadmium concentrations of from 25 to 200 mg/l were used at pH 7. The tubes were shaken for 24 hours at 30°C and 150 rpm and then the mixture was centrifuged to yield a clear supernatant solution. The supernatant was withdrawn for the analysis of cadmium by using Atomic Absorption Spectrometer (VARIAN, model 300/400).

The adsorption of organic contaminant was studied by mixing 0.2 g of SMZ and 20 ml of toluene solution in 16-ml crimp-top glass vials seal with Teflon-lined septa with a minimum the headspace. The initial toluene concentration was in the range of 50 to 500 mg/l at pH 7. The vials were shaken for 48 hours at 30°C and 150 rpm. The supernatant was withdrawn for analysis of toluene by using Head-space Gas Chromatography (PERKIN ELMER, Auto GC system). To study the adsorption of heavy metal and organic contaminants simultaneously (mixed system), both contaminants were added to the adsorption experiments simultaneously and the procedures were performed in the same manner as in the single system.

Regeneration of SMZ

After the batch adsorption of cadmium by SMZ was carried out, the supernatant was removed and analyzed by Atomic Absorption Spectrometer (AAS). The cadmium-loaded SMZ was then resuspended in an equal volume of deionized water, and the pH was adjusted to 1.5 by using 1 M of HNO₃, followed by 24 hours of shaking at 150 rpm and 30°C. The mixture was centrifuged and the supernatant was analyzed. After that, the SMZ was washed with deionized water and dried at 60°C. For the reuse of SMZ, cadmium adsorption on the regenerated SMZ was performed as described previously.

Regeneration of toluene saturated SMZ was done in a 16 ml crimp-top glass vials. After toluene sorption occurred for 48 hours, compressed air was purged into the vials overnight to promote air
stripping of the volatile toluene. The supernatant was analyzed before and after the regeneration by Head-space Gas Chromatography. The SMZ was subsequently washed with deionized water and dried at 60°C. For the reuse of SMZ, toluene adsorption on the regenerated SMZ was performed as described previously.

RESULTS AND DISCUSSION

Surfactant adsorption on clinoptilolite

The adsorption isotherm of cetyltrimethylammoniumbromide (CTAB) on clinoptilolite at 25°C is shown in Figure 1. The maximum adsorption of CTAB on clinoptilolite is approximately 80 µmol of CTAB/gram of clinoptilolite.

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 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.

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 and compare with those obtained from unmodified clinoptilolite. Some fundamental IR absorption frequencies of clinoptilolite and SMZ with various metal ligand:surfactant loading ratios are shown in
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>
<thead>
<tr>
<th>Clinoptilolite</th>
<th>SMZ (PA:CTAB)</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>(0:1)</td>
<td>3631</td>
<td>O-H stretching of aluminum</td>
</tr>
<tr>
<td></td>
<td>3631</td>
<td>hydroxide</td>
</tr>
<tr>
<td>(1:1)</td>
<td>2851</td>
<td>Aliphatic C-H stretching</td>
</tr>
<tr>
<td>(2:1)</td>
<td>2851</td>
<td>Aliphatic C-H stretching</td>
</tr>
<tr>
<td>(4:1)</td>
<td>2919</td>
<td>Quaternary amine salts</td>
</tr>
<tr>
<td>(4:1)</td>
<td>1577</td>
<td>C=O stretching of COO(^-)</td>
</tr>
</tbody>
</table>

All frequencies in cm\(^{-1}\)

The organic carbon contents of SMZ with various PA:CTAB loading ratios are shown in Table 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.

<table>
<thead>
<tr>
<th>SMZ C content, wt %</th>
<th>µmol/g</th>
<th>mole ratio of PA:CTAB adsorbed</th>
</tr>
</thead>
<tbody>
<tr>
<td>(0:1) 0.955</td>
<td>41.885</td>
<td>-</td>
</tr>
<tr>
<td>(1:1) 1.481</td>
<td>41.885/27.370(^a)</td>
<td>0.653</td>
</tr>
<tr>
<td>(2:1) 1.869</td>
<td>41.885/44.895(^b)</td>
<td>1.072</td>
</tr>
<tr>
<td>(4:1) 2.473</td>
<td>41.885/78.775(^b)</td>
<td>1.881</td>
</tr>
<tr>
<td>(6:1) 2.479</td>
<td>41.885a/79.375(^b)</td>
<td>1.895</td>
</tr>
</tbody>
</table>

\(^a\) µmoles of CTAB/g of SMZ. \(^b\) µmoles of PA/g of SMZ.

