รายงานวิจัยฉบับสมบูรณ์

โครงการ

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# (Recovery of Polyelectrolyte from Polyelectrolyte-Enhanced Ultrafiltration by Precipitation Process)

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สัญญาเลขที่ BGJ4480004

# รายงานวิจัยฉบับสมบูรณ์

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ระยะเวลาโครงการ : 1 ปี

กระบวนการตกตะกอนเพื่อนำสารพอลิอิเล็กโตรไลต์กลับคืนจากกระบวนการกำจัดโครเมทออกจากน้ำเสียโดยการกรองแบบอุลตร้าฟิลเตรชั่นที่มีพอลิอิเล็กโตรไลต์เพิ่มการกรองได้มีการศึกษาทั้งการตกตะกอนขนาดแล็บสเกลและการตกตะกอนแบบกะและแบบต่อเนื่องในเครื่องตกผลึกขนาดนำร่อง กระบวนการกรองแบบอุลตร้าฟิลเตรชั่นที่มีพอลิอิเล็กโตรไลต์เพิ่มการกรองเป็นกระบวนการแยกโดยอาศัยเยื่อเลือกผ่านซึ่งสามารถใช้กำจัดโครเมทอิออนออกจากน้ำเสีย ส่วนที่ถูกกักโดยเยื่อเลือกผ่านนั้นประกอบด้วยพอลิอิเล็กโตรไลต์ที่จับอยู่กับโครเมทอิออนที่มีความเข้มข้นสูงจึงต้องทำการแยกสารพอลิอิเล็กโตรไลต์ออกจากโครเมทเพื่อนำพอลิอิเล็กโตรไลต์กลับคืนมาใช้ใหม่ ในกระบวนนั้นจะเติมแบเรียมคลอไรด์ในส่วนที่ถูกกักโดยเยื่อเลือกผ่านเพื่อตกตะกอนโครเมทอิออนให้อยู่ในรูปของตะกอนแบเรียมโครเมท ในงานวิจัยนี้จึงศึกษาความสามารถในการนำพอลิอิเล็กโตรไลต์กลับมาใช้ใหม่และความสามารถในการแยกตะกอนแบเรียมโครเมทออกจากสารละลายโดยเครื่องตกผลึก โดยศึกษาผลกระทบของระยะเวลาของตะกอนในเครื่องตกผลึกหรืออัตราการป้อนของสาร ความสูงของเครื่องตกผลึก อัตราส่วนความเข้มข้นของพอลิอิเล็กโตรไลต์ต่อโครเมท ทั้งนี้พบว่าสัดส่วนการนำพอลิอิเล็กโตรไลต์กลับคืนจากการทดลองขนาดแล็บสเกลมีปริมาณสูงสุดและการทดลองแบบกะให้ผลการนำพอลิอิเล็กโตรไลต์กลับคืนมากกว่าแบบต่อเนื่อง นอกจากนั้นยังพบว่าสารพอลิอิเล็กโตรไลต์ประจุบวกมีผลทำให้เกิดการกระจายตัวของอนุภาคแบเรียมโครเมทซึ่งส่งผลให้ประสิทธิภาพในการแยกตะกอนในเครื่องตกผลึกต่ำ ดังนั้นจึงได้มีการศึกษาเกี่ยวกับผลกระทบของพอลิอิเล็กโตรไลต์ประจุบวกต่อการกระจายตัวของแบเรียมโครเมท โดยได้ศึกษาผลกระทบของอัตราส่วนความเข้มข้นแบเรียมต่อโครเมท ความเข้มข้นของพอลิอิเล็กโตรไลต์ อุณหภูมิและการเติมอิเล็กโตรไลต์ต่อการกระจายของขนาดอนุภาค อัตราการตกตะกอน ความหนืด รูปร่างลักษณะของผลึก ศักย์ซีต้าของอนุภาคแบเรียมโครเมทในกระบวนการตกผลึกแบเรียมโครเมท ทั้งนี้พบว่าการดูดซับของพอลิอิเล็กโตรไลต์บนอนุภาคแบเรียมโครเมทเป็นผลทำให้ขนาดของอนุภาคเล็กลงและเมื่อความเข้มข้นของพอลิอิเล็กโตรไลต์เพิ่มขึ้น ความหนืดของสารละลายจะเพิ่มขึ้นซึ่งทำให้อัตราการตกตะกอนลดลง ดังนั้นการเพิ่มเวลาในการตกตะกอนในเครื่องตกผลึกแบบกะทำให้การแยกตะกอนดีขึ้นหรือทำให้อนุภาคถูกพาออกมากับสารพอลิอิเล็กโตรไลต์น้อยลง

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The recovery of polyelectrolyte from polyelectrolyte-enhanced ultrafiltration (PEUF) for chromate removal was studied as equilibrium experiments in a laboratory scale and batch and continuous operations in a pilot scale crystallizer. PEUF is a membrane separation process, which can be used in the removal of chromate anion from wastewater. 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. In the regeneration step, barium chloride can be added to the retentate to precipitate chromate anion as compact barium chromate solid waste. This study investigates the abilities to recover polyelectrolyte and to separate barium chromate solid from the solution in a crystallizer. The effects of the residence time or feed flow rate, height of the column, and polymer to chromate ratio were studied. The highest percentage of polymer recovery was obtained from the equilibrium precipitation followed by the batch crystallizer operation and the continuous crystallizer operation, respectively. The dispersion of barium chromate particles stabilized by the cationic polyelectrolyte leads to poor separation efficiency in the crystallizer. Therefore, a fundamental study on the effect of cationic polyelectrolyte on barium chromate dispersion was carried out. The effect of barium to chromate ratio, polyelectrolyte concentration, temperature, and added electrolyte on particle size distribution, sedimentation rate, viscosity, crystal morphology, and zeta potential of particle in the barium chromate crystallization process was determined. Polymer adsorption leading to a decreased particle size, as well as increased solution viscosity, causes sedimentation rate to decrease with increasing polyelectrolyte concentration. The increased residence time in a batch crystallizer results in decreased carry-over barium chromate particles or better solid separation.

**Keywords:** Chromate/ Polyelectrolyte/ Precipitation/ Ultrafiltration/ Water treatment

# TABLE OF CONTENTS

CHAPTER PAGE

## LIST OF TABLES

TABLE PAGE

### Chapter IV

### Appendix

# LIST OF FIGURES

FIGURE PAGE

## Chapter II

## Chapter III

FIGURE PAGE

**Chapter IV**

Appendix

FIGURE PAGE

# CHAPTER I

# INTRODUCTION

# INTRODUCTION

Nowadays disposal of chromium-containing wastewater has become a serious environmental problem to the industries. Chromium compounds are widely used in the manufacture of ceramics, catalysts, pigments, wood preservatives and fungicides, in metal finishing, in corrosion control, in tanning industry, in magnetic tapes and in printing and dyeing of textiles (Westbrook, 1993).

Two stable oxidation states of chromium occur in natural environments are chromium (VI) and chromium (III). Hexavalent chromium is more toxic than trivalent chromium (Westbrook, 1993). Occupational exposure to chromium (VI) is of concern because it is non-biodegradable and highly toxic compound; moreover, it has mutagenic and carcinogenic effect. Effects on the body include skin ulceration, inflammation of air passages, allergic reactions, and lung cancer.

Various methods have been used to remove chromium from industrial waste water. The traditional techniques for removal of chromium ion from aqueous effluents, which are lime precipitation or process of reduction, are incapable of reducing concentration to the levels required by law. Drinking water standards have been set at 0.1 mg/L total chromium (Page and Loar, 1993). Although these conventional processes generate the large amount of hydroxide solid at the end of the process, they have been widely used in industries. The other methods including electrochemical precipitation (Kongsricharoern and Polprasert, 1995, 1996), ion exchange (Zhao *et al.*, 1998) and activated carbon adsorption (Lalvani *et al.*, 1998) are prohibitively expensive. Moreover, these processes are still in developing stages.

The use of membrane separation process in treating wastewater containing metal ions is today an attractive and suitable technique because the separation can be carried out at room temperature, the modular membrane can be easily adjusted to the wastewater flows; and various industrial membranes are now available. In order to retain chromium ions, reverse osmosis is used. Reverse osmosis is a membrane process, which applies pressure forces water to pass through a semi-permeable membrane, which prevents the passage of dissolved and suspended constituents (Tucker, 1992). But the usual permeate fluxes of reverse osmosis membranes are limited and require high transmembrane pressure (200-800 psi), which makes the process expensive. In addition, the reverse osmosis process is often affected by fouling, scaling, and chemical deterioration of the membrane.

Ultrafiltration is an attractive industrial separation technique for removing molecules from wastewater; however; traditional ultrafiltration is not effective in removing solutes having molecular weight less than 500 Daltons (Christian *et al.*, 1995). A new class of ultrafiltration techniques developed is called colloid-enhanced ultrafiltration (CEUF) (Christian *et al.*, 1990, 1995). These technologies all involve adding water-soluble colloids to aqueous stream and subsequently using ultrafiltration to remove target ions and molecules that could not be effectively removed by ultrafiltration. The techniques that have been investigated up to the present include micellar-enhanced ultrafiltration (MEUF) (Scamehorn *et al.*, 1986, 1994; Dunn *et al.*, 1985, 1987; Bhat *et al.*, 1987; Smith *et al.*, 1987; Christian *et al.*, 1988; Choi *et al.*, 1998; Gzara and Dhahbi, 2001), polyelectrolyte-enhanced ultrafiltration (PEUF) (Sasaki *et al.*, 1989; Novikov *et al.*, 1989; Tucker *et al.*, 1992a, 1992b; Mundker and Watters, 1993; Volchek *et al.*, 1993; Zhou *et al.*. 1994; Tabatabai *et al.*, 1995a, 1995b; Geckeler and Volchek, 1996, Juang and Chen, 1996; Sriratana *et al.*, 1996; Uludag *et al.*, 1997; Muslehddinoglu *et al.*, 1998; Tangvijitsri *et al.*, 2002), polectrolyte-surfactant complexes in CEUF(Guo *et al.*, 1997) , ligand-modified micellar-enhanced ultrafiltration (LM-MEUF) (Klepac *et al.*, 1991; Fillipi *et al.*,1997, 1998), ligand-modified polyelectrolyte-enhanced ultrafiltration (LM-PEUF) (Tuncay *et al.*, 1994a, 1994b) and ion-expulsion ultrafiltration (IEUF) (Christian *et al.*, 1989; Krehbiel *et al.*, 1992).

In PEUF, a water-soluble polyelectrolyte, of charge opposite to that of the soluble target ion, is added to the polluted water. The target ion binds or adsorbs onto the polyelectrolyte. The solution is then treated by ultrafiltration with membrane pore size small enough to reject the polyelectrolyte. The purified water (permeate) may be released to the environment. If the permeate is not sufficiently low, the process can be staged to achieve any desired degree of purity.

Ions, which have been studied in PEUF, include divalent cations such as copper (Sasaki *et al.*, 1989; Mundker and Watters, 1993; Volchek *et al.*, 1993; Geckeler and Volchek, 1996; Juang and Chen, 1996), nickel (Volchek *et al.*, 1993; Geckeler and Volchek, 1996), cadmium (Volchek *et al.*, 1993; Geckeler and Volchek, 1996; Müslehddinoglu *et al*, 1998), cobalt (Volchek *et al.*, 1993; Geckeler and Volchek, 1996), zinc (Volchek *et al.*, 1993; Geckeler and Volchek, 1996), mercury (Geckeler and Volchek, 1996; Uludag *et al.*, 1997; Müslehddinoglu *et al*, 1998), calcium (Tabatabai *et al.*, 1995; Geckeler and Volchek, 1996; Müslehddinoglu *et al.*, 1998), magnesium (Tabatabai *et al.*, 1995; Geckeler and Volchek, 1996) (with an anionic polyelectrolyte), divalent anions such as chromate (Tucker *et al.*, 1992a, 1992b; Sriratana *et al.*, 1996; Tangvijitsri *et al.*, 2002), sulfate (Tangvijitsri *et al.*, 2002), monovalent anion such as nitrate (Tangvijitsri *et al.*, 2002), and multivalent anions such as arsenic or arsenate (Shkinev *et al.*, 1987; Geckeler and Volchek, 1996; Legault *et al.*, 1993), actinides (Novikov *et al.*, 1989)and selenite or selenate (Geckeler and Volchek, 1996) (with a cationic polyelectrolyte).

In the purification of water containing chromate, the cationic polyelectrolyte poly (diallyldimethylammonium chloride) or QUAT is used in removing chromate over a wide range of chromate and QUAT concentrations, as well as different concentrations of added NaCl. In the absence of other added electrolytes, chromate rejections of up to 99.8% were observed. The presence of added NaCl reduces the chromate rejection substantially. The results also gave high gel concentration and high rejection (Sriratana *et al.*, 1996; Tangvijitsri *et al.*, 2002).

An efficient and economic process would consist of a further step to separate the polymer/chromate mixture to provide a compact chromate waste for disposal and a polyelectrolyte-rich stream, which could be returned to the process. The most direct route toward freeing the chromate from the polyelectrolyte and producing a compact chromate waste appears to be a precipitation step. The precipitant for chromate, which might be least environmentally harmful in low concentration, appears to be barium chloride. The chloride ion will reconstitute the polyelectrolyte with its chloride counterion and barium chromate may be separated as a solid waste, which settles out, so that inexpensive gravity settling is feasible. The integrated PEUF and regeneration processes were demonstrated in a field test to treat groundwater, which contained chromate from electroplating waste at the Elizabeth City Coast Guard Base in North Carolina; however, the overnight settling in a quiescent was used for the precipitating step (Tucker *et al.*, 1992a, 1992b).

For industrial operation, a continuous, steady state separation using high flow rate is generally less expensive to operate than a batch process. So this research work was focused on the feasibility of the continuous polyelectrolyte recovery process using a continuous crystallizer. In addition, the studies of the equilibrium precipitation of barium chromate in a laboratory scale, the polymer recovery in a batch crystallizer, and the effect of polyelectrolyte on barium chromate dispersion stability were parallelly carried out in order to comprehend phenomena occurred in the continuous polyelectrolyte regeneration process.

