CHAPTER III
A POLYMER RECOVERY PROCESS IN
POLYELECTROLYTE-ENHANCED ULTRAFILTRATION (PEUF)
FOR CHROMATE WASTEWATER TREATMENT:
BATCH AND CONTINUOUS CRYSTALLIZERS

ABSTRACT

Polylectrolyte-enhanced ultrafiltration (PEUF) is a membrane separation process, which can be used in the removal of chromate anion from wastewater. In the process, a water-soluble cationic polyelectrolyte is added to bind to chromate. The bound chromate-polymer is ultrafiltered from the solution, resulting in the purified water (permeate) passing through the membrane, which contains very low chromate concentration. For an economical operation, the retentate solution not passing through the membrane can be treated to separate the polyelectrolyte and chromate ions to permit reuse of the polyelectrolyte and/or concentrate the pollutant ions for disposal. In the regeneration step, barium chloride can be added to the retentate to precipitate chromate anion as compact barium chromate solid waste. The solution containing the concentrated polymer can be directly recycled after the solid barium chromate is separated from the solution. Gravity settling is much less expensive than filtration or centrifugation, so study investigates the abilities to recover polymer and to separate barium chromate solid from the solution in both batch and continuous crystallizers/setters. The effects of the residence time, the [QUAT]/[chromate] ratio and the outlet height were examined. The compositions of batch and continuous crystallization effluent streams were compared to that estimated at equilibrium

INTRODUCTION

Polyelectrolyte-enhanced ultrafiltration (PEUF) can be used to remove chromate in wastewater. In the process, a water-soluble cationic polyelectrolyte, poly (diallyldimethylammonium chloride), is added to the wastewater containing chromate anions. The chromate will bind or adsorb onto the polyelectrolyte. Then the solution is forced to pass through the ultrafiltration membrane which has a pore size small enough to reject the bound polyelectrolyte and chromate ions. The solution passing through the membrane (permeate) is relatively pure water which can be directly distributed to the environment. The removal of chromate, which is a toxic heavy metal, by the PEUF process with rejection more than 99% was obtained from previous work at high polyelectrolyte concentration (1, 2). In this study the retentate solution, which does not pass through the membrane, can be treated to separate the polyelectrolyte and chromate ions to permit the polyelectrolyte to be reused in order to obtain an economic process.

The PEUF process is further developed by adding the regeneration unit (crystallizer) for recovering polyelectrolyte as shown in Fig.1. The addition of the regeneration unit, the cationic polyelectrolyte named poly(diallyldimethylammonium chloride) or QUAT used, can be regenerated and returned to the process. The method for freeing the chromate from the polyelectrolyte and producing a compact chromate waste appears to be a precipitation process (3-7). A barium chloride solution is added to precipitate the chromate out from the retentate stream as barium chromate. The solution containing the concentrated polymer can be directly recycled after the solid barium chromate is separated from the solution. Gravity settling is much less expensive than filtration or centrifugation, so this study investigates the abilities to recover polymer and to separate barium chromate solid from the solution in a crystallizer by gravity settling. A batch as well as a continuous crystallizer for regenerating the polymer was investigated in order to describe the influence of different operational conditions on the polymer recovery and on the solid settling. The effects of the residence time and [QUAT]/[chromate] ratio were examined for batch and continuous operations, but the outlet height effect was examined for only

batch crystallizer. The compositions of batch and continuous crystallization effluent streams were compared to that estimated at equilibrium.

