

CHAPTER III

METHODOLOGY

3.1 Materials

The natural zeolite (clinoptilolite) used in this study was purchased from Marineland (Moorpark, CA). To obtain the desired particle size of 0.42-0.83 mm, clinoptilolite was ground and sieved by using 20 and 40 mesh. The specific surface area of clinoptilolite was determined from the 10-points adsorption isotherm of N₂ gas on clinoptilolite using a BET surface analyzer. From the BET results, it was found that the surface area of clinoptilolite is 10.15 m²/g. Cetyl trimethyl ammonium bromide or CTAB (C₁₉H₄₂BrN) and disodium hexadecyl diphenyloxide disulfonate or DOWFAX 8390 (C₁₆H₃₃C₁₂H₇O(SO₃Na)₂), Sodium dodecyl diphenyl oxide disulfonate or DOWFAX 2A1 (C₁₂H₂₅C₁₂H₇O(SO₃Na)₂), and sodium dodecylbenzenesulfonate or SDBS (C₁₂H₂₅C₆H₄SO₃Na) were used as the surface modifying agents to modify clinoptilolite surface. The chemical structures of the surfactants are listed in Table 3.1. CTAB with a purity of 96% and SDBS with a purity of 88% were purchased from Aldrich (Milwaukee, WI), DOWFAX 8390 with active ingredient of 36% and DOWFAX 2A1 with active ingredient of 46% were purchased from DOW Chemical (Midland, MI). All chemicals were used without further purification to study adsorption characteristic of SMZ for heavy metal and toxic organic. The model heavy metals used were cadmium and lead. Toluene was used as model toxic organic contaminants. Cadmium chloride (CdCl₂·2½H₂O) and toluene (C₆H₅CH₃) with a purity of 99.5% were purchased from Carlo Erba (Milan, Italy). Lead chloride (PbCl₂), with a purity of 99.0%, was purchased from APS (NSW, Australia). The physical and chemical properties of the contaminants are listed in Table 3.2.

Table 3.1 Surfactants used in this research


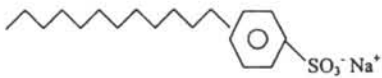
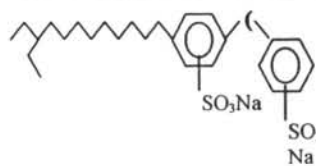
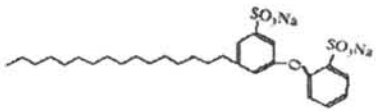
Name	Formula	Structure	Mw.
CTAB	$C_{19}H_{42}BrN$		364.46
SDBS	$C_{12}H_{25}C_6H_4SO_3Na$		348.48
DOWFAX 2A1	$C_{12}H_{24}C_2H_5C_{12}H_7O(SO_3Na)_2$		576
DOWFAX 8390	$C_{16}H_{33}C_{12}H_7O(SO_3Na)_2$		642

Table 3.2 Physical and chemical properties of the contaminants used in this research

Name	Formula	Mw. (g/mol)	Boiling point (°C)	Melting point (°C)	Density (g/cm ³)	Water solubility at 20°C (%)
Lead chloride	$PbCl_2$	278.1	950	501	5.85	0.99
Cadmium chloride	$CdCl_2 \cdot 2\frac{1}{2}H_2O$	228.34	960	564	40.08	140
Toluene	$C_6H_5CH_3$	92.14	110.6	-93	0.8669	0.05

From material safety data sheets (MSDS)

3.2 Experimental

3.2.1 Preparation of Surfactant-Modified Zeolite (SMZ)

The first step of surface modification is cationic 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 second step is anionic surfactant adsorption. CTAB-modified clinoptilolite obtained from the first step was reacted with anionic surfactants as DOWFAX 8390, DOWFAX 2A1, and SDBS, which can be anchored onto the CTAB-modified clinoptilolite surface through hydrophobic interaction. The anionic surfactant concentration was used by various from 1 to 10 times of CTAB concentration.

3.2.1.1 *Adsorption of Cetyl trimethyl ammonium Bromide (CTAB) on Clinoptilolite*

An adsorption isotherm was carried out by the batch equilibration technique 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 concentrations were used in the range of 50-6000 μM . The mixtures were equilibrated on a shaker at 150 rpm at 30°C for 24 hours, which were found to be sufficient to achieve equilibrium. After equilibration, they were centrifuged and 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 analyzer (Shimadzu, model 5000 A). A simple mass balance was used to determine the amount of CTAB adsorbed onto the clinoptilolite. The adsorption isotherm was constructed by plotting the amount of CTAB adsorbed on clinoptilolite ($\mu\text{mol/g}$) versus the equilibrium concentration of CTAB in the solution (μM).