## Objectives

The objectives of this research were to study the recovery of polyelectrolyte from polyelectrolyte-enhanced ultrafiltration as batch experiments in a laboratory scale. The factors affecting the polymer regeneration were studied as follows: barium to chromate concentration ratio, QUAT to chromate concentration ratio, and added electrolyte concentration. Moreover, the recovery process was subsequently scaled up to batch and continuous operations in a steady state crystallizer. The effect of residence time, feed flow rate, drainage flow rate, QUAT to chromate concentration ratio, and height of the crystallizer was studied. In addition, the fundamental study was carried out to investigate the effect of cationic polyelectrolyte on barium chromate dispersion. The effect of barium to chromate concentration ratio, polyelectrolyte concentration, temperature, and added electrolyte on particle size distribution, sedimentation rate viscosity. crystal morphology, and zeta potential of particle in the barium chromate crystallization process was determined. Moreover, comparisons between results obtained from batch experiments in a laboratory scale and from batch and continuous operations in a crystallizer were present.

# 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 $(H_2C{=}CHCH_2)_2N(CH_3)_2Cl$. 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, 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 [QUAT]/[$CrO_4^{2-}$] 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 [QUAT]/[$CrO_4^{2-}$] ratio and the [$Ba^{2+}$]/[$CrO_4^{2-}$] 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 [$Ba^{2+}$]/[$CrO_4^{2-}$] ratios of 1.0 (stoichiometric ratio), 1.1, and 1.2. Where as, lower fractions of chromate precipitated are obtained at [$Ba^{2+}$]/[$CrO_4^{2-}$] ratios of 0.8 and 0.9 (sub-stoichiometric), which are 84.96 and 90.54%, respectively. In the presence of QUAT, at any [$Ba^{2+}$]/[$CrO_4^{2-}$] ratios, the precipitation of barium chromate decreases as the [QUAT]/[$CrO_4^{2-}$] 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 ($2.1 \times 10^{-10}$). For example, at a [$Ba^{2+}$]/[$CrO_4^{2-}$] ratio of 1.0 (stoichiometric ratio), fractions of chromate precipitated are 93.13, 88.52, 84.53, and 81.46 % at [QUAT]/[$CrO_4^{2-}$] ratios of 5, 10, 15, and 20, respectively. On the other hand, the chromate rejection increases as the [QUAT]/[$CrO_4^{2-}$] ratio increases in the previous PEUF work (1, 2). For example, at retentate [QUAT] of 300 mM, chromate rejections are 91.45, 98.20, and 99.45 % at [QUAT]/[$CrO_4^{2-}$] ratios of 5, 10, and 20, respectively. It demonstrates that the [QUAT]/[$CrO_4^{2-}$] ratio is an optimized parameter in the integrated PEUF and regeneration processes. In addition, the higher fraction of chromate precipitated is obtained with increasing [$Ba^{2+}$]/[$CrO_4^{2-}$] ratio. For example, at a [QUAT]/[$CrO_4^{2-}$] ratio of 20, percentages of polyelectrolyte recovery are 58.24, 69.77, 81.46, 89.02, and 94.51 % at [$Ba^{2+}$]/[$CrO_4^{2-}$] 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 $[Ba^{2+}]/[CrO_4^{2-}]$ 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 $[Ba^{2+}]/[CrO_4^{2-}]$ ratio of 1.6 and a $[QUAT]/[CrO_4^{2-}]$ ratio of 5, fractions of chromate precipitated are 99.94, 99.96, 99.97, 99.97, and 99.97 % at [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 $[QUAT]/[CrO_4^{2-}]$ ratio of 20, chromate rejections are 99.60, 98.51, 89.76, and 71.01 % at [NaCl] of 0.01, 0.05, and 0.10 M, respectively. For an integrated process, [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 [NaCl] of 0.04 M, the fraction of chromate precipitated are 99.97, 99.94, 99.92, and 99.90 % at $[QUAT]/[CrO_4^{2-}]$ 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 [QUAT]/[$CrO_4^{2-}$] 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 [$Ba^{2+}$]/[$CrO_4^{2-}$] 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.

## ACKNOWLEDGMENTS

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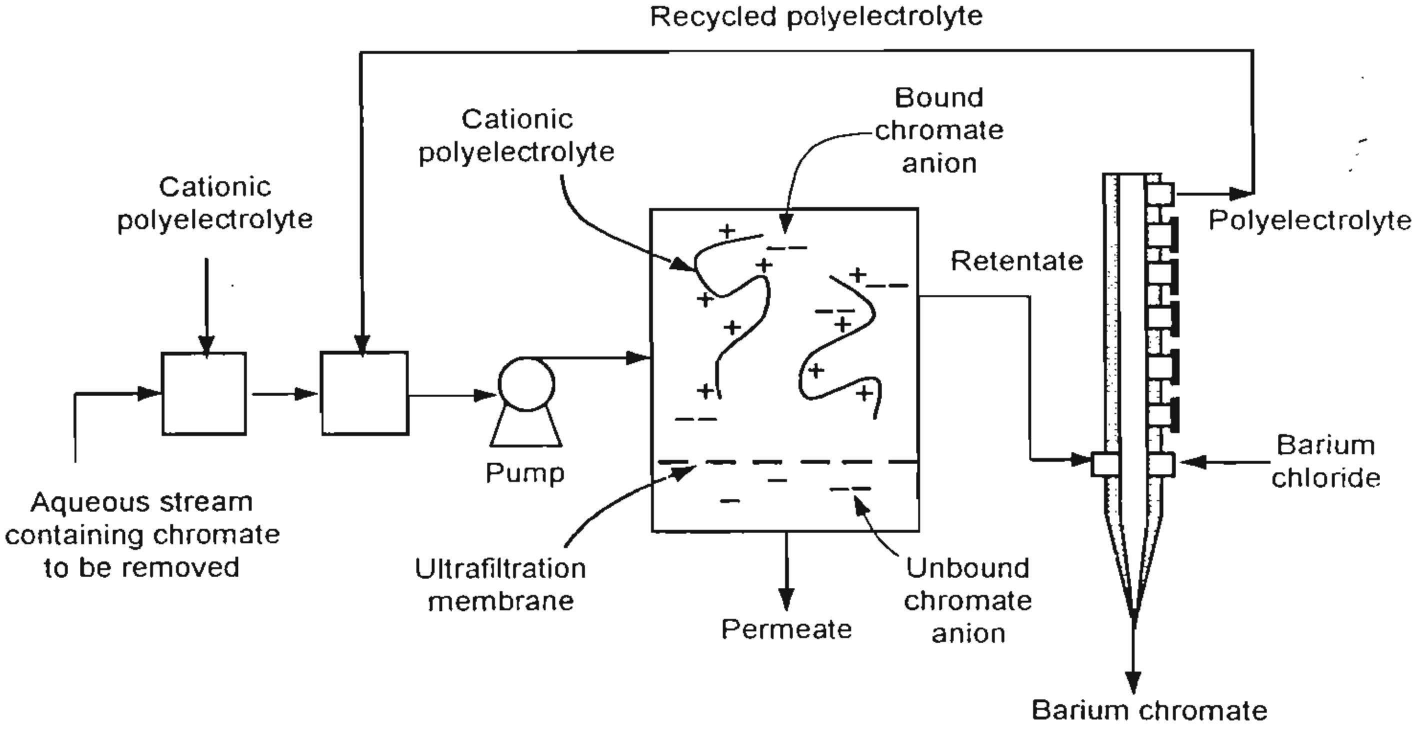

Figure 1. Schematic diagram of PEUF and polyelectrolyte regeneration processes to remove chromate from water.

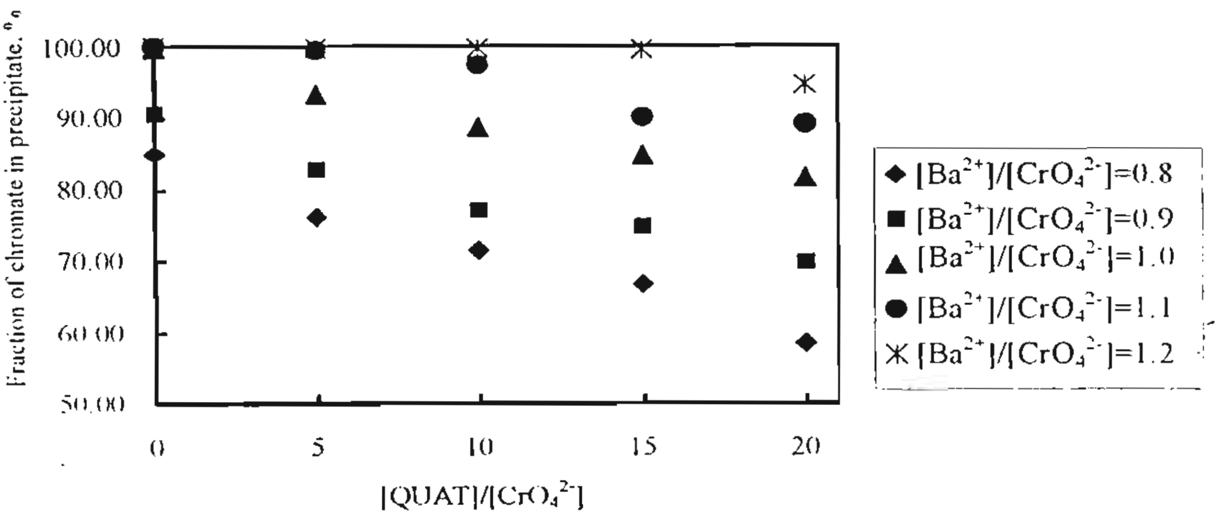

Figure 2. Fraction of chromate in precipitation at different $[QUAT]/[CrO_4^{2-}]$ ratios.

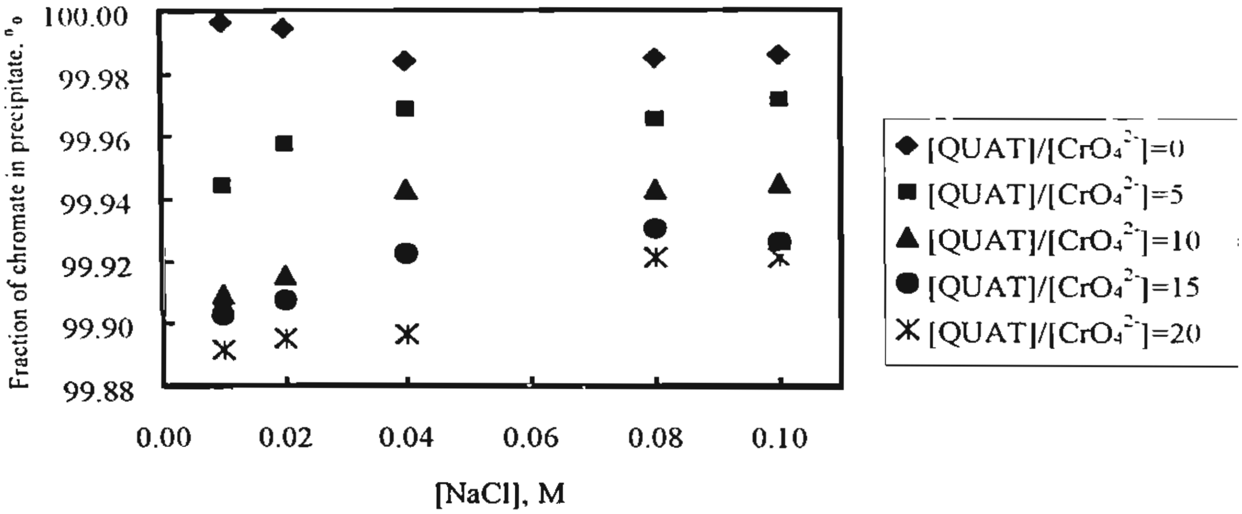

Figure 3. Fraction of chromate in precipitate at different [NaCl].

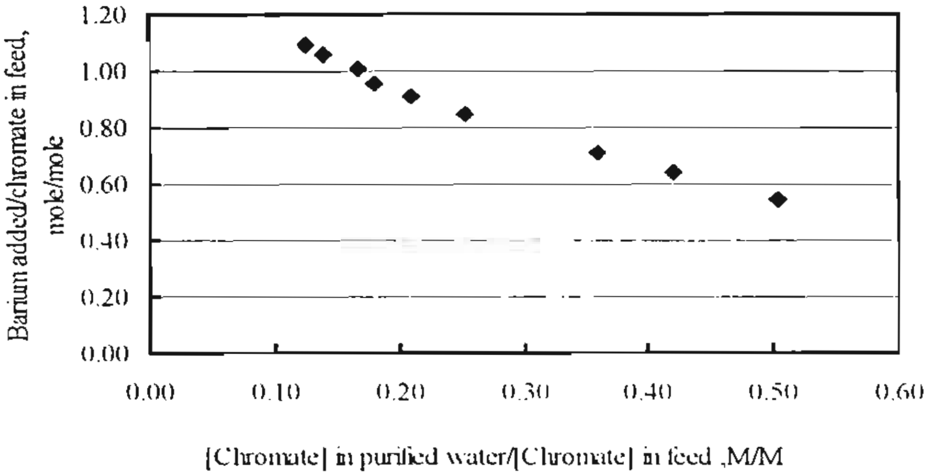

Figure 4. Added barium in crystallizer/chromate in feed at different chromate removal levels.

