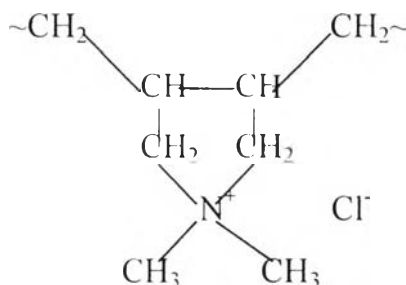


CHAPTER III EXPERIMENTAL SECTION

3.1 Materials

Poly(diallyldimethyl ammonium chloride) or MerQUAT 100, 40 weight percent in an aqueous solution, was obtained from Calgon Corporation. Its average molecular weight is 240 K daltons and its empirical formula of monomer is shown below



Membrane for purification of QUAT was Prep/Scale-TFF Cartridges supplied by Millipore Corporation. The membrane was PLGC cellulose with 6 ft² area and 10 K molecular weight cut-off (MWCO). Sodium chromate was analytical grade supplied by Seelze-Hannover, Germany. Barium chloride dihydrate (AR grade), absolute methanol (99.8 %), standard barium solution (1000 mg/l) for AAS analysis and nitric acid were obtained from Merck company. Sym-diphenylcarbazide, glacial acetic acid, and hydrochloric acid were supplied by J.T.Baker. Potassium chloride (AR grade) used in atomic absorption spectroscopy was purchased from Fluka. Silver nitrate (AR grade) from BHD Laboratory was used to determine chloride ion. Deionized and

distilled water was used to rinse glassware and prepared all solutions in all experiments.

3.2 Preparation

3.2.1 Purification

The QUAT solution was purified in a Prep/Scale-TFFspiral wound ultrafiltration (UF) column. It was operated at the pressure of 25 psig and the flow rate of 300 ml/min. Permeate and retentate existed vertically at the top of the column. Moreover retentate returned to the feed reservoir and permeate was released. Initial QUAT concentration was 0.0742 M and 85% of initial volume was removed as permeate. Distilled water was added to the feed reservoir to original solution volume, this solution then being treated. The purification process was repeated for at least 6 cycles.

3.2.2 Determination of Chromium (VI) Ion

The concentration of chromate in solid precipitation and in the solution at the outlet of the crystallizer was colorimetrically determined by UV/VIS spectrophotometer. This method followed ASTM D1687-92 for determination of chromium (VI) in wastewater (ASTM Test Method D1687-92, 1993). The supernatant was filtered (Whatman No.42) and the clear solution was taken to analyze. Barium chromate particles were filtered, washed 2-3 times with water, and dissolved in a hot solution of 10% HCl.

Sym-diphenylcarbazine reagent was prepared by dissolving 0.1 mg sym-diphenylcarbazine in 50 ml absolute methanol and adjusted to 250 ml by adding the solution of 10% acetic acid in distilled water.

At the low chromate (VI) concentration sym-diphenylcarbazine reagent was used to develop color of red-violet complex with chromium(VI). Then the absorption of complex solution was determined with a UV/VIS

spectrophotometer (Perkin Elmer, Lamda 16) at 542 nm. Determination of chromium (VI) at high concentration was directly measured from its absorbance at 346 nm.

3.2.3 Determination of Barium (II) Ion

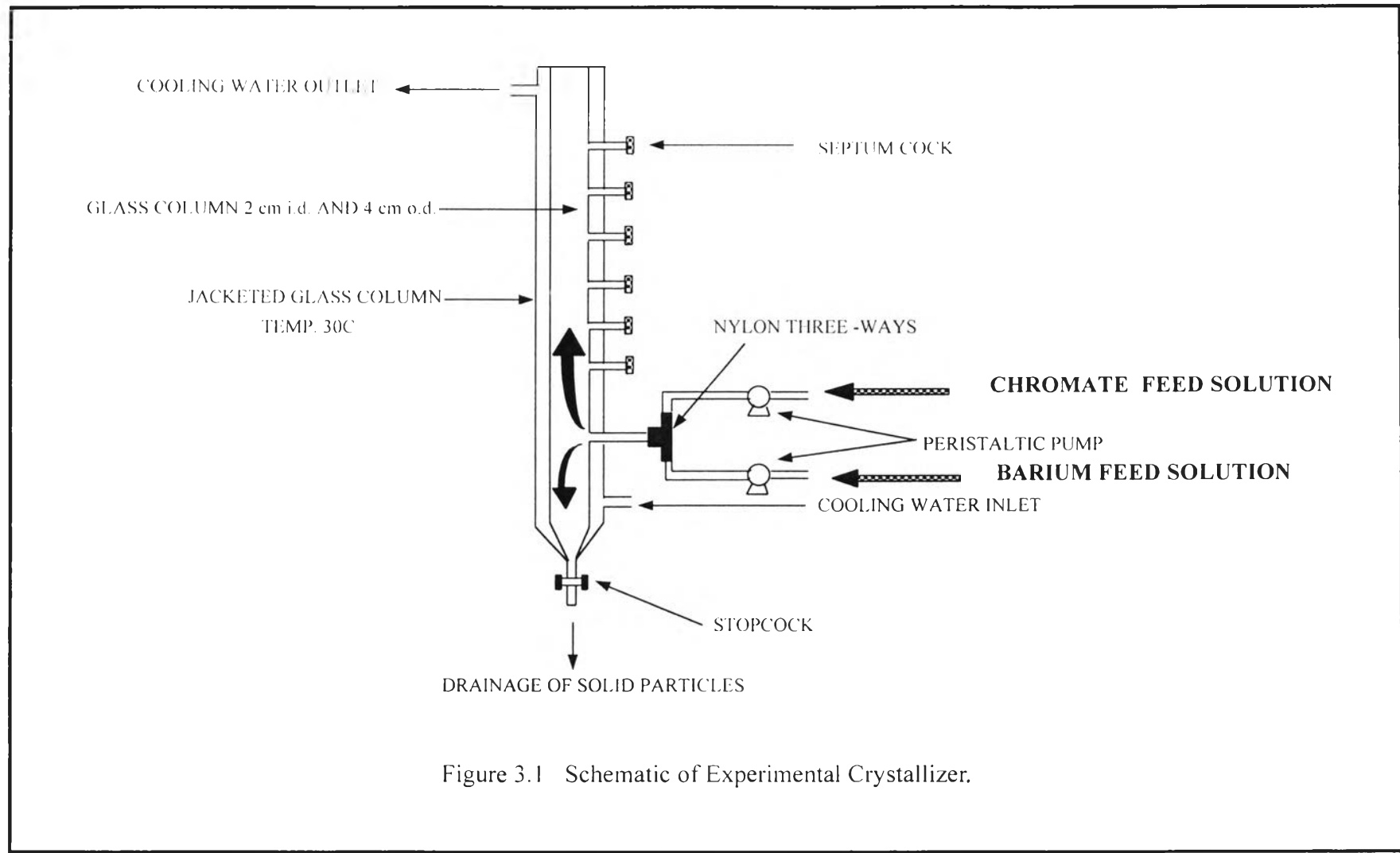
The concentration of barium ion at the outlet of the crystallizer was determined by an atomic absorption spectrophotometer (Varian Spectr AA-300). This method followed ASTM D3651-92 for determination of barium (II) in wastewater (ASTM Test Method D3651-92, 1993). Barium solution was prepared according to the analytical method recommended by the instrument manufacturer and analyzed by using a nitrous oxide-acetylene flame at 553.6 nm.

