



CHAPTER II
RECOVERY OF POLYELECTROLYTE FROM
POLYELECTROLYTE-ENHANCED ULTRAFILTRATION (PEUF)
BY CRYSTALLIZATION PROCESS:
EQUILIBRIUM PRECIPITATION AND OPTIMIZATION

ABSTRACT

Polyelectrolyte-enhanced ultrafiltration (PEUF) is an effective process, which 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. The solution is then 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 PEUF process has potential to be more economical than other competitive methods because it is a low-energy separation method and it results in a very low volume of ultimate waste in the form of a barium chromate wet cake. 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. To regenerate polyelectrolyte, a barium chloride solution is added to precipitate the chromate out from the retentate stream as barium chromate. The optimization of an integrated design of ultrafiltration and crystallization unit operations is studied by using the equilibrium precipitation results.

INTRODUCTION

Polyelectrolyte-enhanced ultrafiltration (PEUF) (1-17) is a useful separation process for removing solutes species from water. This process requires the addition of a soluble polyelectrolyte with opposite charge of the target ions or molecules to the feed stream to bind with low molecular weight solutes, followed by ultrafiltration to produce a filtrate (permeate) containing a very low concentration of the target molecules or ions compared to a concentration in the feed stream. The polyelectrolyte and bound ions or molecules, which not passing through the membrane, is called retentate. In the previous work (1, 2), the removal of a toxic heavy metal chromate anion (CrO_4^{2-}) by PEUF process using the cationic polyelectrolyte, poly(diallyldimethylammonium chloride) or QUAT over wide range of chromate and QUAT concentrations, as well as different concentrations of sodium chloride, was investigated. The high rejection (99%) and a substantial reduction in rejection with added sodium chloride were observed (1). In order to obtain the high water recovery (permeate/feed ratio), the retentate must have a high QUAT concentration (approximately one-third or one half of the gel concentration) (2). Therefore, for an economic issue, the effective method is required to recover the polyelectrolyte for reuse and to separation chromate anions for disposal

To regenerate the polymer, barium chloride is added to the retentate containing the QUAT and chromate in high concentrations. The chloride ion will reconstitute the polyelectrolyte with its chloride counterion and chromate will be separated out as a compact barium chromate waste (3-5), which settles out, so that inexpensive gravity settling is feasible. The PEUF process can be further developed by adding a regeneration unit (crystallizer) for continuously recovering polyelectrolyte as shown in Fig 1

In addition, the results from the batch field test at Elizabeth City Coast Guard Base, North Carolina supported the feasibility of developing a large scale continuous process to treat industrial wastewater and groundwater containing chromate and sulfate, producing a purified aqueous permeate and a compact barium chromate and barium sulfate (3-5). The equilibrium quantities of chromate and barium in supernatant, amount of barium chromate solid or chromate removed, and amount of

added barium chloride at different degrees of purity can be calculated by modeling (4). A set of simultaneous equations consisting of equations of solubility product of barium chromate and charge balances was modeled.

In this study, the effects of chemicals, which are QUAT concentration, barium to chromate concentration ratio, and sodium chloride concentration on the equilibrium precipitation of barium chromate, were investigated in laboratory scale experiments. The amount of added barium chloride, amount of barium chloride remained in the purify water, the optimum condition of the integrated PEUF and recovery processes were predicted from a processing engineering calculation base on the equilibrium precipitation results obtained from this study and the PEUF results obtained from the previous work (2), before starting up the integrated operation.

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 $(\text{H}_2\text{C}=\text{CHCH}_2)_2\text{N}(\text{CH}_3)_2\text{Cl}$. 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, barium chloride dihydrate, and sodium chloride were analytical grade (purity of 99%) supplied by Reidel-DeHaen (Seelze, Germany), Merck (Darmstadt, Germany), and Carlo Erba (Milan, Italy), 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.