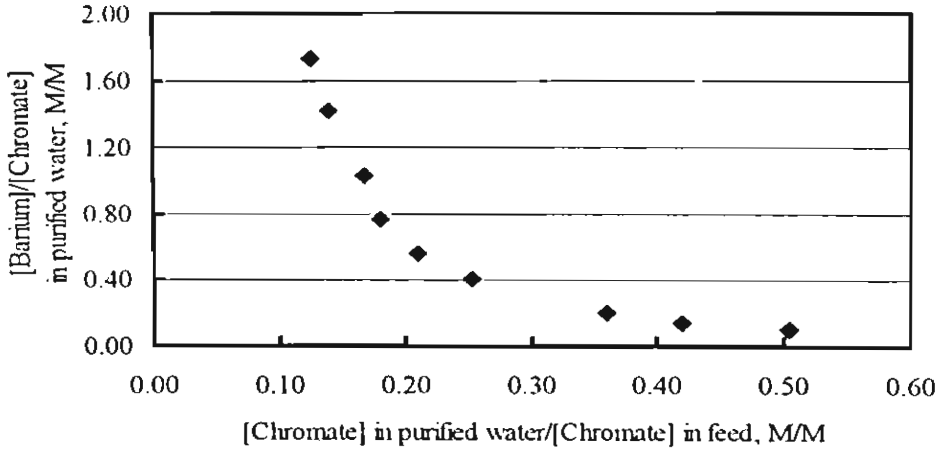

Figure 5. Barium concentration/chromate concentration in purified water at different chromate removal levels.

# 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. The initial solutions of sodium chromate, barium chloride, and QUAT were prepared at 30°C. The equilibrated initial solutions were mixed together in a test tube 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 emptied 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 $2.4 \times 10^5$ 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

Fig. 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. Fig. 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

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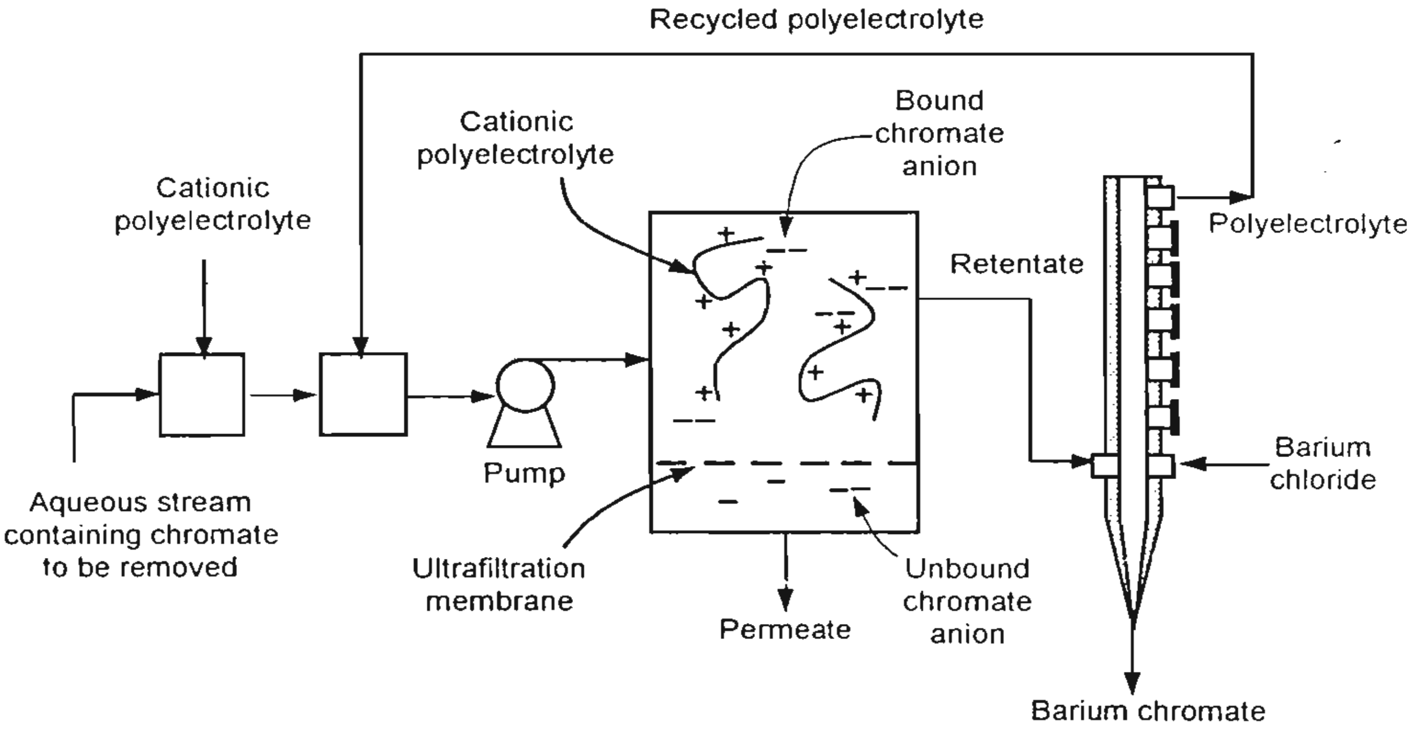

Figure 1. Schematic diagram of PEUF and polyelectrolyte regeneration processes to remove chromate from water.

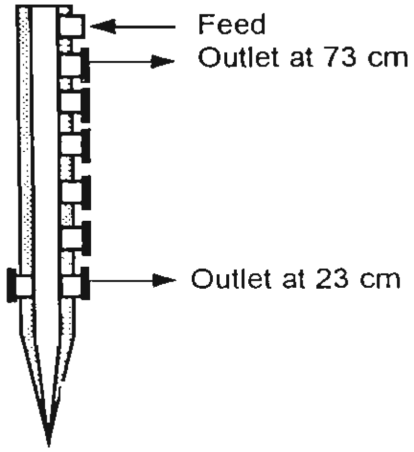

Figure 2. Experimental setup of the batch crystallizer

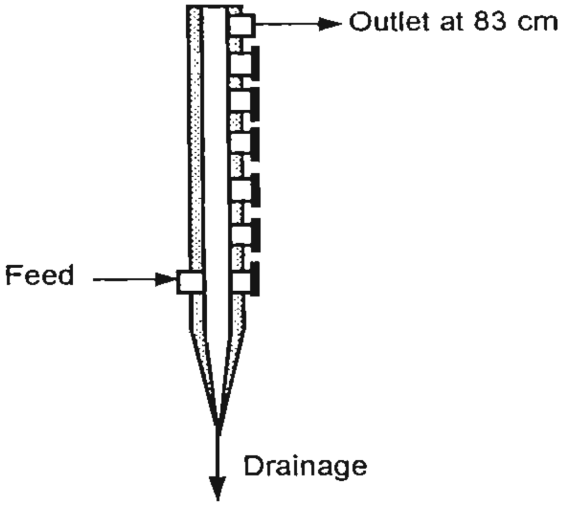

Figure 3. Experimental setup of the continuous crystallizer

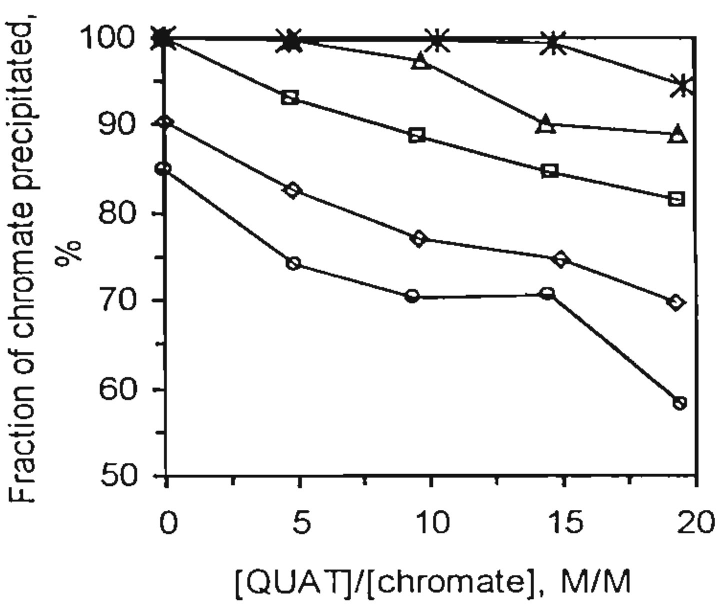

Figure 4. Fraction of chromate in precipitate at different QUAT to chromate ratios and at various barium to chromate ratios. (O) 0.8, (◇) 0.9, (□) 1.0, (△) 1.1, (✳) 1.2.

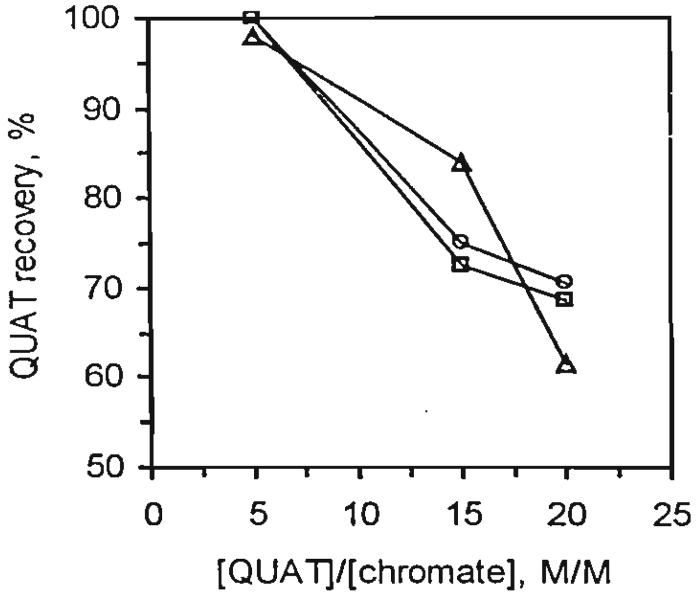

Figure 5. Fraction of QUAT in solution at different QUAT to chromate ratios at various residence times. (O) 30 min, (□) 60 min, (△) 120 min.

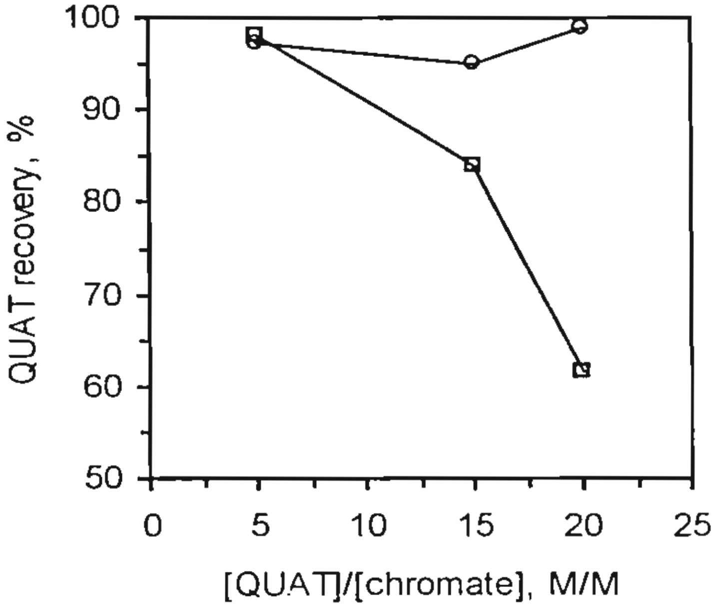

Figure 6. Fraction of QUAT in solution at different QUAT to chromate ratios at various outlet heights. (O) 23 cm, (□) 73 cm.

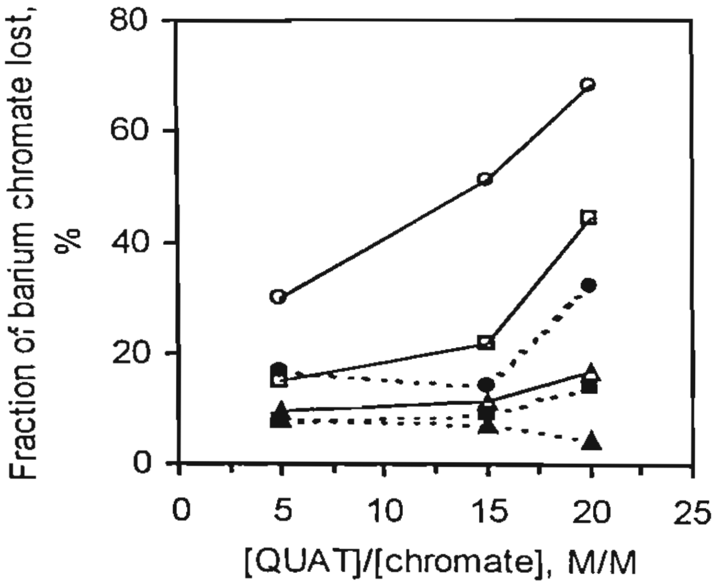

Figure 7. Fraction of barium chromate in solution at different QUAT to chromate ratios at various outlet heights and residence times. (O) 23 cm/30 min, (□) 23 cm/60 min, (△) 23 cm/120 min, (●) 73 cm/30 min, (■) 73 cm/60 min, (▲) 73 cm/120 min.

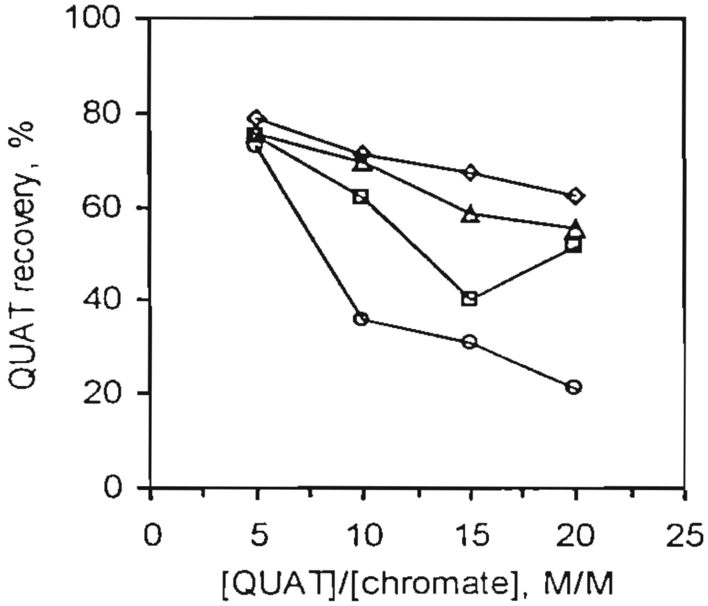

Figure 8. Fraction of QUAT in solution at different QUAT to chromate ratios at various feed flow rates. (○) 4 mL/min, (□) 8 mL/min, (△) 12 mL/min, (◇) 16 mL/min.

