

## CHAPTER III EXPERIMENTAL

### 3.1 Materials

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, clinoptilolite was ground and sieved by using 20 and 40 mesh. Cetyltrimethylammoniumbromide or CTAB ( $C_{19}H_{42}BrN$ ) 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 heavy metal and organic contaminants, respectively. Cadmium chloride ( $CdCl_2 \cdot 2\frac{1}{2}H_2O$ ) and toluene ( $C_6H_5CH_3$ ), with a purity of 99.5%, were purchased from Carlo Erba (Milan, Italy).

### 3.2 Experimental

#### 3.2.1 Clinoptilolite characterization

The chemical composition of clinoptilolite was analyzed by using X-ray diffraction (Ringaku, RINT-2200). An external surface area of clinoptilolite was estimated by BET surface area analyzer (Autosorb-1, Quantachrome). To eliminate adsorbed volatile compound, 0.5 g of clinoptilolite was dried at 200 °C for 24 h. The external surface area of clinoptilolite was evaluated at 0.1 P/P<sub>0</sub> in N<sub>2</sub> atmosphere.

#### 3.2.2 Study the adsorption isotherm of cetyltrimethylammoniumbromide (CTAB) on clinoptilolite.

Adsorption isotherms were 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 a 24-ml

screw-cap glass vial. The initial CTAB concentration was in the range of 50-9000  $\mu\text{M}$ . Samples were equilibrated on a shaker at 150 rpm at 25°C for 8 h, which was 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 analyzer (Shimadzu, model 5000 A). The amount of CTAB adsorbed onto clinoptilolite was determined by a simple mass balance. The adsorption isotherm was then constructed by plotting the amount of CTAB adsorbed on clinoptilolite ( $\mu\text{mol/g}$ ) and equilibrium concentration of CTAB in the solution ( $\mu\text{M}$ ).

To reflect the extent of adsorption and the orientation of adsorbed CTAB on clinoptilolite, the surface potential of clinoptilolite was measured by zeta meter (Zeta meter, model 3.0<sup>+</sup> unit).

### 3.2.3 Preparation of surfactant-modified zeolite (SMZ)

A cationic surfactant (CTAB) and long chain carboxylic acid (palmitic acid) were used to modify the surface of clinoptilolite. CTAB replaces the counterion on the exchange sites of the clinoptilolite and converts the clinoptilolite surface to become strongly hydrophobic. Subsequently, palmitic acid can be anchored onto the modified clinoptilolite surface through hydrophobic interaction.

First, clinoptilolite was initially treated with CTAB at a concentration equivalent to the external cation-exchange capacity (ECEC) of clinoptilolite (90-100 mequiv/kg). The mixture of clinoptilolite and CTAB solution was agitated at 25 °C and 150 rpm for 8 h and then the mixture were centrifuged for phase separation.

Modified-clinoptilolite obtained from the first step was then reacted with palmitic acid. A 2-fold excess of palmitic acid was used 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 h and then centrifuged. The modified-clinoptilolite complex (SMZ) was washed with DI water before being air-dried at 60°C.

#### 3.2.4 SMZ Characterization

The amount of surfactant and palmitic adsorbed on clinoptilolite were analyzed by Elemental Analyzer (EA). Identification of surfactant and palmitic acid bound on the clinoptilolite surface and mode of contaminant adsorption on SMZ was done by Fourier Transform Infrared spectrophotometer (BRUKER EQUINOX, model 55/S). The morphology of the surface of clinoptilolite before and after modification was examined by Scanning Electron Microscope (JEOL, model JSM-5200).

#### 3.2.5 Batch adsorption experiments for contaminants

For adsorption of heavy metal, 0.2 g of adsorbent (clinoptilolite or SMZ) and a 40 ml of cadmium solution were mixed in a 50-ml polycarbonate centrifuge tube. The initial cadmium concentrations ranging from 50 to 400 mg/l were used at pH ranging from 4-8. The pH was adjusted by using 1 M of NaOH or 1 M of HNO<sub>3</sub>. The tubes were shaken for 24 h at 25°C and 150 rpm and then the mixture were centrifuged to yield a clear supernatant solution. The supernatant was then withdrawn for the analysis of cadmium by Atomic Absorption Spectrometer (VARIAN, model 300/400).

To study the effect of ionic strength on cadmium adsorption, NaCl solution were added in the system. The ionic strength of the system was adjusted in the range of 10-100 mM. The mixture were shaken for 24 h at 25°C and 150 rpm also. And then the procedures were performed same as previous part.

Adsorption of organic contaminant was studied by mixing a fixed amount of SMZ and a fixed volume of toluene solution in 16 ml crimp-top glass vials sealed with Teflon-lined septa with a minimum of headspace. The initial toluene concentration used was in the range of 500 to 6000 µM, while the pH was in the range of 4-8. The mixture was shaken on a shaker for 48 h the conditions as described previously. It was then centrifuged to yield a clear supernatant solution. Supernatant was withdrawn for analysis of toluene by Head-space Gas

Chromatography (PERKIN ELMER, Auto GC system). To study the simultaneous adsorption of heavy metal and organic contaminants, both contaminants were loaded on SMZ simultaneously and then the procedures were performed in the same manner as in the single system.

### 3.2.6 Regeneration of SMZ

Batch adsorption experiments for contaminants were carried out. 0.2 g of adsorbent (clinoptilolite or SMZ) and a 40 ml of cadmium solution were put into 50-ml polycarbonate centrifuge tube. The initial cadmium concentrations ranging from 50 to 400 mg/l were used at pH ranging from 4-8. The pH was adjusted by using 1 M of NaOH or 1 M of HNO<sub>3</sub>. The tubes were shaken for 24 h at 25°C and 150 rpm and then the mixture were centrifuged to yield a clear supernatant solution. The supernatant was then withdrawn for the analysis of cadmium by Atomic Absorption Spectrometer (VARIAN, model 300/400).

Regeneration of toluene saturated SMZ was done in a 16-ml crimp-top glass vials sealed with Teflon-lined septa. After toluene sorption for 48 h, the supernatant was analyzed by Head-space Gas Chromatography. The rubber septum was then removed and the jet of air was bubbled through the mixture overnight to promote air stripping of the volatile toluene. The supernatant was analyzed by Head-space Gas Chromatography again.