



CHAPTER III

MATERIALS AND METHODS

3.1 Materials

3.1.1 Ion Exchange Resin

In this study, ion pairs selected as model metal ions were $\text{Ca}^{2+}/\text{H}^+$ and $\text{Mg}^{2+}/\text{H}^+$ while a strong acid Dowex50-x8 was used as a model ion-exchange resin.

The Dowex50-x8 resin used in all experiments was an H type of strong acid synthetic resin, manufactured by the Dow Chemical Co., Ltd. The ion-exchange resins had to be pretreated before it was used in the experiments. It was washed several times using deionized water to remove chemical impurities and then treated with HCl solution to get the H^+ saturated resin. The resin was then dried in an oven for over 5 hours at 70°C , and was put in a dessicator.

3.1.2 Other Chemicals

Two aqueous solutions were used in the experiments. The first solution, a metal solution, was prepared by adding appropriate amount of CaCl_2 , MgCl_2 or $\text{CaCl}_2/\text{MgCl}_2$ into deionized water. The second solution, a regenerating solution, was prepared by adding 37% hydrochloric acid in deionized water into produce a hydrogen ion concentration of 0.2 N. All of the chemicals used in these experiments were A.R. grade, which were obtained from the Merck Corporation.

Tris buffer solution, which was used to control the pH of the solution equal 7.2 and ionic strength 0.05 M solution, was prepared by adding allocate amount of Trizama hydrochloride obtained from Aldrich Chemical Company, Inc. and Tris (hydroxyl methyl) aminomethane obtained from Carlo ERBA into deionized water.

The chemicals, which were used in AAS (atomic adsorption spectrometer), were potassium chloride, and calcium and magnesium standard solution. All of the chemicals were obtained from the Merck Corporation.

3.2 Experimental Setup

The experiment setup of the ion exchange column used in this study is shown in Figure 3.1. A positive-displacement-metering pump (Masterflex) with fine adjustment scale of 10-1,000 was used for flow control. The pump inlet and outlet tubing could easily be disconnected from system with two quick disconnect fittings. Dowex50-x8 resins of nominal capacity 1.7 meq/ml of resin bed were completely packed in a glass column (2.8 cm. ID, 24 cm. height). The void fraction in the compacted bed (before fluidization) is 0.41. Three stock jars contained deionized water, HCl, Ca^{2+} , Mg^{2+} and $\text{Ca}^{2+}/\text{Mg}^{2+}$ solution. Three shut-off valves and one four-way flow-selection valve were used to direct the flow of any of the three liquids through the bed, either in upflow or downflow mode, or bypass the ion exchange bed entirely for pH electrode calibration or storage. The pH electrode mounted at the bed exit was used to measure the pH of the solution as a function of time. The height of the resin bed was monitored by means of the scale mounted outside of the column.

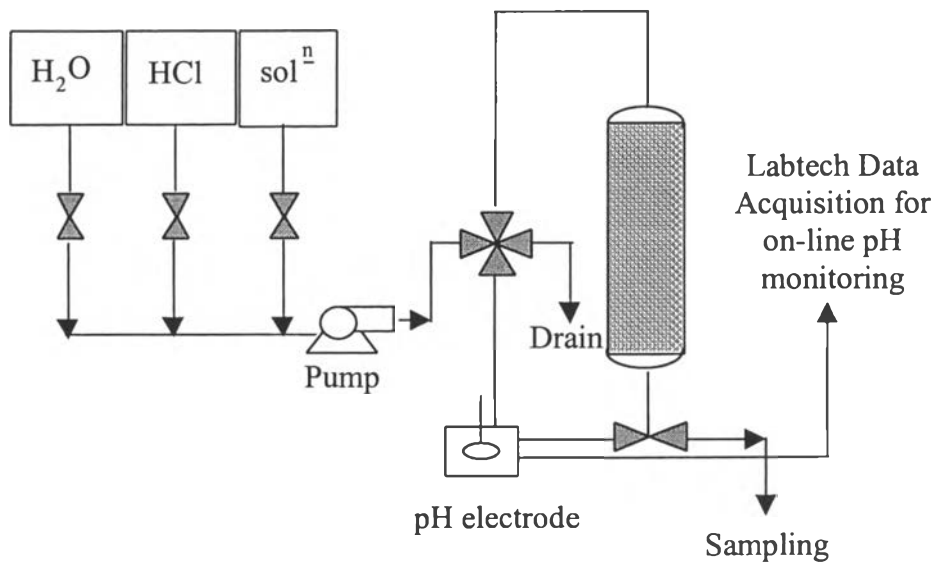


Figure 3.1 Schematic diagram of experimental apparatus for continuous flow operation

3.3 Methods

3.3.1 Determination of Response Time of the pH Electrode

3.3.1.1 *Batch operation mode*

The experiment was carried out by adding 600 cm³ of 0.2 N HCl into a 1000 cm³ baffled beaker, agitated by an electrical stirrer at a controlled mixing speed. The mixing speed was first set to 250 rpm. The pH electrode was placed in the solution to measure the pH value as a function of time. The process was stopped when the pH value showed no further changes. The mixing speed was changed to 500, 750 and 1000 rpm, and the experiment was carried out in the same manner. The response time constant of the pH electrode was calculated by performing a hydrogen balance around the pH electrode according to equation (2.9).

3.3.1.2 *Continuous operation mode*

The equipment setup for continuous operation is shown in Figure 3.2. Firstly, the deionized water was flowed past the pH electrode until the effluent pH value was constant. Secondly, instead of the deionized water 0.2 N HCl was flowed in, starting with a flow rate of 100 ml/min. The pH value was measured as a function of time until it became constant. The HCl flow rate was changed to 100, 150, 170, 200, 220, and 250 ml/min. Finally, the response time constant of the pH electrode was calculated by performing a hydrogen balance around the pH electrode according to equation (2.9).