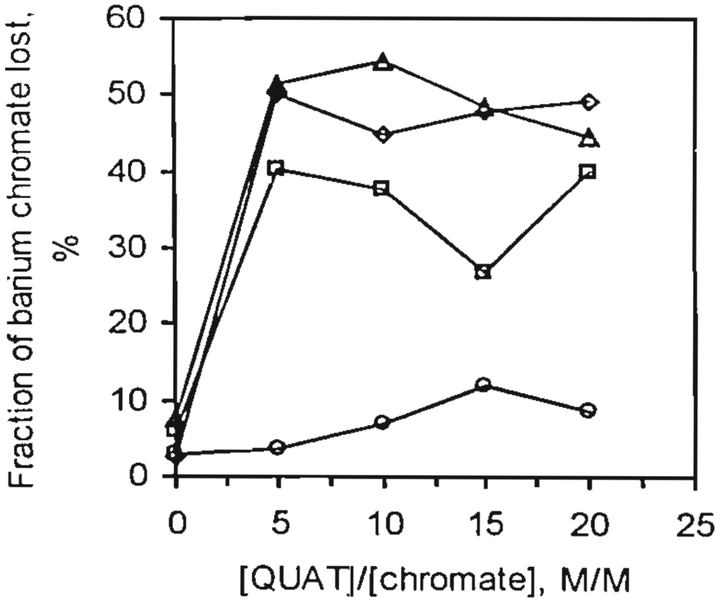

Figure 9. Fraction of barium chromate solid in solution at different QUAT to chromate ratios and at various feed flow rates. (○ ) 4 mL/min, (□) 8 mL/min, (△) 12 mL/min, (◇) 16 mL/min.

# CHAPTER IV

# AQUEOUS DISPERSION BEHAVIOR OF BARIUM CHROMATE CRYSTALS: EFFECT OF CATIONIC POLYELECTROLYTE

## ABSTRACT

In polyelectrolyte-enhanced ultrafiltration (PEUF), a cationic polyelectrolyte binds to chromate and is ultrafiltered from solution. The permeate passing through the membrane can contain a very low chromate concentration; the retentate solution not passing through the membrane must be treated to recover a large fraction of the polymer for reuse for economical operation. In the regeneration step, barium chloride can be added to the retentate to precipitate chromate anion as a compact barium chromate solid waste. The solution containing the 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 investigation studies the ability to separate solid from solution in a settling unit. Unfortunately, the polyelectrolyte can act as a dispersing agent that stabilizes the dispersion of barium chromate particles, resulting in poor separation efficiency in the settler. The adsorption of cationic polyelectrolyte on barium chromate particles increases with increasing polymer concentration, increasing ionic strength, and decreasing barium to chromate ratio. In addition, adsorption of the polyelectrolyte onto the barium chromate particles inhibits the growth of crystals and affects the crystal morphology. The average particle size of barium chromate crystals formed in the presence of the polymer is less than in the absence of the polymer. As a consequence, slower settling of the smaller particles occurs in the presence of polymer. The sedimentation rate of barium chromate increases with decreasing polymer concentration, increasing temperature and increasing electrolyte concentration, and reaches a maximum when there is a stoichiometric ratio of barium to chromate present. At this stoichiometric ratio in the absence of polymer, the zeta potential is zero, confirming that the rapid settling is due to the absence of electrostatic repulsion between the particles. Even though the barium chromate settles rapidly in the absence of polymer, the polymer adsorbs on the crystals and acts like a dispersant as well as causing a solution viscosity increase, resulting in slow settling rates in the PEUF process where the polyelectrolyte must be present.

# INTRODUCTION

Chromate removal using the polyelectrolyte-enhanced ultrafiltration process (PEUF) requires the addition of a soluble cationic polyelectrolyte to the feed chromate-laden wastewater to bind chromate anions electrostatically, followed by ultrafiltration to produce a filtrate (permeate) containing a very low concentration of the chromate anions and which can be discharged to the environment. From our previous work,[1, 2] the removal of chromate, a carcinogenic heavy metal, by the PEUF process with rejections above 99% was demonstrated. High polymer concentrations in the retentate are possible, while maintaining high flux, which is desirable because it leads to high water recovery (permeate/feed) and a minimization of the volume of retentate effluent to be further treated. Other electrolytes present (e.g., NaCl) result in lower chromate rejection due to the competition of dissimilar anions with chromate for binding sites on the polymer.

Economical operation of PEUF requires that a substantial fraction of the separating agent (polymer) be recovered from the retentate for reuse. This can be achieved by adding a cation with a very low $K_{sp}$ to precipitate the chromate. We have identified barium as an effective precipitating cation to form barium chromate precipitate. After the solid barium chromate is separated from the solution, the concentrated polyelectrolyte solution can be recycled to the feed to the ultrafiltration unit. The solid barium chromate can be removed from solution by centrifugation or filtering, but these methods tend to be expensive. So, we have focused on developing a gravity settling process to achieve solid/liquid separation. In a batch field test at the U.S. Coast Guard Support Base in Elizabeth City, North Carolina for treating industrial process wastewater and groundwater containing chromate and sulfate, this gravity settling was demonstrated to work effectively[3-5] (where overnight settling in a quiescent environment was used). We desire to develop a continuous, steady state separation process, which would be required to economically treat high flow rate streams. We have found that excellent separations are observed in a continuous crystallizer for barium chromate crystals in the absence of the polymer, but poor separations are observed in the presence of the polyelectrolyte since it acts as a dispersant.[6] Understanding the interaction between the polymer and barium chromate crystals and effect on dispersion stability, particle size distribution produced during crystallization, and other properties is the purpose of this study to support the development of an effective separation process.

Dispersions of solid particles are important in many areas.[7-16] Examples include inhibition of calcium phosphate deposition in industrial water systems, the treatment of barium sulfate scale problem in oil industries, suspensions in pharmaceutical applications, and modification of solid surfaces by polyelectrolyte-based coatings and adhesives. Dispersions can be undesirable in some applications and additives can cause coagulation; e.g., removal of clay fines from drinking water.[17, 18]

Polyelectrolytes can have the tendency to adsorb at the surface of solid dispersed particles, the level of adsorption depending on factors such as the nature of the particle surface, the concentration and chemical structure of polymer, and the solvent quality of the dispersion medium.[19] The effect of additives; sodium tripolyphosphate (STP), ethylenediaminetetramethylenephosphonic acid (ENTMP), and 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP), on the crystallization of barium chromate was studied conductometrically, where stoichiometric concentrations of barium and chromate were present at 298 K.[20, 21] Increasing the additive concentration decreases the growth rate due to the blocking of the active sites for crystallization on the crystal surface through adsorption, which could be interpreted in terms of a Langmuir type adsorption isotherm. It has been reported that the barium chromate crystallization occurs by a surface-controlled growth mechanism.[20] The study of adsorption behavior of polyelectrolytes in relation to the crystal growth kinetics of barium sulfate indicate that the adsorption of polyphosphinoacrylate, poly(acrylic acid), poly(styrenesulfonic acid), poly(vinylsulfonic acid), and a copolymer of maleic acid and vinylsulfonic acid disturb the growth rate of barium sulfate.[7, 8, 15, 16] Williams and Harrop[9] described the adsorption of an amphoteric polymer, a copolymer of diallyldimethylammonium chloride (QUAT) and acrylic acid, on barium sulfate crystals, and demonstrated its ability to greatly enhance the colloid stability of a barium sulfate dispersion. Moreover, the adsorption capacity for the polymer increases with increasing ionic strength. The influence of QUAT on the precipitation of amorphous calcium phosphate exhibits no pronounced effect on the induction period preceding amorphous calcium phosphate precipitation, while the adsorption of polyacrylic acid and benzene hexacarboxylic acid on calcium phosphate is significant.[10] The study of the adsorption of QUAT and copolymers of N-methyl-N-vinyl-acetamide and QUAT on colloidal silica particles showed that the adsorbed levels as well as the hydrodynamic layer thickness of the adsorbed polyelectrolyte layer increases with the ionic strength and the pH of the suspension at high salt concentration. At low salt concentration, the adsorption increases with decreasing charge density of the polyelectrolyte.[11, 13, 14] Terayama *et al.*[12] studied the effect of surfactant and polymer on dispersion stability of aqueous suspensions of 5-(3-ethoxy-4-pentyloxyphenyl)-2,4-thiazolidinedione (CT112), a drug particle, by measuring the adsorbed amount of surfactant and polymer, zeta potential, particle size, and sedimentation rate. The addition of cellulose rather than sodium dodecyl sulfate (SDS) produces a highly stable suspension, while mixed systems of cellulose and SDS enhance CT112 dispersion stability even more effectively.

In this study, the effect of the barium/chromate concentration ratio, QUAT concentration, temperature, and added electrolyte on particle size distribution, sedimentation rate, viscosity, crystal morphology, and zeta potential of particles in the barium chromate crystallization process was measured in support of development of a crystallization/settling process for separation of chromate from QUAT in a PEUF retentate solution.

# EXPERIMENTAL

## Materials

Poly(diallyldimethylammonium chloride) or QUAT having an average molecular weight of approximately 240,000 Dalton 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 Dalton 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 Dalton 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 used in barium chromate solid preparation were analytical grade (purity of 99%) supplied by Reidel-DeHaen (Seelze, Germany) and Merck (Darmstadt, Germany), respectively. Sodium chloride (99.5%) was obtained from Carlo Erba (Milan, Italy). 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. All chemicals were used as received. Deionized and distilled water was used to prepare solutions.

## Sedimentation rate measurement

The sedimentation rate of barium chromate particles at different conditions was measured in screw cap test tubes by observing the heights of suspended solutions and the interface between clear liquid and suspended solids as a function of time. This was measured until this height was constant: the experiment is known as the batch settling test.[22-24]

### Polyelectrolyte adsorption measurement

Adsorption isotherms of QUAT on barium chromate particles were measured at 30°C using the solution depletion method.[13, 14] The barium chromate precipitate was prepared by the rapid mixing of molar solutions of analytically pure barium chloride and sodium chromate, followed by washing with methanol/water mixtures and finally drying at 105°C.[25] The barium chromate solids at [barium]/[chromate] ratios of 0.5 and 1.5 were prepared in the same manner. The equilibrium polymer concentrations were determined by mixing 1.0 g of barium chromate powders with varied QUAT concentrations, ranging from 0.5 to 100 mM. The suspended solutions were shaken by a Vortex-Genie2 vortex mixer (Scientific Industries, Inc., Bohemia, NY) for 1 minute and were subjected to an ultrasound treatment[9] by a Branson 2200 ultrasonic cleaner (Branson Ultrasonics Corporation, Danbury, CT) for 1 minute at 120 W and 47 kHz before equilibrating in a shaking bath at controlled temperature (30.0 ± 0.2°C) and 100 rpm shaking speed for 24 hours to allow adsorption equilibrium to be reached. After centrifuging at 2000 rpm for 10 minutes by a Centrifuge 4236 (A.L.C. International, Milan, Italy), barium chromate powder was then separated by filtering using a 0.2 μm pore size cellulose acetate membrane filter[10, 15] (Lida Manufacturing Corporation, Kenosha, WI), and the supernatant was sampled to determine the equilibrium polyelectrolyte concentration. The quantity of polyelectrolyte adsorbed was then calculated from the change in concentration of the polymer 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. So the molecular weight used to convert mass concentration to molar concentration was 96.08 Dalton, not $2.4 \times 10^5$ Dalton (molecular weight of polymer).

### Particle size measurement

The particle sizes of barium chromate particles with and without adsorbed polymer were determined using a Coulter® LS 230 counter particle size analyzer with a small volume module (Coulter Corporation, Hialeah, FL). This LS 230 uses laser light at a wavelength of 750 nm to obtain the size of particles with diameter from 0.4 μm to 2000 μm by light diffraction (Fraunhofer diffraction). When particles are smaller than 0.4 μm in diameter, polarization intensity diffraction scattering (PIDS) is used, which provides polarized monochromatic light at 450 nm, 600 nm, and 900 nm. Measurements were carried out in both aqueous solution and electrolyte solution at different ionic strengths. The suspended solutions, containing synthesized barium chromate, were equilibrated in a water bath at the desired temperature for 24 hours. The suspensions were shaken homogeneously by the vortex mixer before loading into the Coulter counter particle size analyzer. The particle size distributions and mean diameter of particles were obtained graphically from the instrument.

### Crystal morphology characterization

The morphologies of barium chromate crystals in aqueous solution and in polyelectrolyte solution were investigated using a JSM-6400 scanning electron microscope or SEM (Jeol Ltd., Tokyo, Japan).

### Zeta potential measurement

The zeta potential measurements were made with a zeta meter 3.0+ unit (Zeta-Meter, Inc., Staunton, VA). The determination of surface charges of the barium chromate particles in water at different barium to chromate ratios was made in diluted suspensions to avoid a salting out effect. Even though the dilution is not recommended because the concentration of the dissolved ions significantly affects the charge of the colloid, the dilution can be a valuable tool for comparative study. In this study the dilution ratio used for all samples was 10 to 1.

### Viscosity measurement

The viscosity of the polyelectrolyte solution at the studied condition was measured using a Brookfield digital rheometer DV-III (Brookfield Engineering Laboratories, Inc., Stoughton, MA). The polymer solutions were equilibrated in a water bath at controlled temperatures (10°C, 25°C, and 50°C) before transferring 500 mL of sample into a 600 mL low form beaker. Three rotational speeds of the spindle (RV-1) were used: 100, 125, and 200 rpm. The viscosity of the polyelectrolyte solution at zero shear rate was determined by a linear extrapolation of these measured values. The measuring time used was 10 minutes. The temperature was measured by a temperature probe during the viscosity determination.

# RESULTS

## Sedimentation rate

The rate of barium chromate sedimentation, which is presented as the percentage of solid volume as a function of time, is shown in Figs. 1-7. An average of required settling time to obtain a solid volume below 20% is summarized in Table 1 for the conditions studied. The measurement of sedimentation rate of the particle were carried out 3 times with standard deviation ± 30 seconds for 0 to 0.1 M QUAT and up to ± 3 minutes for 0.2 to 0.4 M QUAT.

