

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, the clinoptilolite was ground and sieved by using 20 and 40 mesh. The specific surface area of clinoptilolite was determined from the 5-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 12.38 m²/g. Cetyltrimethylammonium-bromide or CTAB (C₁₉H₄₂BrN) and palmitic acid (C₁₆H₃₂O₂) 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 (CdCl₂·2½H₂O) and toluene (C₆H₅CH₃) with a purity of 99.5%, were purchased from Carlo Erba (Milan, Italy).

3.2 Experimental

3.2.1 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 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 ($\mu\text{mol/g}$) versus the equilibrium concentration of CTAB in the solution (μM).

3.2.2 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 4-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 DI water before being air-dried at 60°C.

3.2.3 SMZ Characterization

The amount of surfactant and palmitic acid adsorbed on clinoptilolite was analyzed by Elemental Analyzer (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).

3.2.4 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.

3.2.5 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.