EXPERIMENTAL

Materials

Poly(diallyldimethylammonium chloride) or QUAT having an average molecular weight of approximately 240,000 Daltons was supplied by Calgon Corporation (Pittsburgh, PA) and has the trade name MERQUAT®. The empirical formula of the repeating unit of the polymer is $(H_2C=CHCH_2)_2N(CH_3)_2Cl$. The polyelectrolyte was purified using a 10,000 Daltons molecular weight cut-off, spiral wound membrane in order to remove the lower molecular weight components as had been done in studies of the ultrafiltration step in PEUF studies (1, 2). A stirred cell equipped with a 10,000 Daltons molecular weight cut-off Spectrum™ cellulose acetate (type C) ultrafiltration membrane from Spectrum Medical Company (Houston, TX) was used to concentrate the purified polymer solution up to the desired polymer concentration for preparing stock solutions. Sodium chromate and barium chloride dihydrate were analytical grade (purity of 99%) supplied by Reidel-DeHaen (Seelze, Germany), Merck (Darmstadt, Germany), respectively. Silver nitrate (99.8%) supplied from Merck (Darmstadt, Germany) was used to prepare the titrant to double check polyelectrolyte concentration obtained from total organic carbon or TOC measurement. Sym-diphenylcarbazide supplied from Fluka (Buchs, Switzerland), ethyl alcohol (99.8%) obtained from Carlo Erba (Milan, Italy), and acetic acid obtained from J.T. Baker (Phillipsburg, NJ) were used to prepare the sym-diphenylcarbazide solution to form complex with chromate anion giving a violet color for UV/VIS measurement. All chemicals were used as received. Deionized and distilled water was used to prepare solutions.

Crystallizer design

A crystallizer is shown in Fig. 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 design to have

the different outlet heights and have a micro-valve at the bottom to drain solid particles at a desired flow rate.

Equilibrium precipitation

The equilibrium precipitation was studied by precipitating chromate with barium chloride at controlled temperature of 30°C in a test tube. The initial solutions of sodium chromate, barium chloride, and QUAT were prepared at 30°C. The equilibrated initial solutions were mixed together at different concentration ratios to investigate the effect of [QUAT]/[chromate] ratio and [barium]/[chromate] ratio on barium chromate precipitation. The mixed solution was equilibrated until it reached equilibrium. After centrifuging at 2000 rpm for 10 minutes by a Centrifuge 4236 (A.L.C. International, Milan, Italy), the supernatant was separated by filtration and was analyzed for chromate and QUAT concentrations.

Batch crystallizer operation

The experimental setup of the batch crystallizer is shown in Fig.2. Barium chloride solution and mixture of QUAT and sodium chromate solutions in different reservoirs were simultaneously fed into the empty crystallizer at the column height of 83 cm. The mixed solution was left in the column at various residence times (30, 60, and 120 minutes) after it has reached the height of 73 cm, while the microvalve at the bottom of the column was closed. The sample was collected at outlet heights of 23 and 73 cm to determine chromate and QUAT concentrations.

Continuous crystallizer operation

The experimental setup of the continuous crystallizer is shown in Fig.3. Barium chloride solution and mixture of sodium chromate and QUAT solutions contained in different reservoirs were continuously fed into the column at the column height of 23 cm at the studied feed flow rate (4, 8, 12, and 16 mL/min). The drainage flow rate was kept constant at 0.25xtotal feed flow rate. After the solution has

reached the outlet height of 83 cm, the solution was allowed to overflow for 30 minutes to reach steady state. Then the sample for the determination of chromate and QUAT concentrations was withdrawn at the height of 83 cm.

Analysis

Supernatant solutions were analyzed for chromate concentration using UV/VIS spectrophotometer (Perkin Elmer, Lamda 16, Uberlingen, Germany) at a wavelength of 541.2 nm after complexation with sym-diphenylcarbazide solution. Sym-diphenylcarbazide reagent was prepared by dissolving 0.1 g sym-diphenylcarbazide in 50 mL ethyl alcohol and adjusted to 250 mL by adding 10% acetic acid aqueous solution. A Shimadzu TOC-5000A total organic carbon (TOC) analyzer (Kyoto, Japan) was used to determine the QUAT concentration in supernatant solutions. The QUAT concentration reported in this work is based on the concentration of monomer or diallyldimethylammonium chloride molecules. The molecular weight used to convert mass concentration to molar concentration was 96.08 Daltons, not 2.4×10^5 Daltons (molecular weight of polymer).

RESULTS AND DISCUSSION

Equilibrium precipitation

The fraction of chromate precipitated or the percentage of polyelectrolyte recovery as a function of [QUAT]/[chromate] ratio at different [barium]/[chromate] ratios is shown in Fig. 4. At a fixed [barium]/[chromate] ratio, when [QUAT]/[chromate] ratio increases, the precipitation of barium chromate decreases due to the increased polyelectrolyte in the solution, which provides more binding sites for the chromate ions resulting in less free-chromate ions. For example, at a [barium]/[chromate] ratio of 0.8, the fraction of chromate in precipitate are 76 % and 58 % for [QUAT]/[chromate] ratios of 5 and 20, respectively. On the other hand, the fraction of chromate in precipitate was obtained with increasing [barium]/[chromate] ratio above its stoichiometric ratio of 1. For example, at a [QUAT]/[chromate] ratio of 20 and a [barium]/[chromate] ratio of 0.8, the percentage of polyelectrolyte recovery is 58 %, while at a [barium]/[chromate] ratio of 1.2, the recovery is 95 %.