For a stoichiometric ratio of [barium]/[chromate]=1, Figs. 1 and 2 show the rate of sedimentation at 10°C, 25°C, and 50°C in the absence of QUAT and in the presence of 0.1 M QUAT. In either the presence or absence of QUAT, as the temperature increases, the rate of sedimentation increases. In the absence of QUAT, barium chromate particles were visibly flocculated, showing rapid settling. Conversely, in the presence of QUAT, flocculation was not observed, leading to a slower sedimentation. Particle size distribution is described quantitatively later. The sedimentation rate decreases substantially when [QUAT] is increased, as shown in Fig. 3. For example, at 50 °C in the absence of QUAT, the residence time required for suspended solids to settle to a solid volume below 20% is only 1 minute, while in the presence of [QUAT] of 0.1, 0.2, 0.3, and 0.4 M, settling times of 8, 23, 55, and 90 minutes were required, respectively (Table 1).

Figures 4 and 5 illustrate the rate of barium chromate sedimentation at [barium]/[chromate] ratios of 0.5, 1.0, 2.0, 5.0, and 10.0 in the absence and in the presence of QUAT. The results at [barium]/[chromate] ratios of 0.5, 1.0, and 2.0 in the absence of QUAT are similar; however, it should be noted that at a [barium]/[chromate] ratio of 1.0 (stoichiometric), the highest sedimentation rate is observed. The higher [barium]/[chromate] ratios (5.0 and 10.0) give a lower sedimentation rate than lower ratios. In the presence of 0.2 M QUAT at any [barium]/[chromate] ratio, sedimentation is slower than in the absence of QUAT. For example, at 50°C at [barium]/[chromate] ratios of 0.5, 1.0, 2.0, 5.0, and 10.0, in the absence of QUAT, the respective residence time requires for suspended solid to settle to a solid volume below 20% are 2, 1, 2, 8, and 14 minutes. In the presence of 0.2 M QUAT, settling times of 23, 40, 55, and 75 minutes were required at analogous [barium]/[chromate] ratios of 1.0, 2.0, 5.0, and 10.0, respectively. In the presence of 0.2 M QUAT, the most rapid sedimentation occurs at the stoichiometric ratio of barium to chromate. Interestingly, at [barium]/[chromate] ratio of 0.5, no solid settling occurred within the time period studied.

For a stoichiometric [barium]/[chromate] ratio, rates of barium chromate sedimentation at various ionic strengths (added [NaCl] levels) in the absence of QUAT and in the presence of QUAT are shown in Figs. 6 and 7. In the absence of QUAT, the sedimentation rates do not change with ionic strength. In contrast, with 0.2 M QUAT, increasing electrolyte concentration leads to an increase in the barium chromate sedimentation rate.

### Viscosity

The viscosity of the polymer solution at different polymer concentrations, salt concentrations, and temperatures, which is presented in term of relative viscosity (viscosity/viscosity of water) at zero shear rate, is shown in Table 2. The viscosity of the polyelectrolyte solution increases with increased polyelectrolyte concentration, decreased temperature, and decreased ionic strength.

Actually, the viscosity of suspended solution can differ substantially from the particle-free solution since the viscosity of a dispersed system also depends on hydrodynamic interactions between particles and solvent, particle-particle interaction, and interparticle attractions that promote the formation of aggregaies.[26] However, in order to measure the viscosity of the dispersed system, a vibrating viscometer and a specially designed device are needed to maintain the stability of the suspended solution during viscosity measurement.[27, 28] The viscosity reported in this work is the viscosity of the polymer solution in the absence of barium chromate particles, which are useful to qualitatively explain observed effects on dispersion stability.

### Zeta potential

The average zeta potential of barium chromate particles in aqueous solution as a function of [barium]/[chromate] ratio is shown in Fig. 8 in the absence of QUAT. At the stoichiometric ratio, the zeta potential is zero, which represent no net charge on the surface of particles, whereas a negative charge is observed at a [barium]/[chromate] < 1, and a positive charge at a [barium]/[chromate] >1. The average zeta potential shown in this work was obtained from 30 measurements. Most of the sample has a high uniformity of charge (electrophoretic mobility); a standard deviation of the zeta potential values is around ± 0.5 to ± 2.0 mV. At a [barium]/[chromate] ratio of 1, the heterogeneity of the particles as indicated by their electrophoretic mobility was greater (some particles moved toward the anode and some to the cathode), but the average velocity (and hence zeta potential) is approximately zero. It can also be confirmed by an interpolation of the zeta potential at [barium]/[chromate] ratios of 0.8 and 1.2, which gives zero zeta potential at a [barium]/[chromate] ratio of 1. Due to high viscosity, the zeta potential of the solid could not be measured in the presence of the QUAT with our instrument. Moreover, in the presence of polyelectrolyte there was a non-horizontal particle movement along a tracking path between the two electrodes because of an excess cationic charge on the particles.

### Particle size distribution

The barium chromate particle size distribution, which is presented as volume fraction as a function of the logarithm of particle diameter, is shown in Figs. 9-16. Average particle diameter, and range of particle diameters are summarized in Table 1 for the conditions studied. Each value of the average particle diameter represents the average from five particle size measurements with standard deviations reported in Table 1.

The effect of QUAT concentration on the barium chromate particle size at low concentration range from 1 to 100 mM and at high concentration range from 100 to 400 mM are shown in Figs. 9 and 10, respectively at 50°C. The average particle size is shown as a function of [QUAT]. There is clearly a critical [QUAT] range of 10 to 50 mM over which the particles sharply decrease in size and above which the average particle size levels off at around 0.9 μm (compared to 2.0 μm with no QUAT). Qualitatively similar results were observed in the study of the adsorption of SDS or cellulose on 5-(3-ethoxy-4-pentyloxyphenyl)-2,4-thiazolidinedione (CT112).[12] The particle diameter of CT112 was 47 μm without additives and decreased below 10 μm in the presence of 1 mM SDS or 0.2 g/L cellulose.

Figures 11 and 12 present the particle size distribution of barium chromate at different temperatures in the absence and in the presence of QUAT. Without QUAT, increased temperature generated a broader particle size distribution and a larger average particle diameter of barium chromate shown in Fig. 11 and Table 1; however, in the presence of 0.1 M QUAT, increased temperature does not cause a significant effect on barium chromate particle size distribution. The particle diameter observed here compares reasonably with the particle diameter of barium chromate reported by Packter and Alleem,[29] which was in between 1.5 μm and 7.0 μm at pH from 3 to 8 and initial overall metal concentration from 0.13 to 10 mM at 22°C.

The effect of [barium]/[chromate] ratio on particle size distribution of barium chromate is presented in Figs. 13 and 14 in the absence and the presence of QUAT; this [barium]/[chromate] ratio has an insignificant effect on the particle size distribution. It should be noted that the initial barium chloride concentration used in this experimental part (1.0 M) was higher than other experiments (0.2 M) in order to be able to prepare samples to give a [barium]/[chromate] ratio up to 10, where the initial sodium chromate concentration was 0.2 M throughout this work. This higher initial barium chloride concentration results in a larger average particle diameter both in the absence and in the presence of QUAT even at the same [barium]/[chromate] ratio. For example, at 50°C in the absence of QUAT, the average particle diameters are 2.0 μm for a 0.2 M barium chloride solution and 3.8 to 4.9 μm for a 1.0 M barium chloride solution. Similarly, in the presence of QUAT, the average particle diameters are 0.9 μm for a 0.2 M barium chloride and 1.1 to 1.2 μm for a 1.0 M barium chloride solution.

Figures 15 and 16 show the ionic strength effect on barium chromate particle size in the absence and in the presence of QUAT by varying added [NaCl]. From Fig. 15 and Table 1, in the absence of QUAT, the average particle diameters vary little with [NaCl], but the particle size distribution is broader at higher ionic strengths. At 0.2 M

QUAT, there is little change in particle size distribution and average particle diameter with electrolyte concentration. Interestingly, in the absence of QUAT, the average particle diameter of barium chromate with added salt is slightly higher (2.2 to 2.6 μm) than without added salt (2.0 μm). Conversely, in the presence of 0.2 M QUAT, the average particle diameters are 0.9 μm for no added salt and 0.5 to 0.6 μm for the system with added salt.

**Polymer adsorption**

The adsorption isotherms of QUAT on barium chromate solid in water and in 0.1 M NaCl are shown in Fig. 17. The adsorption increases with increasing polyelectrolyte concentration in a Langmuirian fashion and reach a plateau with different adsorption densities at different equilibrium QUAT concentrations. For example, at a [barium]/[chromate] ratio of 0.5 and 1.0, the equilibrium concentrations are around 70 mM and 50 mM, respectively. However, at a [barium]/[chromate] ratio of 1.5, there is an insignificant amount of polyelectrolyte adsorbed on the barium chromate. It was found that the adsorption of polymer on solid decreases with increased [barium]/[chromate] ratio and increases with increased ionic strength.

Figure 18 shows the effect of QUAT concentration on sedimentation rate of barium chromate, barium chromate particle size, relative viscosity, and polymer adsorption to permit simultaneous comparison of several properties. QUAT concentration in the region of 0.001 to 0.1 M provides a significant influence on every parameters studied. For example, the sedimentation rate decreases dramatically with increasing QUAT concentration to 0.1 M and slowly declines when QUAT is increased from 0.1 M to 0.4 M, the average particle size of barium chromate decreases and reaches a certain value around 0.05 to 0.1 M, the adsorption of polymer on barium chromate solid increases sharply with increasing QUAT concentration and remains constant at around 2 mg/g of $BaCrO_4$ at approximately 0.05 M of QUAT, and the relative viscosity increases sharply until 0.05 M QUAT is reached and continues to increase steadily at higher [QUAT].

## Crystal Morphology

The barium chromate crystal morphology is shown in scanning electron micrographs in Figs. 19 and 20 in the absence and in the presence of 0.2 M QUAT, respectively. A defective crystalline structure is observed in the presence of QUAT. It should be noted that in the presence of QUAT, there was a dried polymer layer coated on the top of the barium chromate particle, resulting in blurred SEM pictures in Fig. 20. At [barium]/[chromate] of 1 in the absence of QUAT, the result from EDX shows that the particles only consist of barium, chromium and oxygen.[30] Moreover, atomic absorption spectroscopy measurements have shown that the molar ratio of barium to chromate in the solid is always 1 to 1 at any QUAT concentration.[30]

# DISCUSSION

## Dispersion stability

Simultaneous consideration of rate of sedimentation, particle size distribution, zeta potential, polymer viscosity, polymer adsorption, and crystal morphology of barium chromate suspensions can provide insight into dispersion stabilization of the crystal particles in water and hints to strategies for more rapid settling in an industrial separation process.

In the absence of added polymer, particles are relatively large and settle rapidly. As expected, the most rapid settling occurs for the electrically neutral barium chromate crystals in a stoichiometric mix of barium and chromate, where the particles have no net electrical charge (zero zeta potential), where the average particle diameter is a maximum also. Heterocoagulation (coagulation of oppositely charged particles) may also contribute to flocculation at zero net zeta potential since the charge distribution of particles is not exactly homogeneous. A little surprising is the increased settling rate with increasing temperature as Brownian motion might be expected to keep particles in suspension longer. However, for dispersions of fine solids in liquid, instability is caused mainly by coagulation resulting from the Brownian motion (sticky collision). Collision between particles will lead to growth of the particle. Because of their close contact, clusters of aggregates and/or primary particles form.[31-33] This phenomenon was also found in removal of kaolinite clay dispersed particles from water in a settling tube experiment; the effective settling velocity is higher when temperatures increases.[34] As the [QUAT] increases, polymer adsorption on the crystals increases, average particle size decreases, particle size distribution narrows, viscosity increases, and sedimentation rates decrease dramatically. There is a range of [QUAT] over which polymer adsorption increases sharply and particle size decreases sharply. Above this concentration, polymer adsorption plateaus, particle sizes stabilize, but sedimentation rates continue to decline. This latter important effect is due to solution viscosity increase caused by increasing polymer concentration.[11] Further addition of the polymer to the full coveraged-particle system will cause an increase in the concentration of the free polymer in the suspending fluid and hence increase the viscosity of the suspension. Therefore, the stability of colloidal dispersions in the presence of polymer is not only affected by the adsorption density of the polymer onto the surface of the particles, but also by the concentration of free polymer chains in the suspending fluid.[35] This is consistent with the increased sedimentation rate with increasing temperature inducing a viscosity reduction. The effect of viscosity on settling rate of ground silica particle has been study by other researchers[27] in hydrocyclone classifiers; they reported that the settling rate of particles decreases as slurry viscosity increases. Moreover, the viscosity of the slurry can be altered by factors other than temperature variation, such as changing solid fraction. The adsorption of polymer mainly inhibits the crystal growth of barium chromate, which can be shown by SEM and particle size measurements of bare and covered barium chromate particles, where at sufficiently high polyelectrolyte concentration, polyelectrolyte is able to retard or to block the crystallization process by adsorption at active growth sites of the crystal surface,[16] leading to smaller barium chromate particles in the presence of QUAT. Since the mechanism of the barium chromate crystallization is a surface-controlled growth mechanism,[20] the decrease in the particle size resulted from the inhibition of particle growth rather than the lack of aggregation of primary particles.