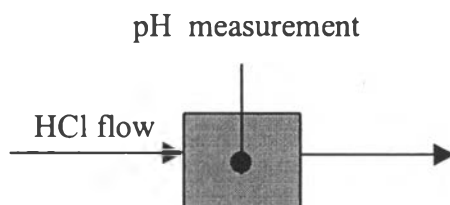


Figure 3.2 Schematic diagram of apparatus of response time constant of the pH electrode for continuous system

3.3.2 Batch Adsorption Experiments

The ion exchange experiments were conducted in a 1000 cm³ beaker of equipped with acrylic sheet baffles in order to ensure complete mixing. The liquid in the beaker was kept well mixed using a magnetic stirrer at 750 rpm. For each experiment, 600 cm³ of various initial concentrations, 0.1-0.6 N, of single and mixed ion solution of Ca²⁺/Mg²⁺ was added to the beaker. The H⁺ ion saturated resins were placed into the beaker. Samples were taken as a function of time from the batch using a syringe, which had a sieve net to screen out the resins. The pH values of all such samples taken manually were measured by allowing the pH electrode to reach equilibrium. An atomic absorption spectrometer (AAS) was also used to measure the ion concentrations in samples for comparison. The process was ended when the pH value showed no further changes. All experiments were performed at ambient temperature. The experimental setup for this mode is shown in Figure 3.3.

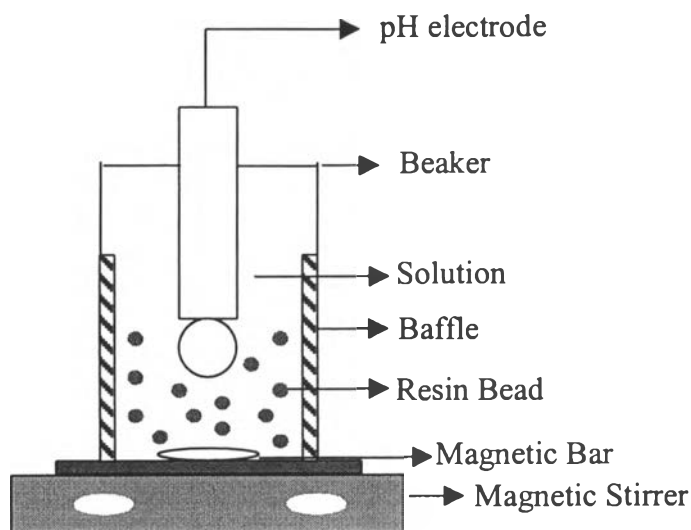


Figure 3.3 Schematic diagram of experimental apparatus for batch operation

3.3.3 Adsorption Isotherm

0.2 g of H⁺ ion saturated resins was weighed into a vial. The vial was added with the known volume of CaCl₂, MgCl₂ and/or CaCl₂/MgCl₂ stock solution in Tris buffer solution at various initial metal concentrations. The control (blank) was

made in the same manner but without the resin in the vial. The total volume for this experiment was controlled at 20 cm³. After that the solution was kept shaking over night at speed about 200 min⁻¹ and 25 °C. The final concentration of metal ions was then measured by atomic absorption spectrometer (AAS). By using method of difference, amount of metal ions adsorbed per gram of the resin was determined. Adsorption isotherm was then constructed by plotting the amount of metal ions adsorbed (q^e) and the corresponding equilibrium metal concentration (c^e).

3.3.4 Continuous Flow Experiments

3.3.4.1 *No adsorption experiment with downflow operation*

The first step in preparing the column for operation was to get rid of the air bubbles in the column. The four-way shut-off valve was switched to 0.2 N HCl solution to allow the resin bead to contact with H⁺ ions in the downflow direction. The pH value of the effluent was continuously monitored until there was no further change in its value, at which stage the resin beads were totally in their active form. The deionized water was allowed to flow through the column by adjusting the four-way shut-off valve to remove the excess hydrogen ions from the bed in the downflow direction. The process was stopped when all the excess hydrogen ions were released from the bed, or there was no further change in the effluent pH value. Again, the four-way shut-off valve was switched to 0.2N HCl to allow the resin beads to contact with 0.2 N HCl in the downflow direction. In this step, the 0.2 N HCl acts as a tracer, since the resin was already saturated with hydrogen ions. The H⁺ concentrations of samples, which were collected manually at all time, were measured by pH electrode after allowing equilibrium to be reached so that the response time effect of the pH electrode can be neglected. The process was stopped when the pH value of effluent was constant. A diagram of apparatus for the continuous system is illustrated in Figure 3.1.

3.3.4.2 *Adsorption experiment with downflow operation*

The experiment was similar to the no adsorption experiment in the downflow direction. After the excess H⁺ ions had already been removed from the system, the four-way shut-off valve was switched to one of the test solutions, either CaCl₂, MgCl₂ or CaCl₂/MgCl₂. The pH values and the samples of the effluent

were measured and collected manually at successive values of time. The pH values of all samples were measured by allowing the pH electrode to reach equilibrium and analyzed the ion concentration by using the AAS (atomic adsorption spectrometer). The process was stopped when the pH value appeared to be constant.

3.3.4.3 Desorption experiment with downflow operation

A method similar to that of section 3.3.4.2 was used but the excess metal ions had been removed from the system by DI water and then the four-way shut-off valve was switched to 0.2 N HCl. The pH values and the samples of the effluent were measured and collected manually at successive values of time. The pH values of all samples were measured by allowing the pH electrode to reach equilibrium. The process was stopped when the pH value was no further changed. Again, the DI water was allowed to flow through the column by adjusting the four-way shut-off valve to remove excess H^+ ions from the system.