3.2.4 Determination of Total Organic Carbon

The concentration of QUAT in the solution at the outlet of the crystallizer was determined by a total organic carbon (TOC) Analyzer (Rosemoust Analytical DC-180). This methods followed ASTM D2579-85 for determination of organic carbon in wastewater (ASTM Test Method D2579-85, 1993). The concentration of QUAT was analyzed as total organic carbon which was obtained from subtraction of inorganic carbon from total carbon concentrations.

3.2.5 Crystallizer Design

A design of a crystallizer is shown in Figure 3.1. It is a jacketed glass column. 3 cm i.d., 4 cm o.d., and 130 cm height. The temperature of the column was kept constant at 30°C by circulating water from a temperature controlled bath. The column was designed to have the outlet at different heights (33, 43, 53, 63, 73 and 83 cm) and have a stopcock at the bottom to drain the solid particles. It can be operated in semi-batch or continuous



system. A semi-batch operation allowed QUAT-chromate solution and barium solution to pre-mix in a small reservoir (300 mL volume) before the overflow solution went to the top and then the precipitate accumulated at the bottom. A continuous operation allowed the solution to feed directly to the crystallizer and drained the precipitate at a constant rate of 1 mL/min at the bottom with the supernatant flow rate constant also since the feed flow rate was constant.

3.3 Procedures

3.3.1 Determination of Equilibration Time

The equilibration time was determined by mixing purified QUAT and sodium chromate solutions in test tubes as shown in Table 3.1. Sodium chromate containing QUAT and barium chloride in separate solutions were equilibrated at 30 °C for 30 min in the temperature controlled bath. Then the barium chloride solution was transferred into the chromate containing QUAT solution using a pipetter (Microlab equipment No.960). The solution was immediately mixed and allowed to stay in the temperature controlled bath for 10 min to 72 hr. The supernatant was withdrawn and filtered by using a syringe and analyzed spectrophotometrically for the chromium (VI) concentration.

Table 3.1 Conditions to determine the equilibration time.

No.	Initial concentration(M)		
	QUAT	CrO ₄ ²⁻	Ba ²⁺
1	0	0.02	0.04
2	0.2	0.02	0.04
3	0.3	0.02	0.04
4	0.4	0.02	0.04

3.3.2 Effect of Flow Rate and Column Height on Precipitation

The precipitation was studied both in semi-batch and continuous systems in the crystallizer. Barium and chromate concentration ratio was fixed at 2 : 1. QUAT-chromate solution and barium solution were introduced into the feed inlet of the crystallizer. The precipitation of barium chromate immediately formed and the liquid up along the column to the outlet at 33, 43, 53, 63, 73, or 83 cm outlet height. Large solid particles traveled gravitationally to the bottom while the liquid with some dispersed particles to the outlet. The feed flow rates were varied from 4 to 14 ml/min. The supernatant and solid particles obtained from the first overheads over (5 mL) was taken and analyzed for QUAT, barium and chromate concentrations.

3.3.3 Effect of Concentration Ratio on Precipitation

The feed barium to chromate concentration ratio was varied from 1 to 2.5 in both systems . The concentration of chromate and QUAT were fixed at 0.02 M and 0.2 M respectively. The solution was fed at the flow rate of 14 ml/min and left the column at 83 cm outlet height.