Polymer adsorption on barium chromate particles can enhance the dispersion stability through electrostatic and/or steric stabilization mechanisms, leading to a slower sedimentation rate due to repulsive forces. At low polymer concentration or at low ionic strength of the aqueous solution, the adsorbed polymers develop a train structure (flat conformation) on the surface because of mutual repulsion of charged segments, hence the adjacent charge on polymer segments adsorbed onto the surface cause electrostatic repulsion forces (large increase in zeta potential). In contrast, at high polyelectrolyte concentration or at high ionic strength, the QUAT adsorbed on the barium chromate surface take the conformation of mainly tails or loops, containing unadsorbed functional groups extending away from the surface, rather than a flat conformation. In this case the high dispersion stability occurs as a consequence of high steric hindrance between the adsorbed polymer layers accompany with high electrostatic repulsion between charges of polymer segments. These phenomena have been reported in other systems as well.[12, 16, 36, 37]

An increase in the sedimentation rate with increasing electrolyte concentration is observed in this work. Addition of electrolyte leads to an increase in the polymer adsorption on the solid particles[9, 11, 13, 14, 37] (see Fig. 17) and results in more steric repulsion between particles due to the coil conformation of polymers. Increasing adsorption due to added electrolyte leads to a smaller average barium chromate particle size. Added electrolyte leads to screening of polymer charges through compression of the electrical double layer next to the surface that can suppress the electrostatic repulsion between the polyelectrolyte segments. If the magnitude of the electrostatic repulsion is lower than the magnitude of the van der Waals attraction, the dispersion will be unstable and particles will form aggregates in the suspension.[35] Increase in the sedimentation rate with increasing [NaCl] in the presence of QUAT indicates that at least some of the dispersion stabilization induced by the polymer is electrostatic in nature. Additionally, the electrolyte added can reduce the dispersed solution viscosity, resulting in poorer dispersion stabilization. This result was also observed in clay system, where the turbidity of the solution decreases with increasing NaCl concentration.[31]

As [barium]/[chromate] ratio increases well above stoichiometric ratios (up to 10), the sedimentation rates of 0.2 M [QUAT] compared to no-polymer systems decreases. For example, the ratio of residence times from Table 1 for no QUAT system to the 0.2 M QUAT system varies from 1/23 to 14/75 as [barium]/[chromate] ratio varies from 1 to 10. At a [barium]/[chromate] ratio of 10 in the presence of QUAT, there is no significant polymer adsorption, so the decrease in the sedimentation rate is mainly due to the increase in viscosity of the polymer solution. The dispersion stability also depends on the solid/solution ratio. For example, the absolute value of the zeta potential of barium chromate at a [barium]/[chromate] ratio of 10 (ZP=+35 mV) is higher than at a ratio of 0.5 (ZP=-15 mV); however, the residence time required for the suspended solid to settle to a solid volume below 20% at a [barium]/[chromate] ratio of 10 (75 minutes) is lower than that at a [barium]/[chromate] ratio of 0.5 (more than 120 minutes). This is expected since the fraction of barium chromate precipitated at a [barium]/[chromate] ratio of 0.5 is 41.7%, while that at a [barium]/[chromate] ratio of 10 is nearly 100.0%.[30] Therefore, less agglomeration occurs due to the lower solid/solution ratio at the lower [barium]/[chromate] ratio.

From Fig. 18, polymer adsorption leading to a decreased particle size, as well as increased solution viscosity, causes sedimentation rate to decrease with increasing QUAT concentration up to about 0.05 M QUAT. Above that concentration, polymer adsorption and particle size level off, so further reductions in sedimentation rate are primarily due to continuing viscosity increase with QUAT concentration.

### Implications for process design

In the PEUF process, the higher the [QUAT] in the retentate stream from the ultrafiltration step (feed stream to the crystallizer/settler), the higher the water recovery (permeate/feed in ultrafiltration) and the smaller the retentate volume to be treated. The maximum retentate [QUAT] is often limited by low flux[2] through the membrane at high [QUAT], which often limits practical [QUAT] to 0.2 to 0.4 M. This work has shown that [QUAT] needs to be about two orders of magnitude lower than that to see poor dispersion stabilities and high settling rates (as observed in a crystallization unit for barium chromate with no added polymer).[6] Operating at stoichiometric ratios of barium and chromate, increasing temperature or increasing added electrolyte concentration decreases dispersion stability. At the [QUAT] necessary for the PEUF process to operate economically (high recovery of QUAT for reuse), dispersion stabilities are always much higher than in the no-polymer case. Therefore, although a continuous, steady-state crystallizer is effective for separation of polymer-free barium chromate crystals from solution, PEUF retentate solutions will probably require semi-batch quiescent settling tanks with long residence times for effective separation of particles from solution.

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Table 1. Summary of dispersion stability results.

| Temperature (°C) | [QUAT] (M) | $\frac{[Ba^{2+}]}{[CrO_4^{2-}]}$ (M/M) | [NaCl] (M) | Residence time[c] (min) | Average particle diameter (μm) | Particle diameter range (μm) |
|---|---|---|---|---|---|---|
| 10 | 0 | 1.0 [a] | 0 | 7 | 1.52 ± 0.04 | 0.38-4.66 |
| 25 | 0 | 1.0 [a] | 0 | 3 | 1.89 ± 0.01 | 0.08-6.16 |
| 50 | 0 | 1.0 [a] | 0 | 1 | 2.06 ± 0.03 | 0.04-6.16 |
| 10 | 0.1 | 1.0 [a] | 0 | 38 | 1.00 ± 0.05 | 0.05-3.21 |
| 25 | 0.1 | 1.0 [a] | 0 | 16 | 0.95 ± 0.09 | 0.05-3.21 |
| 50 | 0.1 | 1.0 [a] | 0 | 8 | 1.00 ± 0.05 | 0.04-3.91 |
| 50 | 0.001 | 1.0 [a] | 0 | 1 | 2.05 ± 0.03 | 0.05-6.97 |
| 50 | 0.005 | 1.0 [a] | 0 | 1 | 1.93 ± 0.08 | 0.05-6.78 |
| 50 | 0.01 | 1.0 [a] | 0 | 2 | 1.67 ± 0.06 | 0.04-5.52 |
| 50 | 0.05 | 1.0 [a] | 0 | 4 | 0.82 ± 0.08 | 0.04-3.21 |
| 50 | 0.2 | 1.0 [a] | 0 | 23 | 0.86 ± 0.02 | 0.04-3.96 |
| 50 | 0.3 | 1.0 [a] | 0 | 55 | 0.91 ± 0.06 | 0.06-3.96 |
| 50 | 0.4 | 1.0 [a] | 0 | 90 | 0.91 ± 0.04 | 0.07-3.96 |
| 50 | 0 | 0.5 [b] | 0 | 2 | 3.82 ± 0.04 | 0.12-12.99 |
| 50 | 0 | 1.0 [b] | 0 | 1 | 4.86 ± 0.03 | 0.04-18.30 |
| 50 | 0 | 2.0 [b] | 0 | 2 | 4.44 ± 0.05 | 0.07-16.67 |
| 50 | 0 | 5.0 [b] | 0 | 8 | 4.05 ± 0.08 | 0.10-14.86 |
| 50 | 0 | 10.0 [b] | 0 | 14 | 4.01 ± 0.07 | 0.04-12.99 |
| 50 | 0.2 | 0.5 [b] | 0 | no settling | 1.24 ± 0.04 | 0.10-3.21 |
| 50 | 0.2 | 2.0 [b] | 0 | 40 | 1.23 ± 0.07 | 0.05-3.21 |
| 50 | 0.2 | 5.0 [b] | 0 | 55 | 1.24 ± 0.01 | 0.12-3.57 |
| 50 | 0.2 | 10.0 [b] | 0 | 75 | 1.14 ± 0.03 | 0.06-3.21 |
| 50 | 0 | 1.0 [a] | 0.01 | 1 | 2.24 ± 0.09 | 0.04-8.94 |
| 50 | 0 | 1.0 [a] | 0.05 | 1 | 2.34 ± 0.05 | 0.04-8.94 |
| 50 | 0 | 1.0 [a] | 0.10 | 1 | 2.65 ± 0.09 | 0.08-8.94 |
| 50 | 0.2 | 1.0 [a] | 0.01 | 24 | 0.47 ± 0.05 | 0.06-4.66 |
| 50 | 0.2 | 1.0 [a] | 0.05 | 20 | 0.65 ± 0.02 | 0.09-4.66 |
| 50 | 0.2 | 1.0 [a] | 0.10 | 15 | 0.53 ± 0.08 | 0.06-4.66 |

[a] Initial barium chloride concentration=0.2 M, initial sodium chromate concentration=0.2 M.

[b] Initial barium chloride concentration=1.0 M, initial sodium chromate concentration=0.2 M.

[c] Required settling time to obtain a solid volume below 20% (± 30 seconds for 0 to 0.1 M QUAT and ± 3 minutes for 0.2 to 0.4 M QUAT). Since this is an interpolated value, more precise standard deviations are not available.

Table 2. Zero-shear relative viscosity of particulate-free QUAT solutions.

| Temperature ( °C) | [QUAT] (M) | [NaCl] (M) | Relative viscosity |
|---|---|---|---|
| 25 | 0 | 0 | 1.0 |
| 25 | 0.001 | 0 | 1.3 |
| 25 | 0.005 | 0 | 1.6 |
| 25 | 0.010 | 0 | 1.8 |
| 25 | 0.020 | 0 | 2.0 |
| 25 | 0.030 | 0 | 2.2 |
| 25 | 0.040 | 0 | 2.4 |
| 25 | 0.050 | 0 | 2.5 |
| 25 | 0.100 | 0 | 2.9 |
| 25 | 0.200 | 0 | 3.9 |
| 25 | 0.300 | 0 | 4.8 |
| 25 | 0.400 | 0 | 5.6 |
| 10 | 0.100 | 0 | 3.5 |
| 50 | 0.100 | 0 | 2.2 |
| 25 | 0.200 | 0.01 | 3.9 |
| 25 | 0.200 | 0.05 | 3.4 |
| 25 | 0.200 | 0.10 | 3.2 |

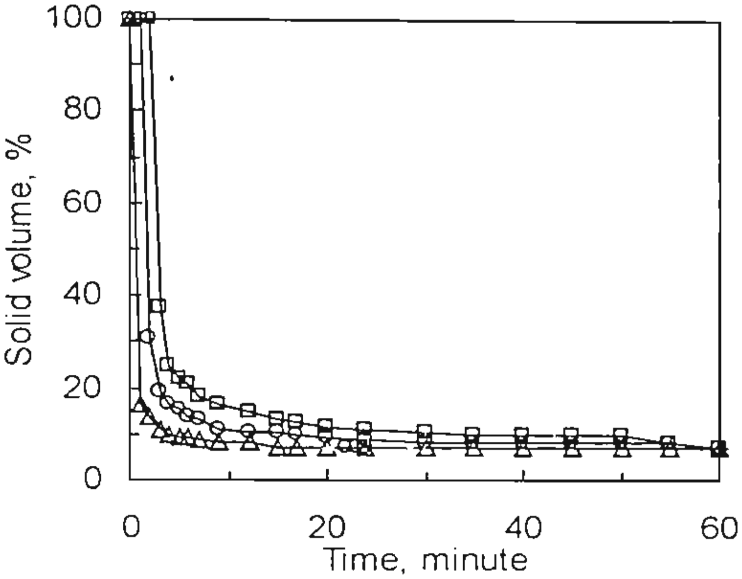

Figure 1. Rate of barium chromate sedimentation in the absence of QUAT at various temperatures. (□) 10°C, (○) 25°C, (△) 50°C

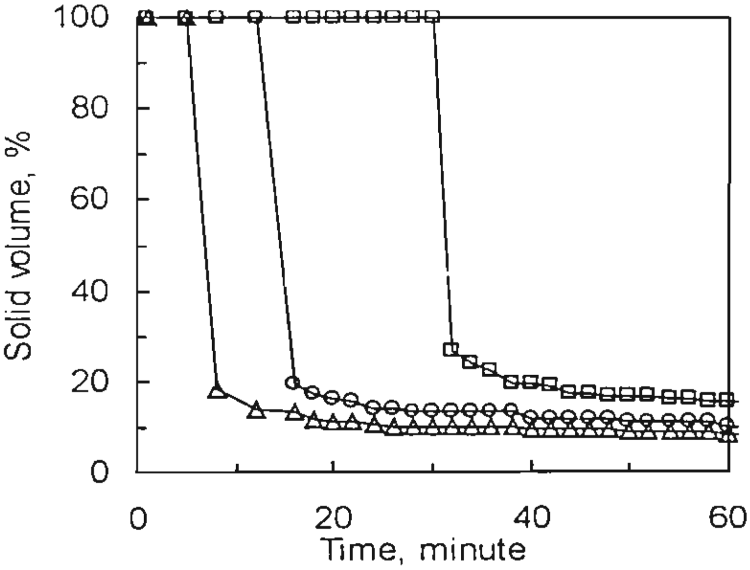

Figure 2. Rate of barium chromate sedimentation in the presence of 0.1 M QUAT at various temperatures. (□) 10°C, (○) 25°C, (△) 50°C.

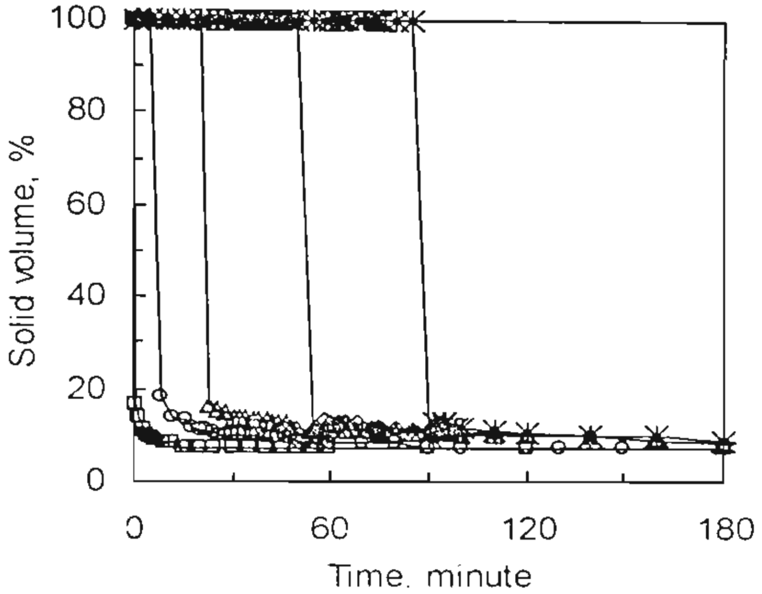

Figure 3. Rate of barium chromate sedimentation at 50°C at various QUAT concentrations. (□) 0 M, (○) 0.1 M, (△) 0.2 M, (◇) 0.3 M, (✳) 0.4 M.