Batch crystallizer operation

Figure 5 illustrates the fraction of QUAT at the outlet height of 73 cm, at [QUAT]/[chromate] ratios of 5, 15, and 20 and at the different residence times of 30, 60, and 120 minutes. [Barium]/[chromate] ratio was fixed at 1.

The fraction of QUAT recovered decreases with increasing [QUAT]/[chromate] ratio corresponding to the result from the equilibrium precipitation study. At low [QUAT]/[chromate] ratio, the fractions of polymer recovered at any residence times are similar to those equilibrium data in Fig. 4; however, at higher [QUAT]/[chromate] ratio, the percentage of polymer recovery is less than that equilibrium data approximately 5 %. The residence time doesn't have a significant effect on polymer recovery. Figure 6 shows the effect of outlet height and [QUAT]/[chromate] ratio on QUAT recovery. The higher fraction of QUAT was obtained at lower outlet height due to the density difference between water (1 g/cm^3) and QUAT (1.3 g/cm^3). Therefore, the QUAT solution tends to flow down to the bottom of the crystallizer

resulting in the lower polymer recovered at the top of the column. When [QUAT]/ [chromate] ratio increases, the polymer recovery at 73 cm outlet decreases since the density of polymer solution also increases. The fraction of barium chromate lost or the fraction of solid in a polymer recycled stream as a function of [QUAT]/ [chromate] ratio at outlet heights of 23 cm and 73 cm and at residence times of 30, 60, and 120 minutes is shown in Fig. 7. As [QUAT]/[chromate] ratio increases, the fraction of solid in the sample increases, which indicates the poor solid settling However, the fraction of solid lost is lower if the sample is collected at higher outlet position. From the previous work (7), the poor settling at high QUAT concentration can be explained by the viscosity effect. The higher QUAT concentration leads to the higher viscosity resulting in slower barium chromate sedimentation rate This phenomenon also corresponds to Stoke's equation Although the fraction of solid in the solution is high, it can be decreased by increasing the residence time The residence time of 120 minutes shows the lowest dispersion of solid at both outlet heights of 23 cm and 73 cm

Continuous crystallizer operation

The percentage of polyelectrolyte recovery obtained from the continuous crystallizer operation by varying [QUAT]/[chromate] ratio and feed flow rate is shown in Fig. 8 [Barium]/[chromate] ratio was fixed at 1

The result shows that the percentage of QUAT recovery decreases with increasing of [QUAT]/ [chromate] ratio at any feed flow rates; however, the increased feed flow rate can enhance the polyelectrolyte recovery since the solution has high viscosity at high polyelectrolyte concentration Therefore the use of the higher flow rate can reduce the shear stress at the inside of the crystallizer wall resulting in the increasing of the amount of polyelectrolyte recovered At low QUAT concentration, [QUAT]/[chromate] ratio of 5, the constant percentage of polyelectrolyte recovery (~75%) is obtained at any feed flow rates because of its low viscosity At [barium]/[chromate] ratio of 1, the results from the crystallizer operations in Fig 5 and Fig 8 are compared with the results from equilibrium precipitation in Fig 4 to determine the efficiency of batch and continuous crystallizer

operations in the polyelectrolyte recovery. The percentages of QUAT recovery from the equilibrium precipitation and the batch crystallizer are 81 to 93 % and 67 to 99 %, respectively. For the continuous crystallizer, the percentage of QUAT recovery is 62 to 79 % at the flow rate of 16 mL/min, which is the feed flow rate that the highest percentage of QUAT recovery can be obtained. Therefore the polymer recovery from the continuous crystallizer is less than that from the equilibrium precipitation about 20 % and 5 % for the batch operation at high [QUAT]/[chromate] ratio and 20 % at lower [QUAT]/[chromate] ratio.

