

CHAPTER III

METHODOLOGY / MATERIALS AND METHOD

3.1 Materials / Sample Preparation

3.1.1 Ion Exchange Resin

The ion pair selected was $\text{Ca}^{2+}/\text{H}^{+}$ because this type of cation (calcium) is found in, and is a principal contaminant of natural water. Dowex50-x8 was selected as the ion-exchange resin because it behaves like a strong acid and the resin beds are spherical in shape.

The ion-exchange resin used in all experiments was an H type of strong acid synthetic resin, manufactured by the Dow Chemical Co., Ltd. under the trade name Dowex50-x8. 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

The aqueous solution for the experiments consisted of two solutions. The first solution was prepared by adding appropriate amounts of CaCl_2 , MgCl_2 or $\text{CaCl}_2/\text{MgCl}_2$ to deionized water. The second, regenerating solution for the experiments was prepared by adding 37% hydrochloric acid in deionized water to 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.



3.2 Experimental Setup

Figure 3.3 shows the equipment used in this study. A positive-displacement-metering pump with fine adjustment scale of 10-1,000 is used for flow control. The pump inlet and outlet tubing can easily be disconnected from system with two quick disconnect fittings. Dowex50-x8 *ion-exchange 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 are provided so that any of the three liquids can be pumped through the bed, either in upflow or downflow mode, or can bypass the ion exchange bed entirely for pH electrode calibration or storage. Two pH electrodes were mounted at the bed inlet and exit for measuring the pH value as a function of time.

3.3 Experimental Procedure

3.3.1 Response Time of the pH Electrode Experiment

3.3.1.1 *Batch Operation Mode*

The experiment was started by adding 600 cm^3 of 0.2 N HCl to a 1000 cm^3 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 dipped into the solution and the pH value of the system was begun to be monitored. The process ceased when the pH value showed no further change. The mixing speed was varied to 500, 750 and 1000 rpm; finally, the response time constant at various mixing speed values was calculated by using equation (2.9).

3.3.1.2 Continuous Operation Mode

A schematic diagram for the equipment used in the continuous operation mode is shown in Figure 3.1.

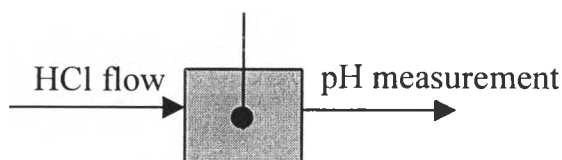


Figure 3.1 Schematic diagram of apparatus of response time constant of the pH electrode for continuous system.

The deionized water flowed past the pH electrode until the effluent pH value was constant, to make sure that the pH electrode measured the pure deionized state. The 0.2 N HCl was then flowed instead of the deionized water for an experimental starting with a flow rate of 100 ml/min. The pH value was measured until it became constant. The 0.2 N HCl flow rate was changed to 150, 170, 200, 220, and 240 ml/min. Finally, the response time constant of the pH electrode was calculated by using equation (2.9).

3.3.2 Batch Experiment

The ion exchange experiments were conducted in a beaker of 1000 cm³ equipped with two acrylic sheet baffles in order to obtain complete mixing. The liquid in the beaker was kept well mixed with a magnetic stirrer at 750 rpm. For each experiment, 600 cm³ of various initial concentrations, 0.05-0.4 N, of prepared aqueous solution was added to beaker. The 50.123 gm. of H⁺ ion saturated resins were put into the beaker. The pH values in the system were measured by withdrawing samples periodically. The pH values of all such samples taken manually were measured by allowing the pH electrode to reach equilibrium. All

experiments were performed at ambient temperature. The experimental setup for this mode is shown in Figure 3.2.