Methods

The equilibrium precipitation was studied by precipitating chromate with barium chloride at the controlled temperature of 30°C. The initial solutions of sodium chromate, barium chloride, QUAT and sodium chloride were prepared at 30 °C for

equilibrium precipitation studies in the presence and in the absence of added salt. The equilibrated initial solutions were mixed together at several different concentration ratios to investigate the effect of chemical species involved in 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. Additionally, the optimum conditions between both PEUF and recovery processes were obtained by engineering calculation from the equilibrium precipitation data.

Analysis

The supernatant solutions were analyzed for chromate concentration using UV/VIS spectrophotometer (Perkin Elmer, Lamda 16, Uberlingen, Germany) at wavelength 541.2 nm after complexation with sym-diphenylcarbazide. 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. This measurement was used to determine the amount of QUAT precipitated with barium chromate solid.

RESULTS AND DISCUSSION

Equilibrium precipitation

The fraction of chromate in precipitate or the percentage of polyelectrolyte recovery as a function of $[\text{QUAT}]/[\text{CrO}_4^{2-}]$ ratios in the absence and in the presence of added sodium chloride are shown in Figs 2 and 3, respectively.

In the absence of added sodium chloride, Fig. 2 shows the effect of the $[\text{QUAT}]/[\text{CrO}_4^{2-}]$ ratio and the $[\text{Ba}^{2+}]/[\text{CrO}_4^{2-}]$ ratio on the barium chromate precipitation in the absence and in the presence of QUAT. In the absence of QUAT, the fraction of chromate precipitated is 100.00% at $[\text{Ba}^{2+}]/[\text{CrO}_4^{2-}]$ ratios of 1.0 (stoichiometric ratio), 1.1, and 1.2. Whereas, lower fractions of chromate precipitated are obtained at $[\text{Ba}^{2+}]/[\text{CrO}_4^{2-}]$ ratios of 0.8 and 0.9 (sub-stoichiometric), which are 84.96 and 90.54%, respectively. In the presence of QUAT, at any $[\text{Ba}^{2+}]/[\text{CrO}_4^{2-}]$ ratios, the precipitation of barium chromate decreases as the $[\text{QUAT}]/[\text{CrO}_4^{2-}]$ ratio increases, since the increased polyelectrolyte concentration provides more binding positive sites for the chromate anions, which increases the difficulty for chromate anions to be freed and to be precipitated. Moreover, the solubility product of barium chromate solid is affected by the addition of QUAT. The high QUAT concentration results in the higher solubility of barium chromate two orders of magnitude comparing to the solubility of barium chromate in pure water (2.1×10^{-10}). For example, at a $[\text{Ba}^{2+}]/[\text{CrO}_4^{2-}]$ ratio of 1.0 (stoichiometric ratio), fractions of chromate precipitated are 93.13, 88.52, 84.53, and 81.46 % at $[\text{QUAT}]/[\text{CrO}_4^{2-}]$ ratios of 5, 10, 15, and 20, respectively. On the other hand, the chromate rejection increases as the $[\text{QUAT}]/[\text{CrO}_4^{2-}]$ ratio increases in the previous PEUF work (1, 2). For example, at retentate $[\text{QUAT}]$ of 300 mM, chromate rejections are 91.45, 98.20, and 99.45 % at $[\text{QUAT}]/[\text{CrO}_4^{2-}]$ ratios of 5, 10, and 20, respectively. It demonstrates that the $[\text{QUAT}]/[\text{CrO}_4^{2-}]$ ratio is an optimized parameter in the integrated PEUF and regeneration processes. In addition, the higher fraction of chromate precipitated is obtained with increasing $[\text{Ba}^{2+}]/[\text{CrO}_4^{2-}]$ ratio. For example, at a $[\text{QUAT}]/[\text{CrO}_4^{2-}]$ ratio of 20, percentages of polyelectrolyte recovery are 58.24,

69.77, 81.46, 89.02, and 94.51 % at $[\text{Ba}^{2-}]/[\text{CrO}_4^{2-}]$ ratios of 0.8, 0.9, 1.0, 1.1, and 1.2, respectively.