The fraction of solid coming out in the solution with the recycled polyelectrolyte stream is shown in Fig.9. In the absence of QUAT, the amount of solid is only 3 to 8 % at different feed flow rates. On the other hand, the fractions of solid coming out in the solution are 4 % at low flow rate and up to 55 % at higher feed flow rate in the presence of polyelectrolyte. The particle agglomeration could be visually observed in the absence of polyelectrolyte while the very fine suspended particles are observed at high QUAT concentration. The inhibition of the barium chromate crystal growth is caused by the adsorption of polyelectrolyte on the solid particle resulting in the dispersion of the particle (7). However, the increase of residence time in the crystallizer by decreasing the feed flow rate can enhance the separation of barium chromate from the effluent stream. From the barium chromate sedimentation study (7), it was found that the barium chromate settles rapidly in the absence of polymer. When the polymer is presented, the polymer adsorbs on the crystals and acts like a dispersant as well as causing a solution viscosity increases, resulting in slow settling rates. Unexpectedly, the fraction of solid lost obtained from the batch crystallizer at the residence time of 30 minutes and the outlet height of 73 cm is 17 to 32 %, which is higher than that obtained from the continuous crystallizer (3 to 12 %) at the lowest studied feed flow rate (4 mL/min). However, the percentage of polymer recovery of the continuous crystallizer at this condition is only 20 % at [QUAT]/[chromate] ratio of 20. While the fraction of polymer recovered from the batch operation is 71 % at the same [QUAT]/[chromate] ratio. In the batch system, if the residence time is longer up to 120 minutes, the solid lost will be reduced to 5 to 8 % and the polymer recovery will be 93 to 99 %.

CONCLUSIONS

The continuous, steady state separation using high flow rate is generally much less expensive to operate than a batch process; however, the dispersion of barium chromate particles stabilized by the cationic polyelectrolyte leads to poor separation efficiency in the continuous crystallizer. The polymer recovery of the batch crystallizer is higher than that of the continuous crystallizer, while the batch crystallizer can provide lower amount of solid in the QUAT-recycled stream. This PEUF process with a polymer regeneration unit shows a high feasibility in substitution of conventional processes in chromate wastewater treatment

ACKNOWLEDGMENTS

REFERENCES

1. Sriratana, S.; Scamehorn, J. F.; Chavadej, S.; Saiwan, C.; Haller, K. J.; Christian, S. D.; Tucker, E. E. Use of Polyelectrolyte-Enhanced Ultrafiltration to Remove Chromate from Water. Sep. Sci. Technol. **1996**, *31* (18), 2493-2504.

2. Tangvijitsri, S.; Saiwan, C.; Soponvuttikul, C.; Scamehorn, J.F. Polyelectrolyte-Enhanced Ultrafiltration of Chromate, Sulfate, and Nitrate. Sep. Sci. Technol. **2002**, *37*(5), 1-15.

3. Christian, S D.; Tucker, E. E.; Scamehorn, J. F. Colloid-Enhanced Ultrafiltration Wastewater and Groundwater. Spec. Chem. **1995**, *15*(3), 148-151.

4. Tucker, E. E.; Christian, S. D.; Scamehorn, J F.; Uchiyama, H.; Guo, W. Removal of Chromate from Aqueous Streams by Ultrafiltration and Precipitation. ACS Symp. Ser. **1992**, *491*, 84-98.

5. Tucker, E.E.; Christian, S.D.; Uchiyama, H.; Guo, W.; Scamehorn, J.F.; Puls, R.W. Toxic Anion Removal from Aqueous Streams, Proceedings of the 3rd Annual Conference on Groundwater Quality Research, Dallas, June, 1992.

6. Soponvuttikul, C.; Saiwan, C.; Scamehorn, J.F. Use of Polyelectrolyte-Enhanced Ultrafiltration to Remove Chromate from Water: Polymer Recycle by Precipitation. 222nd ACS National Meeting, Chicago, August, 2001.