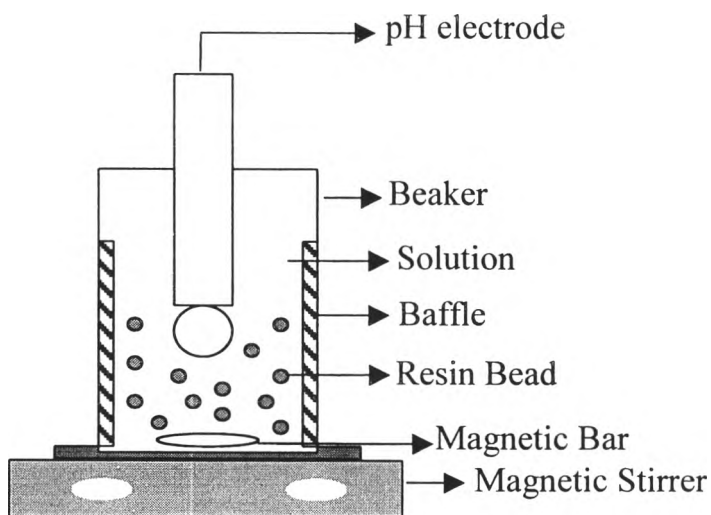


Figure 3.2 Schematic diagram of experimental apparatus for batch operation.

3.3.3 Dynamic Continuous Flow Experiment

The equipment unit was designed to operate in both upflow and downflow direction by using a four-way valve. The chosen liquid was allowed to go to the column by using a selector valve. The two valves at the top and the bottom of the column should be open all the time. An apparatus diagram for the continuous system is illustrated in Figure 3.3.

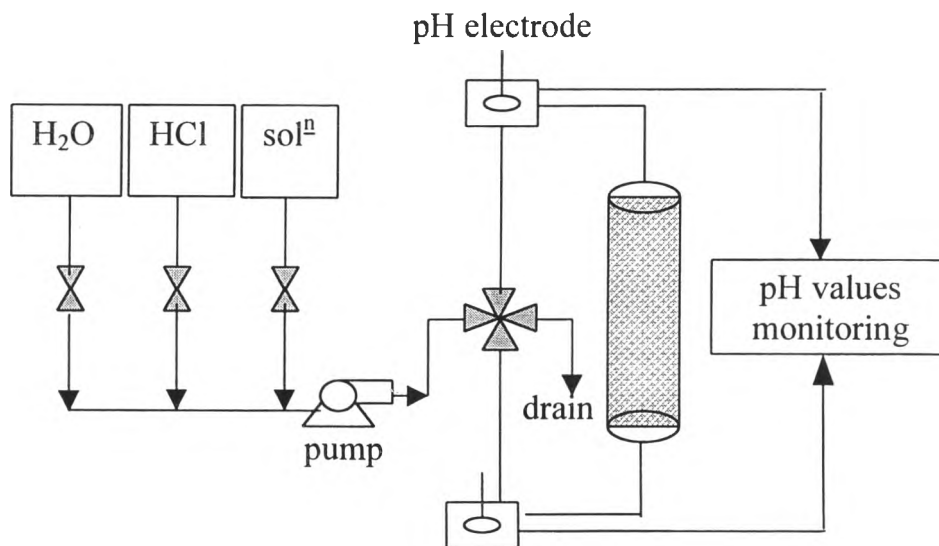


Figure 3.3 Schematic diagram of experimental apparatus for continuous flow operation.

3.3.3.1 No Adsorption Experiment with Downflow

Direction

The four-way shut-off valve was switched to 0.2 N HCl solution to allow the resin bead to contact with more than enough 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 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 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 0.2 N 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 is already saturated with hydrogen ions. The samples were collected manually at successive values of time and measured by a pH electrode after allowing equilibrium to be reached, so that

the response time of the electrode was not a factor. The process was stopped when the pH values of effluent were constant.

3.3.3.2 Adsorption Experiment with Downflow Direction

A procedure similar to the no-adsorption experiment in the downflow direction was conducted, 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 $CaCl_2$, $MgCl_2$ or $CaCl_2/MgCl_2$. The pH values and the samples of the effluent were measured and collected as a function of time. The pH values of all samples were measured by allowing the pH electrode to reach equilibrium. In the case of mixed-ion solutions, the samples were tested to find the Ca^{2+} concentration by using the AAS (atomic absorption spectrometer) technique. The process was stopped when the pH value appeared to be constant (the details of the AAS technique were shown in Appendix H).

3.3.3.3 No Adsorption Experiment with Upflow Direction

A method similar to that of section 3.3.3.1 was used but now operating in the upflow direction.

3.3.3.4 Adsorption Experiment with Upflow Direction

A method similar to that of section 3.3.3.2 was used but now operating in the upflow direction.