Figure 3 shows the effect of the concentration of added sodium chloride on the precipitation of barium chromate in the absence and in the presence of QUAT at a $[\text{Ba}^{2-}]/[\text{CrO}_4^{2-}]$ ratio of 1.6. The fraction of chromate precipitated increases when sodium chloride is added to the system due to the competition of the chloride ions (monovalent) (from the addition of sodium chloride) with chromate ions (divalent) to bind onto the positive site of the polymer, resulting in the lower amount of bound chromate anions with the polymer. Therefore, it's easier for chromate anions to be freed and to be precipitated as barium chromate. For example, at a $[\text{Ba}^{2-}]/[\text{CrO}_4^{2-}]$ ratio of 1.6 and a $[\text{QUAT}]/[\text{CrO}_4^{2-}]$ ratio of 5, fractions of chromate precipitated are 99.94, 99.96, 99.97, 99.97, and 99.97 % at $[\text{NaCl}]$ of 0.01, 0.02, 0.04, 0.08, and 0.10 M, respectively. Oppositely, the addition of salt results in the decrease of the chromate rejection (1) due to the binding completion between chloride ions and chromate ions. For example, at a $[\text{QUAT}]/[\text{CrO}_4^{2-}]$ ratio of 20, chromate rejections are 99.60, 98.51, 89.76, and 71.01 % at $[\text{NaCl}]$ of 0.01, 0.05, and 0.10 M, respectively. For an integrated process, $[\text{NaCl}]$ is another parameter, which is needed to be optimized. In the presence of added salt, the amount of barium chromate precipitated also decreases as the polymer concentration increases. For example, at a $[\text{NaCl}]$ of 0.04 M, the fraction of chromate precipitated are 99.97, 99.94, 99.92, and 99.90 % at $[\text{QUAT}]/[\text{CrO}_4^{2-}]$ ratios of 5, 10, 15, and 20, respectively. In the absence of QUAT, the precipitation of the barium chromate decreases with the increasing of salt concentration due to the activity effect resulting in the higher barium chromate solubility.

Optimization

In the polyelectrolyte regeneration process of the integrated process in Fig. 1, the amount of barium chloride added is concerned. The higher amount of barium chloride is added to attain the high fraction of polyelectrolyte recovery, the higher amount of an excess barium chloride coming out with purified water would be obtained. Although barium is much less toxic than chromate, its drainage to the

environment should be concerned. The optimization of the addition of barium chloride in polymer regeneration process was investigated by using a processing engineering calculation

In order to obtain the continuous operation, an assumption is made, the chromate concentration in a recycled stream is always equaled to the chromate concentration in the feed stream. Normally, the chromate concentration in the feed stream (wastewater) is known, therefore the chromate concentration in the retentate stream can be calculated by using the results of PEUF (2) at the desired chromate rejection, QUAT concentration in the retentate, and the $[\text{QUAT}]/[\text{CrO}_4^{2-}]$ ratio. The chromate concentration in the retentate obtained from the calculation can be used to determine the percentage of chromate precipitated based on the results from the equilibrium precipitation in this study. Finally, the barium concentration, which is required to be added to the retentate stream to recover QUAT and the barium concentration, which comes out with purified water in PEUF process can be determined at any initial chromate wastewater concentrations.

Figure 4 shows a mole ratio of barium added to chromate in the feed stream as a function of a chromate molar ratio in purified water to feed. In order to achieve the high purity of the permeate stream, the addition of the large amount of barium is required in the regeneration step. The amount of excess barium left over from the precipitation will come out with purified water as shown in Fig. 5. The result shows the $[\text{Ba}^{2+}]/[\text{CrO}_4^{2-}]$ in purified water increases as the chromate molar ratio in purified water to feed decreases or the purity of the purified water increases.

The proper amount of barium chloride, QUAT, and sodium chloride, which will be used in the integrated PEUF and polymer recovery processes can be determined at any concentrations of chromate in wastewater to achieve the desired degree of purity of the purified water.