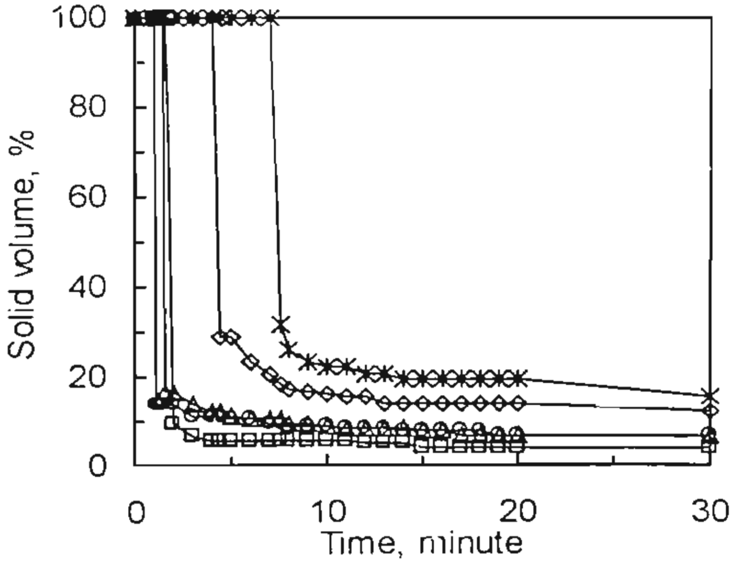

Figure 4. Rate of barium chromate sedimentation in the absence of QUAT at 50°C at various [barium] to [chromate] ratios. (□) 0.5, (○) 1.0, (△) 2.0, (◇) 5.0, (✳) 10.0.

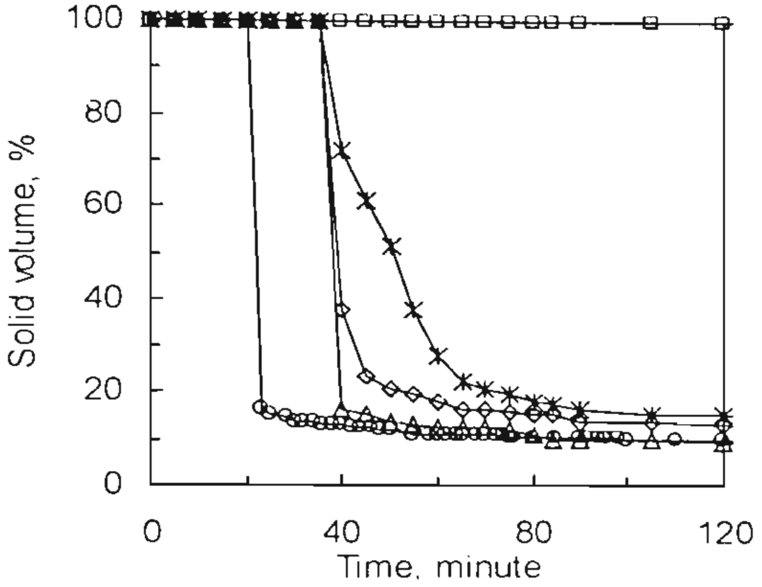

Figure 5. Rate of barium chromate sedimentation in the presence of 0.2 M QUAT at 50°C at various [barium] to [chromate] ratios. (□) 0.5, (○) 1.0, (△) 2.0, (◇) 5.0, (✳) 10.0

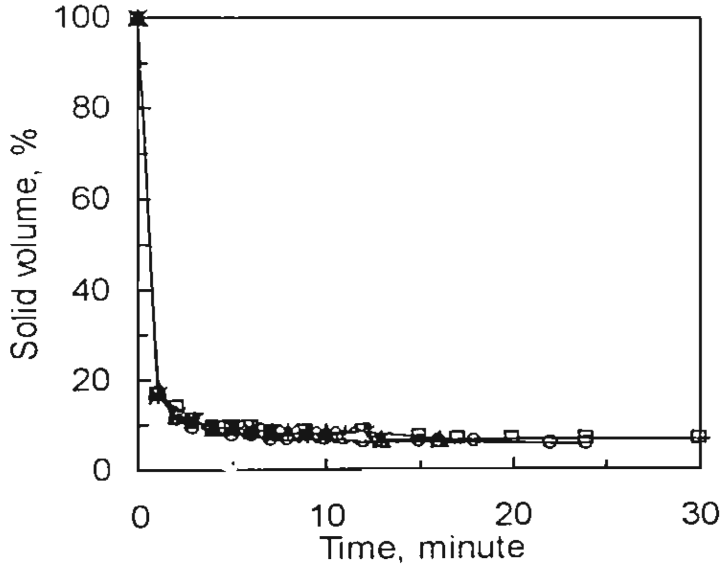

Figure 6. Rate of barium chromate sedimentation in the absence of QUAT at 50°C at various NaCl concentrations. (□) 0 M, (○) 0.01 M, (△) 0.05 M, (✳) 0.10 M NaCl.

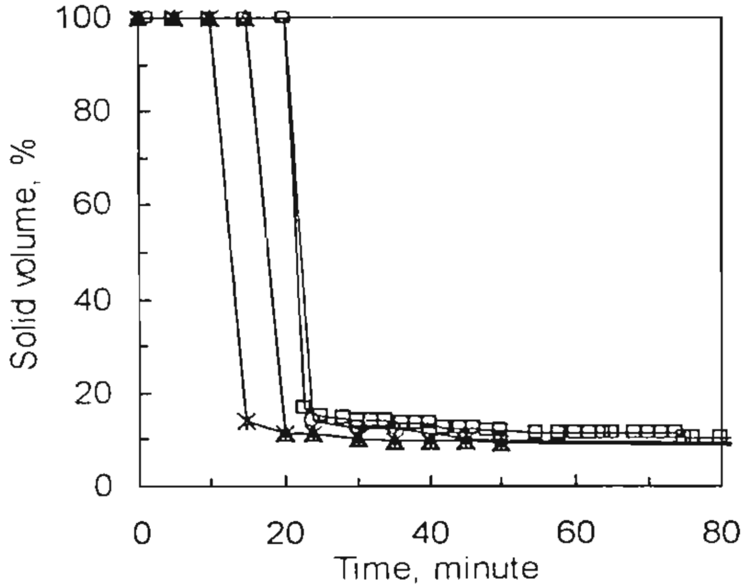

Figure 7. Rate of barium chromate sedimentation in the presence of 0.2 M QUAT at 50°C at various NaCl concentrations. (□) 0 M, (○) 0.01 M, (△) 0.05 M, (✱) 0.10 M NaCl.

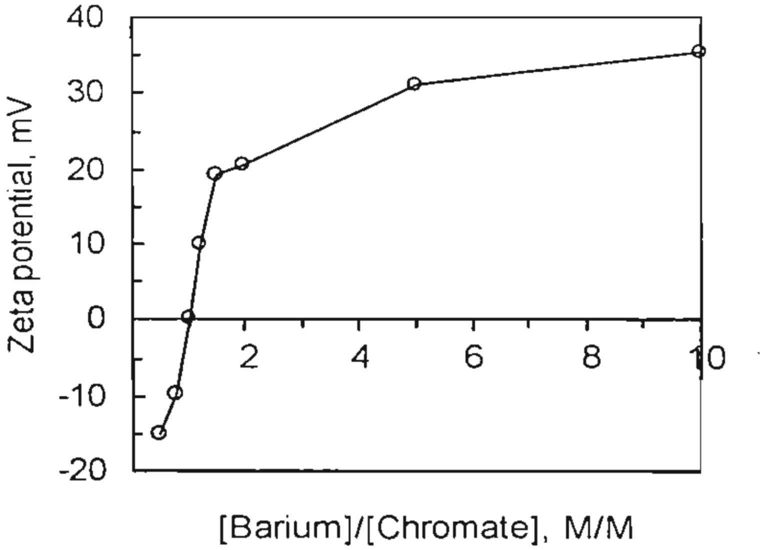

Figure 8. Effect of [barium] to [chromate] ratio on zeta potential of barium chromate particles.

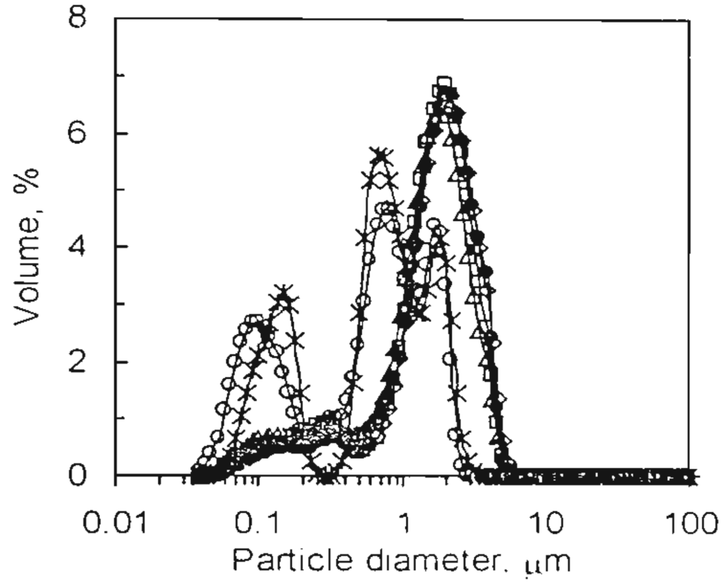

Figure 9. Barium chromate particle size distribution at 50°C at a low QUAT concentration range. (●) 0 mM, (◇) 1 mM, (□) 5mM, (△) 10 mM, (○) 50 mM, (⁎) 100 mM.

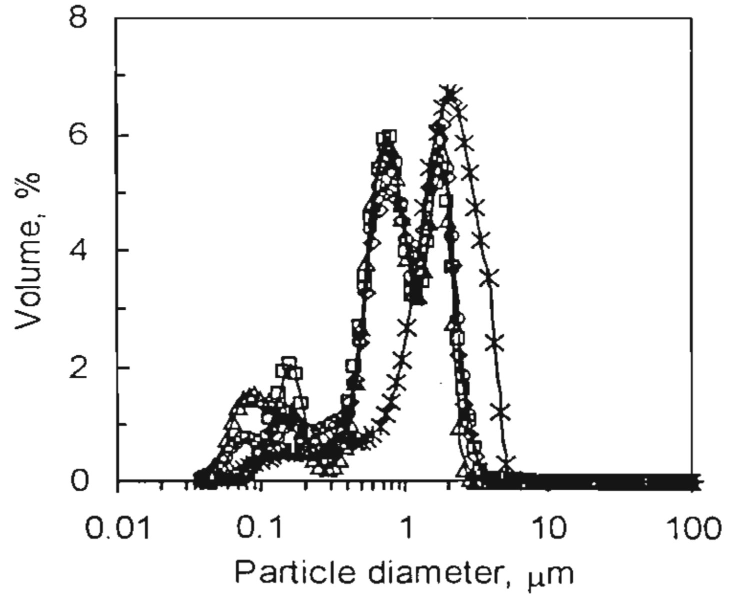

Figure 10. Barium chromate particle size distribution at 50°C at a high QUAT concentration range. (⁎) 0 M, (◇) 0.1 M, (□) 0.2 M, (△) 0.3 M, (○) 0.4 M.

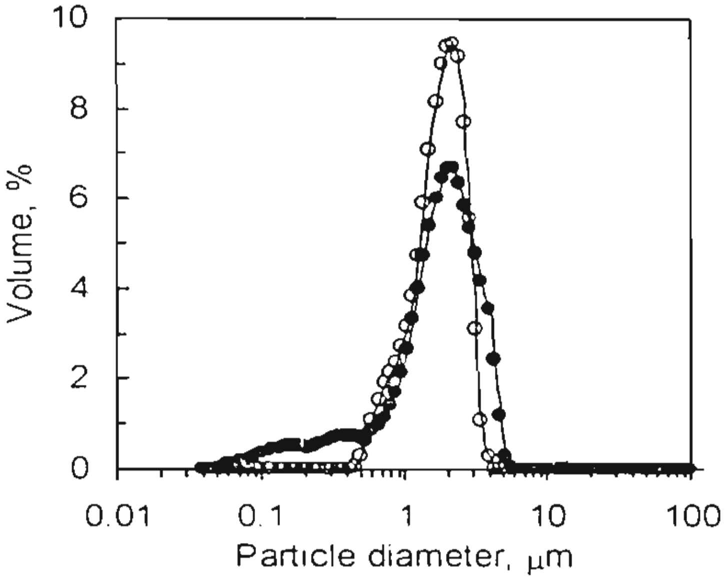

Figure 11. Barium chromate particle size distribution in the absence of QUAT at various temperatures. (○) 10°C, (●) 50°C.

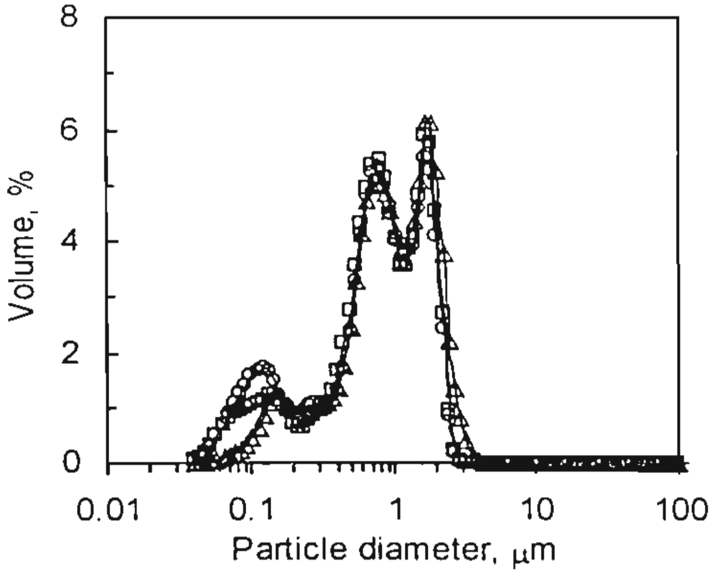

Figure 12. Barium chromate particle size distribution in the presence of 0.1 M QUAT at various temperatures. (□) 10°C, (○) 25°C, (△) 50°C.