The results shown in Table 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.

**Cadmium adsorption on SMZ in single system**

Figure 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:

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

where $q$ is the amount of cadmium adsorbed (mg/g of adsorbent), $C_e$ is an equilibrium cadmium concentration (µM), $Q_{\text{max}}$ 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 3. $Q_{\text{max}}$ 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 ($Q_{\text{max}}$) and low $K$ value, indicating that high adsorbed amount can be achieved at low concentration.

**Table 3. Langmuir parameters for the adsorption of cadmium on SMZ with various PA:CTAB loading ratios.**

<table>
<thead>
<tr>
<th>SMZ(PA:CTAB)</th>
<th>$Q_{\text{max}}$ (mg/g)</th>
<th>$K$ (µM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SMZ(0:1)</td>
<td>3.34</td>
<td>2360.00</td>
</tr>
<tr>
<td>SMZ(1:1)</td>
<td>3.60</td>
<td>625.70</td>
</tr>
<tr>
<td>SMZ(2:1)</td>
<td>4.25</td>
<td>284.10</td>
</tr>
<tr>
<td>SMZ(4:1)</td>
<td>5.22</td>
<td>226.60</td>
</tr>
<tr>
<td>SMZ(6:1)</td>
<td>5.55</td>
<td>260.94</td>
</tr>
</tbody>
</table>
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 $Q_{\text{max}}$ 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 $Q_{\text{max}}$ 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 $Q_{\text{max}}$ 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.

**Toluene adsorption on SMZ in single system**

The adsorption isotherms of toluene on SMZ with various PA:CTAB loading ratios are shown in Figure 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.

**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 5 and 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 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.

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 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.

**Regeneration and reuse of 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 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.

For the regeneration of cadmium saturated SMZ, since cadmium is adsorbed on the carboxylic functional group of palmitic acid which has pKₐ ~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 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 total organic carbon analyzer (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.

**CONCLUSIONS**

The results obtained in this study clearly demonstrated that the adsorption of heavy metal such as Cd^{2+} ions and organic compound such as toluene by SMZ was greatly improved by the surface modification technique to form a bilayer of cationic surfactant (CTAB) and metal ligand (palmitic acid or PA) on natural zeolite surface. From the equilibrium adsorption study, the results showed that the amount of metal ligand (PA) loading on SMZ had significant effect on the metal adsorption of SMZ. The cadmium uptake by SMZ increased significantly with increasing metal ligand to surfactant loading ratio in the range of 1:1 to 4:1. Increasing the metal ligand loading on SMZ beyond this range had insignificant effect on the cadmium adsorption by SMZ. In addition, the sorption of cadmium on SMZ was shown to be through the complexation between cadmium ions and the carboxylic functional group of PA on SMZ. For organic adsorption, increasing metal ligand loading on SMZ resulted in a slight decrease in the amount of toluene adsorbed on SMZ which is believed to be attributed to the tighter packing of the interlayer of PA and CTAB adsorbed on SMZ surface, thus reducing effective volume of the hydrophobic core of the mixed bilayer for toluene. In mixed-solute system, the presence of toluene did not show any effect on the adsorption of cadmium by SMZ whereas the presence of cadmium was found to enhance the adsorption of toluene. The results obtained from the regeneration studies clearly demonstrated that used SMZ containing heavy metal could be regenerated by using low pH solution to desorb sorbed metal ions on SMZ. On the other hand, used SMZ containing toluene could be easily and fully regenerated by simple air purging. All sorbed toluene was stripped out from SMZ and regenerated SMZ could be reused after the regeneration. It can be concluded that SMZ can be regenerated and reused for multiple adsorption cycles.
ACKNOWLEDGEMENTS

The authors wish to thank Postgraduate Education and Research Program in Petroleum and Petrochemical Technology (PPT Consortium) and Thailand Research Fund (TRF) for the partial funding of the thesis work.

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