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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. Sasaki, K. J.; Burnett, S. L.; Christian, S. D.; Tucker, E. E., Scamehorn, J. F. Polyelectrolyte Ultrafiltration of Multivalent Ions. Removal of Cu²⁺ by Sodium Poly(styrenesulfonate). *Langmuir* **1989**, *5*(2), 363-369
7. Scamehorn, J. F., Christian, S. D.; Tucker, E. E.; Tan, B. I. Concentration Polarization in Polyelectrolyte-Enhanced Ultrafiltration. *Colloids Surf.* **1990**, *49*(3&4), 259-267.
8. Tabatabai, A.; Scamehorn, J. F.; Christian, S. D. Water Softening using Polyelectrolyte-Enhanced Ultrafiltration. *Sep. Sci. Technol.* **1995**, *30*(2), 211-224.
9. Tabatabai, A., Scamehorn, J. F.; Christian, S. D. Economic Feasibility Study of Polyelectrolyte-Enhanced Ultrafiltration (PEUF) for Water Softening. *J. Membr. Sci.* **1995**, *100*(3), 193-207.
10. Mundkur, S. D., Watters, J.C. Polyelectrolyte-Enhanced Ultrafiltration of Copper from a Waste Stream. *Sep. Sci. Technol.* **1993**, *28*(5), 1157-1168

11. Volchek, K.; Krentsel, E.; Zhilin, Y.; Shtereva, G.; Dytnerky, Y. Polymer Binding/Ultrafiltration as a Method for Concentration and Separation of Metals. *J. Membr. Sci.* **1993**, *79*(2&3), 253-272.
12. Zhou, R.; Palmer, V.; Geckeler, K. E. Removal of Inorganic Ions by Polymer-Based Colloid-Enhanced Membrane Filtration in Aqueous Solution. *Wat. Res.* **1994**, *28*(5), 1257-1260.
13. Geckeler, K. E.; Volchek, K. Removal of Hazardous Substances from Water using Ultrafiltration in conjunction with Soluble Polymers. *Envir. Sci. Technol.* **1996**, *30*(3), 725-733.
14. Smith, B.F.; Robison, T.W.; Jarvinen, G.D. Water-Soluble Metal-Binding Polymers with Ultrafiltration. *ACS Symp. Ser.* **1999**, *716*, 294-330.
15. Novikov, P.A.; Shiknev, V.M.; Spivakov, B.Ya.; Myasoedov, B.F.; Geckeler, K.E.; Bayer, E. Separation and Concentration of Actinides by a Water Soluble Oxine Polymer Using Membrane Filtration. *Radiochim. Acta* **1989**, *46*, 35-45.
16. Shkinev, V.M.; Vorob'eva, G.A.; Spivakov, B.Ya.; Geckeler, K.; Bayer, E. Enrichment of Arsenic and Its Separation from Other Elements by Liquid-Phase Polymer-Based Retention. *Sep. Sci. Technol.* **1987**, *22*(11), 2165-2173.
17. Nguyen, Q.T.; Aptel, P.; Neel, J. Application of Ultrafiltration to the Concentration and Separation of Solutes of Low Molecular Weight. *J. Membr. Sci.* **1980**, *6*(1), 71-82.