7. Soponvuttikul, C.; Scamehorn, J. F.; Saiwan, C. Aqueous Dispersion Behavior of Barium Chromate Crystals: Effect of Cationic Polyelectrolyte. Langmuir. (in press)
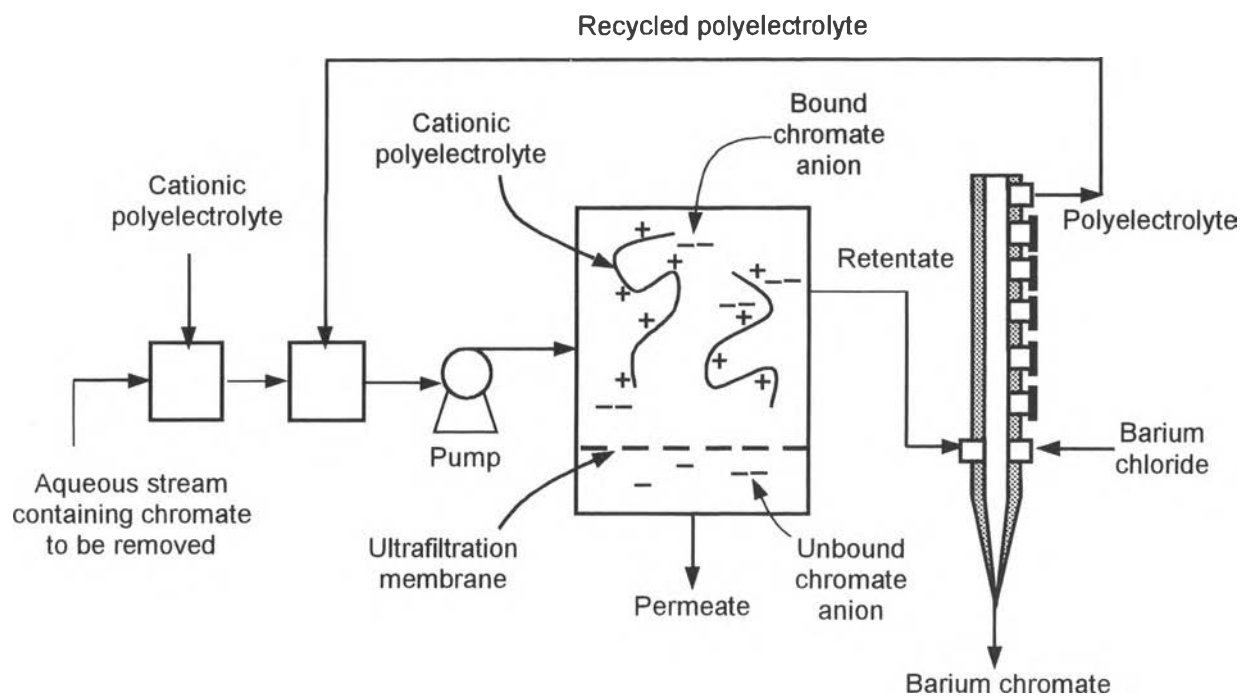
Figure 1. Schematic diagram of PEUF and polyelectrolyte regeneration processes to remove chromate from water.
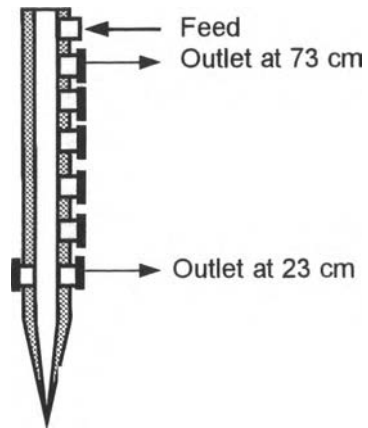
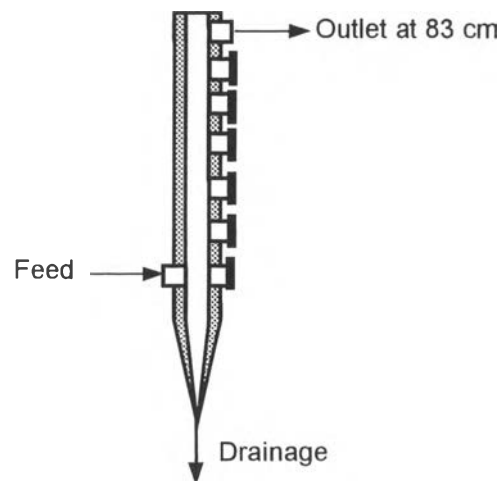Figure 2. Experimental setup of the batch crystallizer

