

CHAPTER III EXPERIMENTAL



3.1 Materials

Clinoptilolite used throughout this thesis was obtained from Marineland Co., Ltd. (Moorpark, CA). For all experiments, the clinoptilolite was dried at 110°C and ground by miller (IKA, Laborfechnik Staufen) to particle size in the range of 0.212-0.425 mm (Endecotts, mesh number of 70 and 120). Acetic acid obtained from Labscan (Patumwan, BKK) and sodium acetate obtained from Carlo ERBA (Rodano, MI) were used to prepare the first buffer solution. Another buffer solution was prepared from tris(hydroxymethyl)aminomethane obtained from Aldrich Chemical Company, Inc (Milwaukee, WI) and tris(hydroxymethyl)aminomethane hydrochloride obtained from Carlo ERBA. Aqueous solutions used in the experiments were ammonium chloride obtained from Carlo ERBA and potassium chloride obtained from APS Finechem (Sevenhills, NSW) in single and mixed system. They were prepared by adding an allocated amount of them to buffer solution. Other chemicals used were calcium chloride and sodium chloride, which were obtained from Scharlau Chomie S.A. (La Jota, BCN) and Carlo ERBA, respectively.

3.2 Experimental Procedure

The experiments were divided into 4 parts:

1. Characterization of clinoptilolite
2. The kinetics of adsorption and desorption of NH_4^+ , K^+ by clinoptilolite at various pH and initial concentrations
3. The equilibrium adsorption and desorption of NH_4^+ , K^+ and NH_4^+/K^+ by clinoptilolite at various pH and initial concentrations
4. The release of NH_4^+ and K^+ from preloaded clinoptilolite at different loading ratios

All of the experiments were performed in the batch liquid operation at ambient conditions.

3.2.1 Characterization

3.2.1.1 *Mineral Purity*

Mineral purity of clinoptilolite sample was determined by X-Ray Diffractometer (Rigaku, RINT-2200).

3.2.1.2 *Surface Area*

Surface area analyzer (Quantachrome, Autosorb-1) was used to determining the specific BET (Brunauer-Emmett-Teller) surface area and pore volume of natural.

3.2.2 Adsorption

3.2.2.1 *Adsorption Isotherm*

The clinoptilolite sample was weighed 0.3 g and placed in 50-ml polypropylene centrifuge tube. After that, a buffer solution and NH_4Cl or KCl solution at the concentration in a range of 50-3000 mg/l were added into the tube. The ratio between clinoptilolite and the solution was fixed at 0.3 g : 15 ml. The centrifuge tube was laid horizontally on an orbital shaker (Rotamix, 50800) and agitated continuously at constant temperature (25°C) for 15 to 20 hours as shown in Figure 3.1. Then, the tube was centrifuged (ALC, 4236) at 2000 x g relative force (RCF) for 10 min for the phase separation. Finally, the concentration of NH_4^+ and/or K^+ in the supernatant was analyzed by ISE (Cole-Parmer) and/or AAS (Varian, spectro AA 300). The amount of NH_4^+ or K^+ sorbed by the sample was calculated from the reduction of NH_4^+ or K^+ in the solution.

In this part of the experiments, effect of pH was also studied by varying pH in a range of 3 to 9. Two buffer solutions were used in the experiments in order to control pH of the solution. The first buffer solution, acetate buffer was used

for pH 3 and 5. The second buffer solution was Trisma buffer solution for pH 7 and 9. The buffer strength was fixed at 0.05 M.

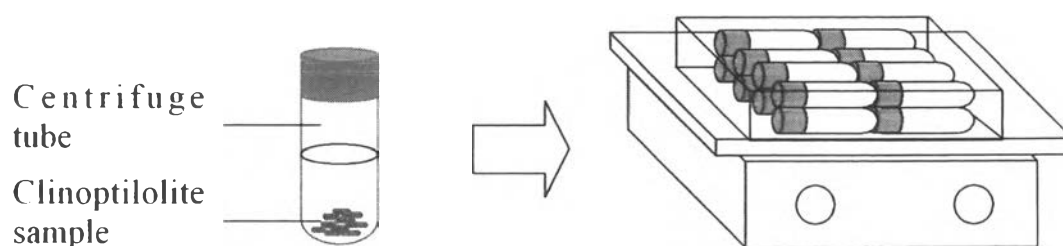


Figure 3.1 Schematic diagram of experimental apparatus for batch operation.

3.2.2.2. Adsorption Kinetics

The sample and solution used were prepared in the same manner as in the previous part. The procedures were also similar to the adsorption isotherm part, except a magnetic stirrer was used instead of an orbital shaker in order to allow the instantaneous measurements. While the mixture was stirred at a constant temperature, the concentration of NH_4^+ or K^+ was continuously monitored by ISE and was recorded at a certain time interval.

3.2.3 Desorption

3.2.3.1 Desorption Isotherm

The desorption experiments were carried out following the adsorption studies. After the adsorption, clinoptilolite remaining in the centrifuge tube was dried. The adsorbed NH_4^+ was desorbed by mixing with NaCl, CaCl_2 or KCl solution. The tube was then shaken on an orbital shaker for 15 to 20 hours followed by centrifugation at 2000 x g relative force (RCF) for 10 min. Similar experiments were carried out for the desorption of K^+ sorbed on clinoptilolite. The supernatant was analyzed for desorbed NH_4^+ or K^+ by ISE and/or AAS.

3.2.3.2 Desorption Kinetics

The sample and solution used were prepared in the same manner as in the previous part. The adsorbed NH_4^+ was desorbed by mixing with NaCl or CaCl_2 or KCl solution followed by stirring at constant temperature. The concentration of NH_4^+ and/or K^+ was continuously monitored by ISE and was recorded at a certain time interval. The solutions of NaCl and CaCl_2 were used to desorb KCl.

3.2.4 Release of NH_4^+ and K^+ at different loading ratios

The natural clinoptilolite was loaded with NH_4^+ and K^+ at the different ratio by these following steps. First, the clinoptilolite with appropriate size was mixed with a predetermined concentration of NH_4Cl in order to obtain the partial coverage. After that, NH_4^+ loaded clinoptilolite was mixed with KCl at desired concentration. While mixing clinoptilolite with NH_4Cl and KCl, pH of the system was fixed at pH of 7. Finally, the loaded clinoptilolite will be dried at 110°C . Clinoptilolite loaded with NH_4^+/K^+ was further used to examine the release of NH_4^+ or K^+ in buffer solution containing CaCl_2 by agitation on the orbital shaker. Then, the sample was centrifuged at $2000 \times g$ RCF for 10 min. The supernatant was analyzed for release of NH_4^+ and K^+ by ISE and/or AAS.