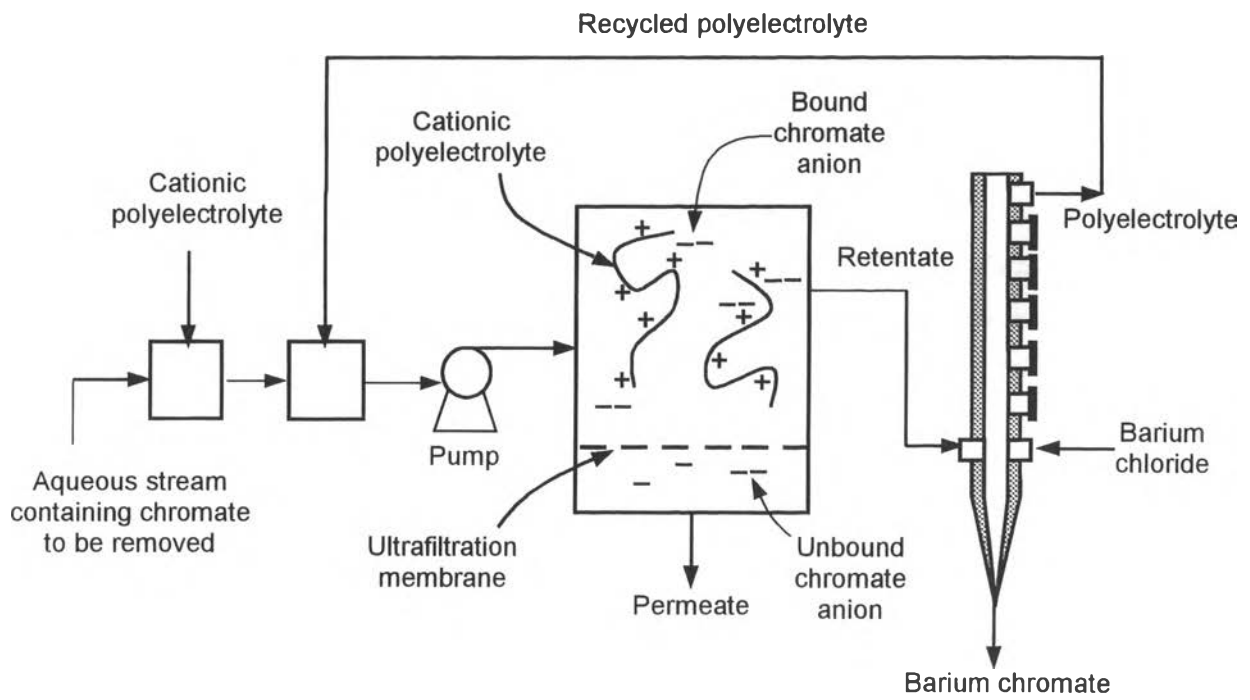


Figure 1. Schematic diagram of PEUF and polyelectrolyte regeneration processes to remove chromate from water.

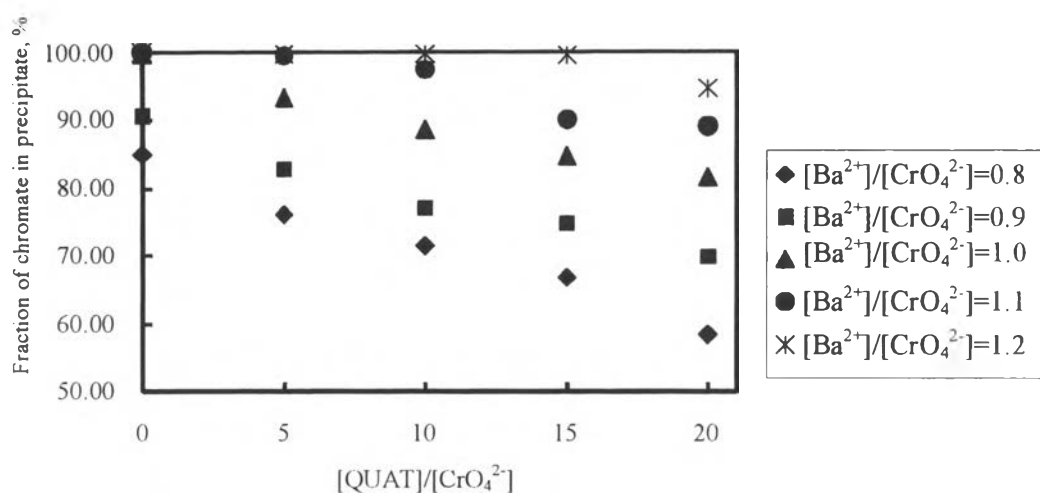


Figure 2. Fraction of chromate in precipitation at different $[\text{QUAT}]/[\text{CrO}_4^{2-}]$ ratios.