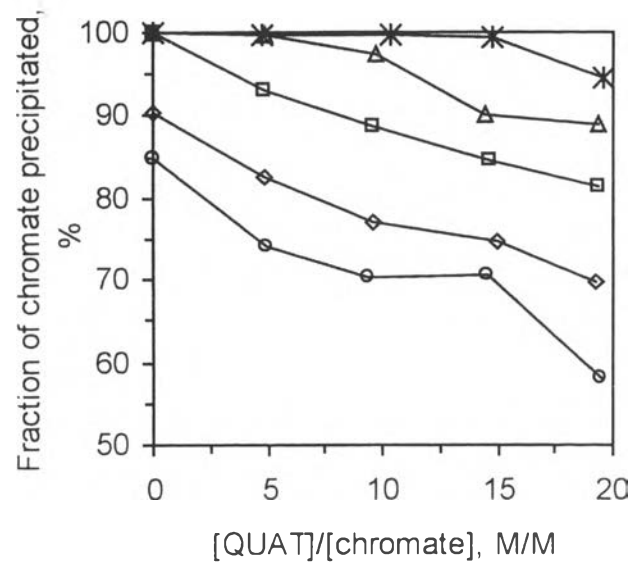Figure 3. Experimental setup of the continuous crystallizer

Figure 4. Fraction of chromate in precipitate at different QUAT to chromate ratios and at various barium to chromate ratios. (O) 0.8, (◇) 0.9, (□) 1.0, (△) 1.1, (✳) 1.2.
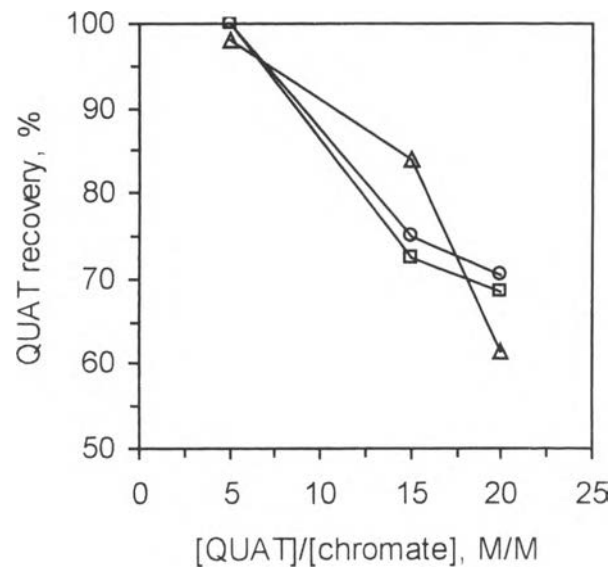

Figure 5. Fraction of QUAT in solution at different QUAT to chromate ratios at various residence times (O) 30 min, (□) 60 min, (△) 120 min
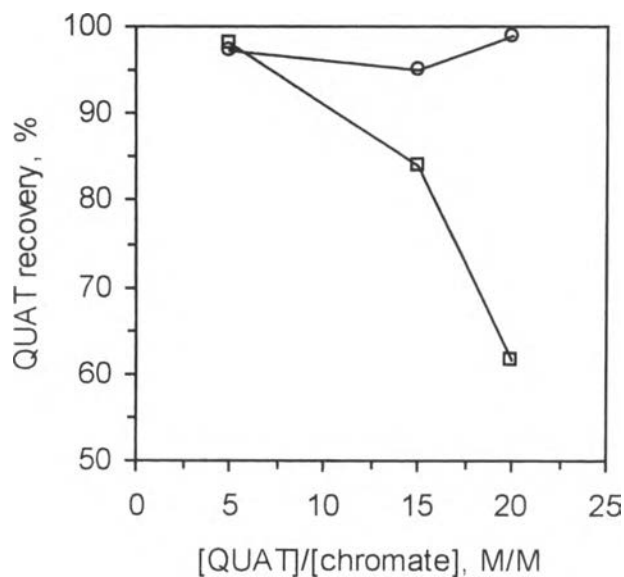
Figure 6. Fraction of QUAT in solution at different QUAT to chromate ratios at various outlet heights. (O) 23 cm, (□) 73 cm.
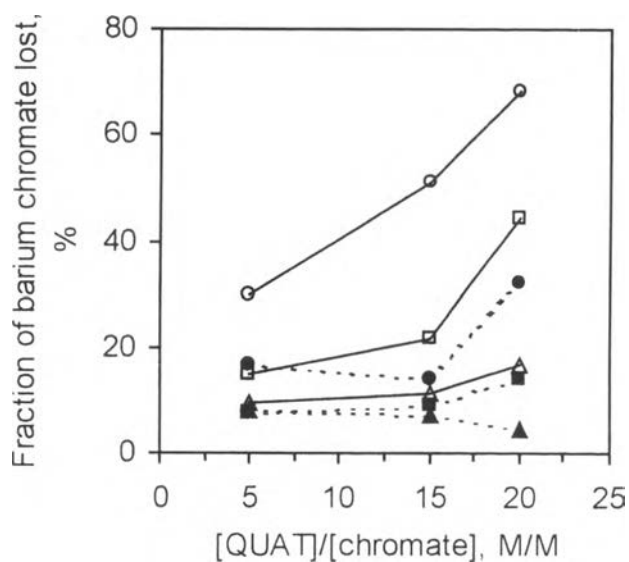

