

CHAPTER III EXPERIMENTAL

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) were used as the surface modifying agents to modify clinoptilolite surface. CTAB with a purity of 96% is purchased from Aldrich (Milwaukee, WI) and DOWFAX 8390 with active ingredients of 36% is purchased from DOW Chemical (Midland, MI). Both 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).

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 DOWFAX 8390, which can be anchored onto the CTAB-modified clinoptilolite surface through hydrophobic interaction. The DOWFAX 8390 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 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 concentrations were used in the range of 50-6000 μM . Vials 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, 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 Adsorption of Disodium Hexadecyl Diphenyloxide Disulfonate (DOWFAX 8390) on CTAB-Modified Zeolite

Firstly, clinoptilolite was initially treated with CTAB solution at the equilibrium CTAB concentration sufficient to provide a complete monolayer. The mixture of clinoptilolite and CTAB solution were agitated at 30°C and 150 rpm for 24 hours until reaching equilibrium. After that, a batch adsorption was constructed to determine DOWFAX 8390 sorption on CTAB-modified clinoptilolite at various DOWFAX 8390 concentrations from 1 to 10 times of CTAB concentration (mole ratio). 0.2 g of modified-clinoptilolite was mixed with 20 ml of DOWFAX 8390 aqueous solution in 24-ml screw-cap glass vial. The mixtures of CTAB-modified clinoptilolite and DOWFAX 8390 solution were agitated at 30°C and 150 rpm for 24 hours. The adsorption of DOWFAX 8390 was quantified by measuring

the surfactant concentration before and after equilibration using a UV-VIS spectrophotometer (Perkin Elmer Lambda 10) at the wavelength 275 nm. A simple mass balance was performed to determine the amount of DOWFAX 8390 adsorbed on the CTAB-modified clinoptilolite.

3.2.2 SMZ Characterization

Identification of surfactant bound on the clinoptilolite surface was done by Fourier Transform Infrared Spectrophotometer (Thermo Nicolet, Nexus 670) with 32 scan at resolution of 4 cm^{-1} in the frequency range of $4000\text{-}400\text{ cm}^{-1}$. Approximately, 0.005 g of a dried sample and 0.065 g of an optical-graded KBr powder used as a standard were mixed and ground together. Prior to the analysis, the specimens were pressed to obtain a transparent thin pellet. 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 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 concentration. The adsorption isotherm was 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 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 different between initial and final concentration. The adsorption isotherm was 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 withdrawn for analysis of organic solute by using Headspace Gas Chromatography (Agilent, 6890N). The sorption of toluene was determined from the different between initial and final concentration.

3.2.3.4 Adsorption of Heavy Metals in Mixed-Solute System

Adsorption of heavy metal (cadmium or lead) and organic contaminant (toluene) 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. Initial concentrations of heavy metal used were in a range of 0.25 to 5.0 mM and fixed toluene concentration at 4000 μM . The pH of the solution was adjusted to 5 by using 0.2 M of HCl and 0.2 M of NaOH. The supernatant was withdrawn for the analysis of heavy metal by using Atomic Absorption Spectrometer (VARIAN, model 300/400). Sorption of heavy metals was calculated from the different between initial and final concentration. The adsorption isotherm was constructed by plotting the amount of heavy metal adsorbed on SMZ (mmol/g) versus the equilibrium concentration of heavy metal in the solution (mM).

The supernatant was withdrawn for analysis of organic solute by using Headspace Gas Chromatography (Agilent, 6890N). The amount of toluene sorbed was determined from the difference between initial and final concentration.