3.2.1.2 *Precipitation Study*

CTAB at the completed monolayer concentration was mixed with anionic surfactant at various concentrations ranging from 1 to 10 times of CTAB concentration (mole ratio) at 30°C. The mixtures were observed everyday for possible precipitation by visualization and the reflection of the precipitates was also checked by using laser pointer.

3.2.1.3 *Adsorption of anionic surfactant on CTAB-Modified Zeolite*

Firstly, clinoptilolite was initially treated with CTAB solution at the equilibrium CTAB concentration sufficient to provide a complete monolayer. From the precipitation study, the ratio of CTAB and anionic surfactants could be selected to avoid precipitation. After that, a batch adsorption was conducted to determine anionic surfactant sorption on CTAB-modified clinoptilolite at various anionic surfactant concentrations. 0.2 g of modified-clinoptilolite was mixed with 20 ml of anionic surfactant as DOWFAX 8390, DOWFAX 2A1, and SDBS aqueous solution in 24-ml screw-cap glass vial. The mixtures of CTAB-modified clinoptilolite and anionic surfactant solution were equilibrated on a shaker at 150 rpm at 30°C and varied equilibrium time for 24 to 96 hours. The adsorption of anionic surfactant was quantified by measuring the surfactant concentration before and after equilibration using an Ion Chromatography (Dionex, model ICS 2500). A simple mass balance was performed to determine the amount of anionic surfactant adsorbed on the CTAB-modified clinoptilolite. Then the surfactant-modified clinoptilolites were washed using reverse osmosis (RO) water before being air-dried at 110°C.

3.2.2 SMZ Characterization

Identification of surfactants bound on the clinoptilolite surface was done by Fourier Transform Infrared Spectrophotometer (Thermo Nicolet, Nexus 670). To reflect the extent of adsorption and the orientation of adsorbed surfactant on clinoptilolite, the surface potential of clinoptilolite was measured by zeta meter (Zeta meter, model 3.0+ unit).

3.2.3 Adsorption Experiments for Heavy metals and Organic contaminant

3.2.3.1 *Adsorption of Heavy Metals in Single-Metal System*

Batch adsorption experiments were performed to determine the heavy metal (cadmium or lead) adsorption. Initial concentrations of heavy metal used were in a range of 0.25 to 5.0 mM. 0.2 g of SMZ and 20 ml of heavy metal solution were mixed in 24-ml screw-cap glass vial. The pH of the solution was adjusted to 5 by using 0.2 M of HCl and 0.2 M of NaOH. The tubes were shaken for 24 hours at 30°C and 150 rpm. The supernatant was then withdrawn for the analysis of heavy metal by using Atomic Absorption Spectrometer (VARIAN, model 300/400). Sorption of heavy metal was calculated from the difference between initial and final concentrations. The adsorption isotherms were constructed by plotting the amount of heavy metal adsorbed on SMZ (mmol/g) versus the equilibrium concentration of heavy metal in the solution (mM). For heavy metal adsorption using clinoptilolite, the procedures were performed in the same manners as SMZ.

3.2.3.2 *Adsorption of Heavy Metals in Mixed-Metals System*

Batch adsorption experiments were performed to determine the mixed heavy metal (cadmium and lead) adsorption. Initial concentrations of both heavy metal used were in a range of 0.25 to 3.0 mM at the equal-molar ratios of cadmium and lead. 0.2 g of SMZ and 20 ml of mixed heavy metal solution were mixed in 24-ml screw-cap glass vial. The pH of the solution was adjusted to 5 by using 0.2 M of HCl and 0.2 M of NaOH. The tubes were shaken for 24 hours at 30°C and 150 rpm. The supernatant was then withdrawn for the analysis of each heavy metal ions by using Atomic Absorption Spectrometer (VARIAN, model 300/400). Sorption of each heavy metal was calculated from the difference between initial and final concentrations. The adsorption isotherms were constructed by plotting the amount of heavy metal adsorbed on SMZ (mmol/g) versus the equilibrium concentration of heavy metal in the solution (mM).

3.2.3.3 *Adsorption of Toluene in Single-Solute System*

Adsorption of organic contaminant was studied by mixing 0.2 g of SMZ and 20 ml of organic solute (toluene) in 20-ml crimp-top glass vials seal with Teflon-lined septa with a minimum the headspace. The initial organic solute

concentrations were used in the range of 500 to 5500 μM . The vials were shaken for 48 hours at 30°C and 150 rpm. The supernatant was then withdrawn for analysis of organic solute by using Headspace Gas Chromatography (Agilent, 6890N). The amount of adsorbed toluene was determined from the difference between initial and final concentrations.