Figure 7. Fraction of barium chromate in solution at different QUAT to chromate ratios at various outlet heights and residence times. (O) 23 cm/30 min, (□) 23 cm/60 min, (△) 23 cm/120 min, (●) 73 cm/30 min, (■) 73 cm/60 min, (▲) 73 cm/120 min
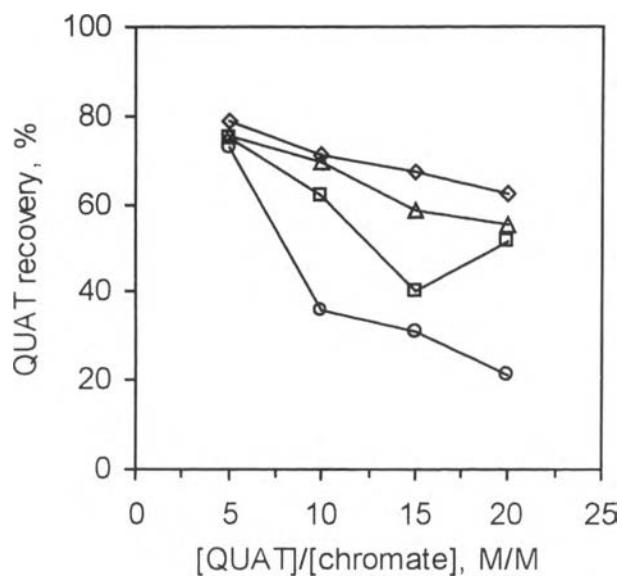
Figure 8 Fraction of QUAT in solution at different QUAT to chromate ratios at various feed flow rates. (O) 4 mL/min, (□) 8 mL/min, (△) 12 mL/min, (◇) 16 mL/min
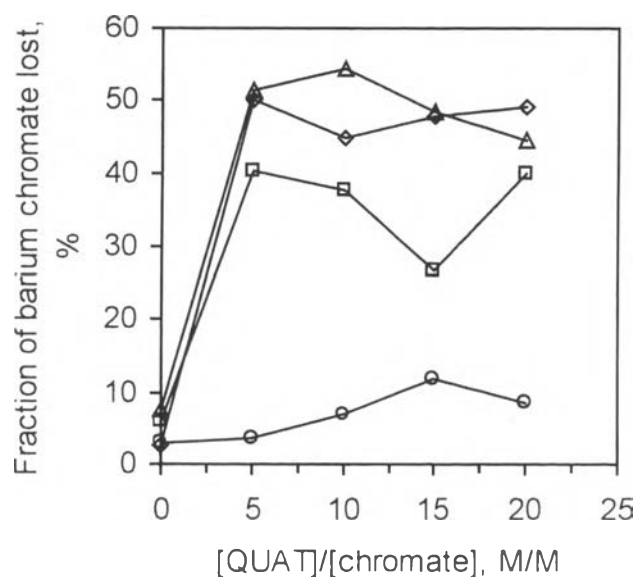

Figure 9 Fraction of barium chromate solid in solution at different QUAT to chromate ratios and at various feed flow rates. (O) 4 mL/min, (□) 8 mL/min, (△) 12 mL/min, (◇) 16 mL/min.