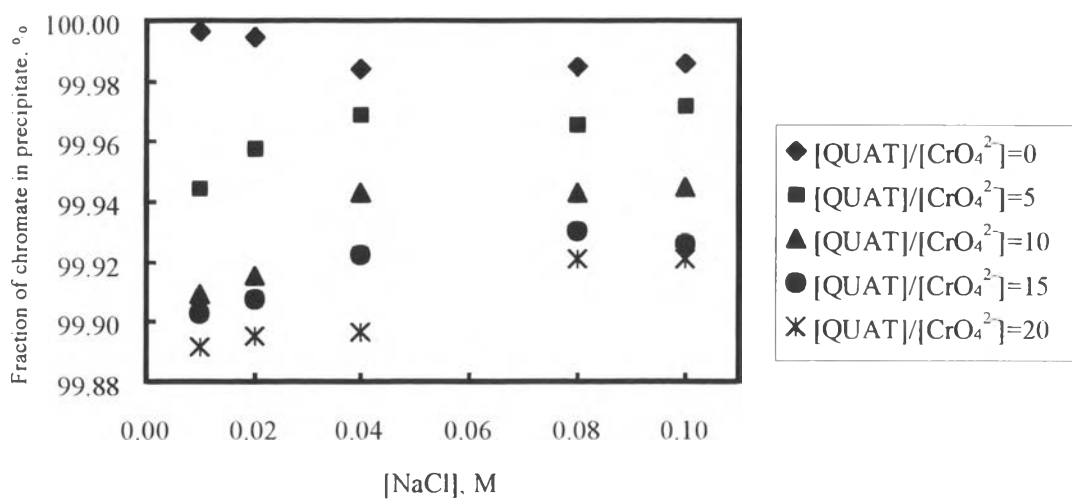


Figure 3. Fraction of chromate in precipitate at different $[\text{NaCl}]$.

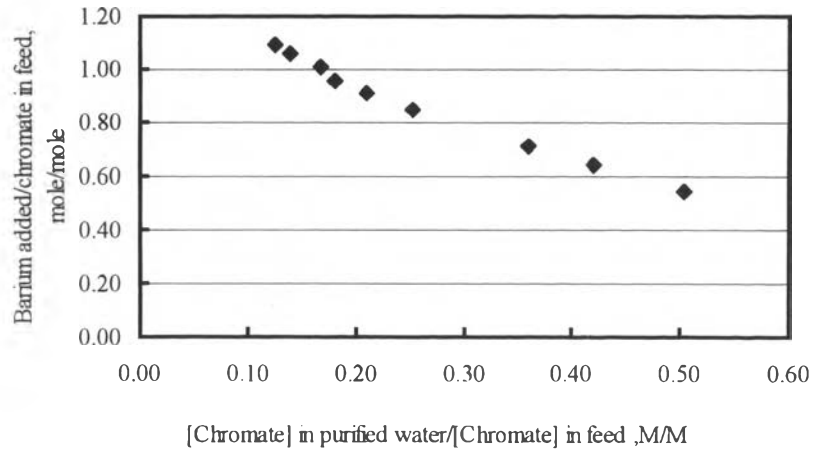


Figure 4. Added barium in crystallizer/chromate in feed at different chromate removal levels.

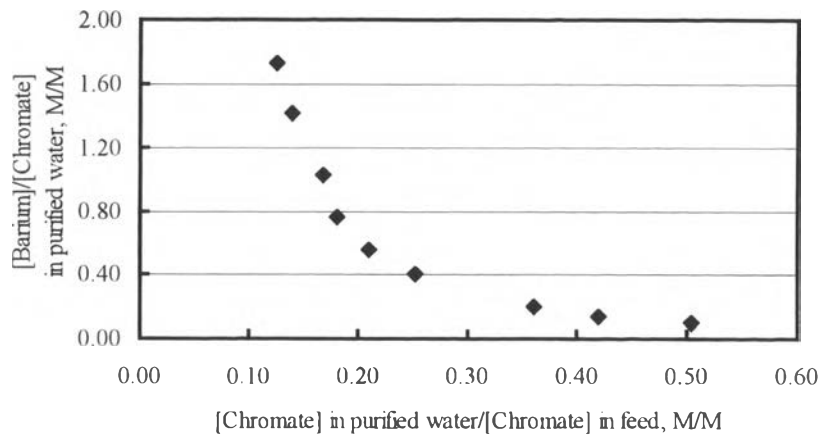


Figure 5. Barium concentration/chromate concentration in purified water at different chromate removal levels.