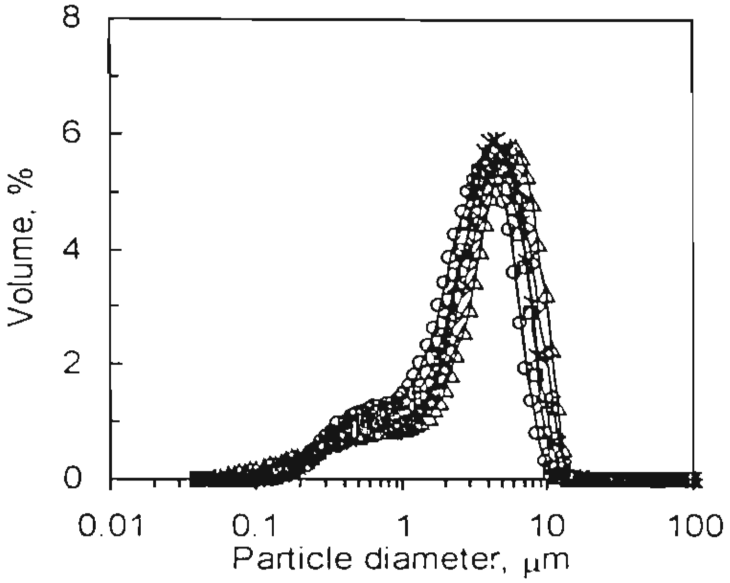

Figure 13. Barium chromate particle size distribution in the absence of QUAT at 50°C at various [barium] to [chromate] ratios (○) 0.5, (△) 1.0, (◇) 2.0, (✳) 5.0, (□) 10.0.

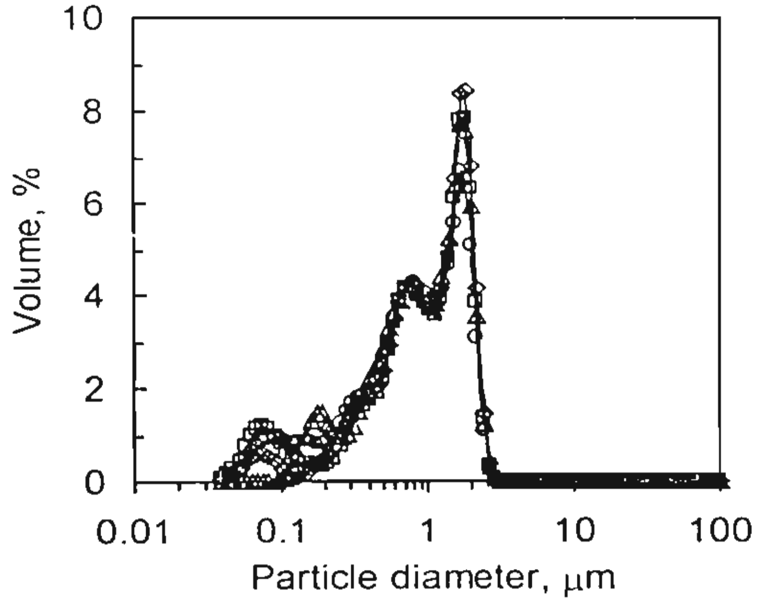

Figure 14. Barium chromate particle size distribution in the presence of 0.2 M QUAT at 50°C at various [barium] to [chromate] ratios. (◇) 0.5, (□) 2.0, (△) 5.0, (○) 10.0.

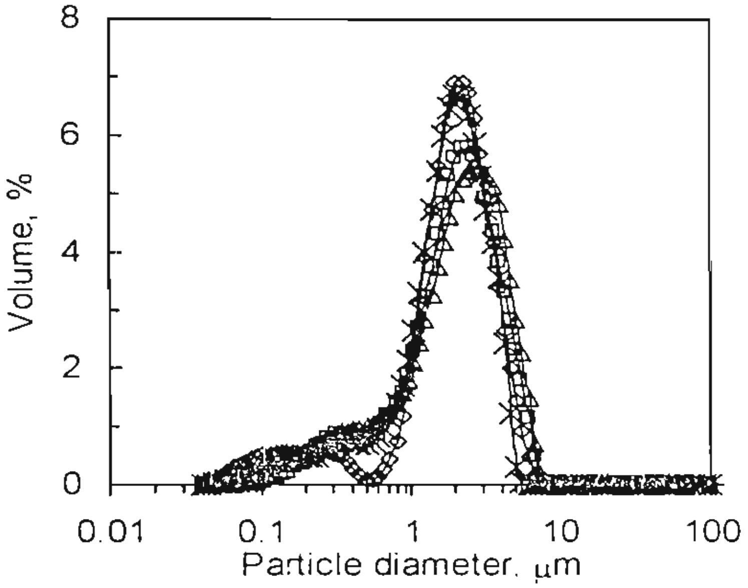

Figure 15. Barium chromate particle size distribution in the absence of QUAT at 50°C at various NaCl concentrations. (✳) 0 M, (◇) 0.01 M, (□) 0.05 M, (△) 0.10 M NaCl.

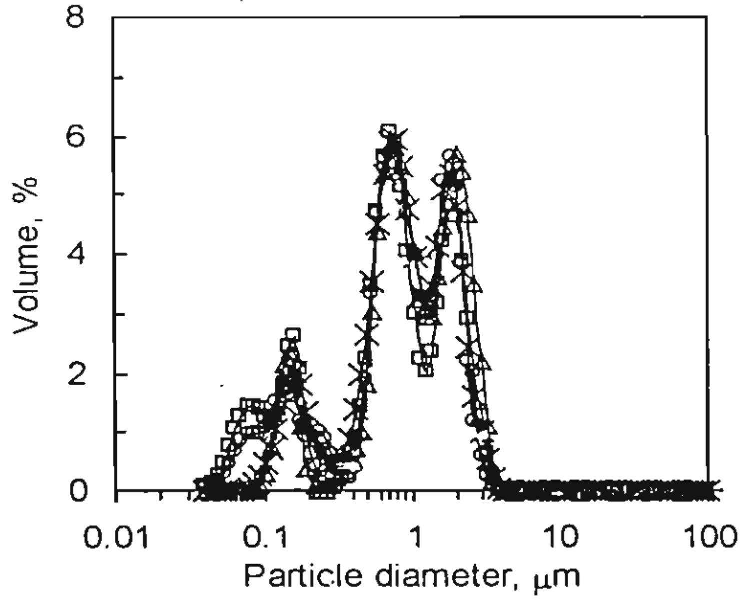

Figure 16. Barium chromate particle size distribution in the presence of 0.2 M QUAT at 50°C at various NaCl concentrations. (✳) 0 M, (□) 0.01 M, (△) 0.05 M, (○) 0.10 M NaCl.

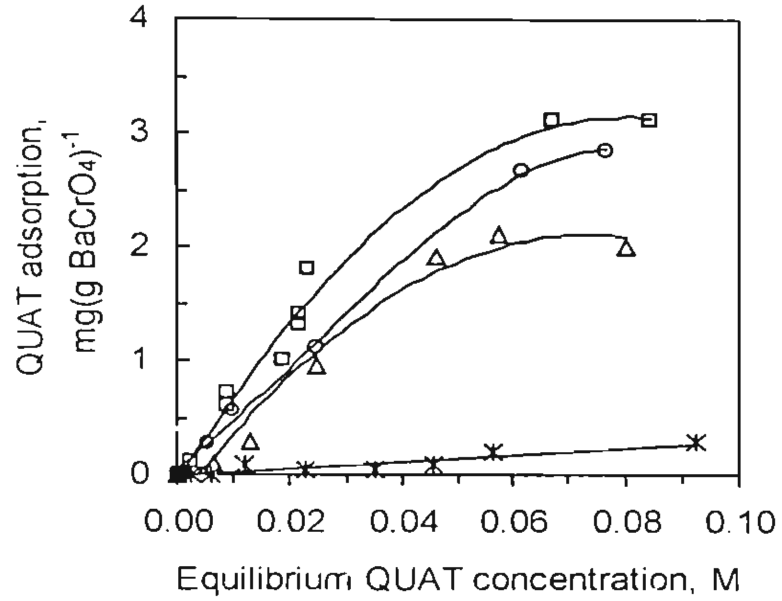

Figure 17. Adsorption isotherm of QUAT on barium chromate in water and in 0.1 M NaCl at various [barium] to [chromate] ratios. (□) 0.5 in water, (Δ) 1.0 in water, (✱) 1.5 in water, (○) 1.0 in 0.1 M NaCl.

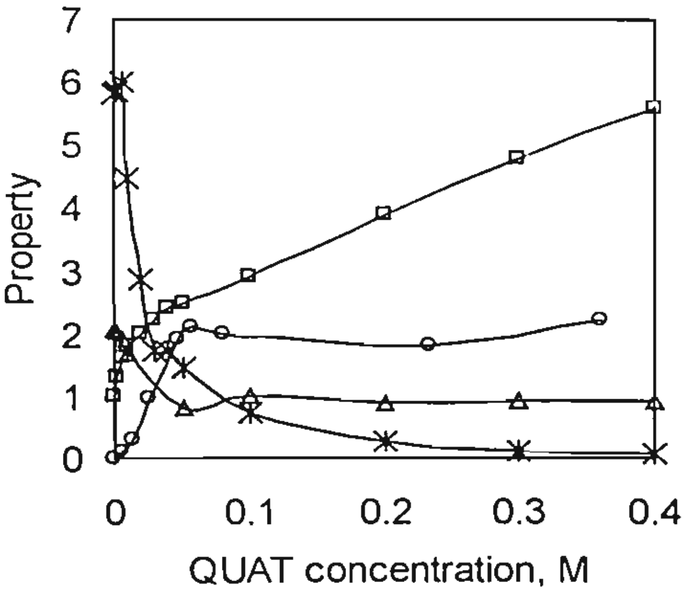

Figure 18. Effect of QUAT concentration on barium chromate sedimentation, barium chromate particle size, polymer adsorption, and relative viscosity of polymer solution. (✱) sedimentation rate (cm/min), (Δ) average particle diameter (μm), (○) QUAT adsorption ($mg(gBaCrO_4)^{-1}$), (□) relative viscosity.

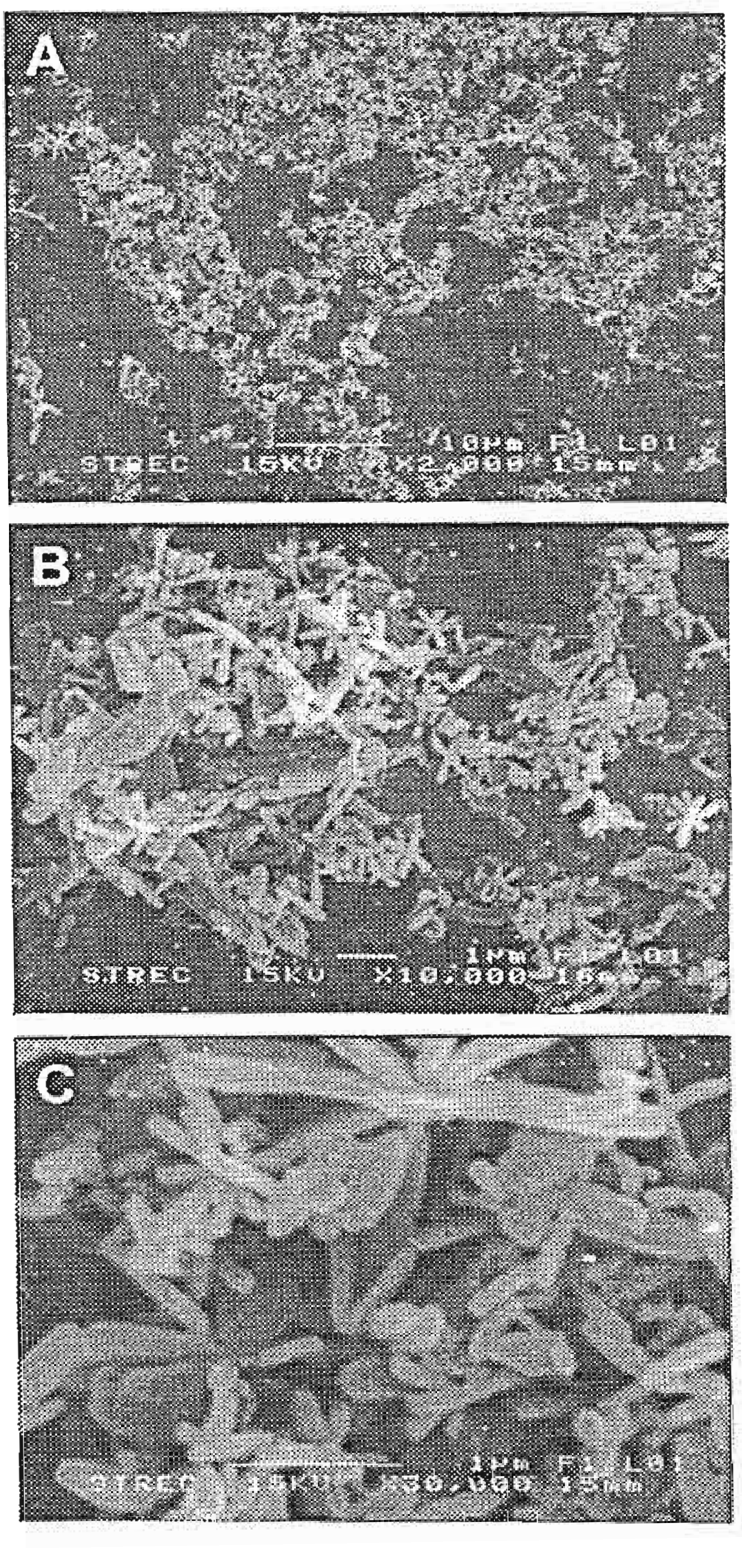

Figure 19. SEM views of barium chromate crystals in the absence of QUAT. Magnification (A) 2000X, (B) 10000X, (C) 30000X.

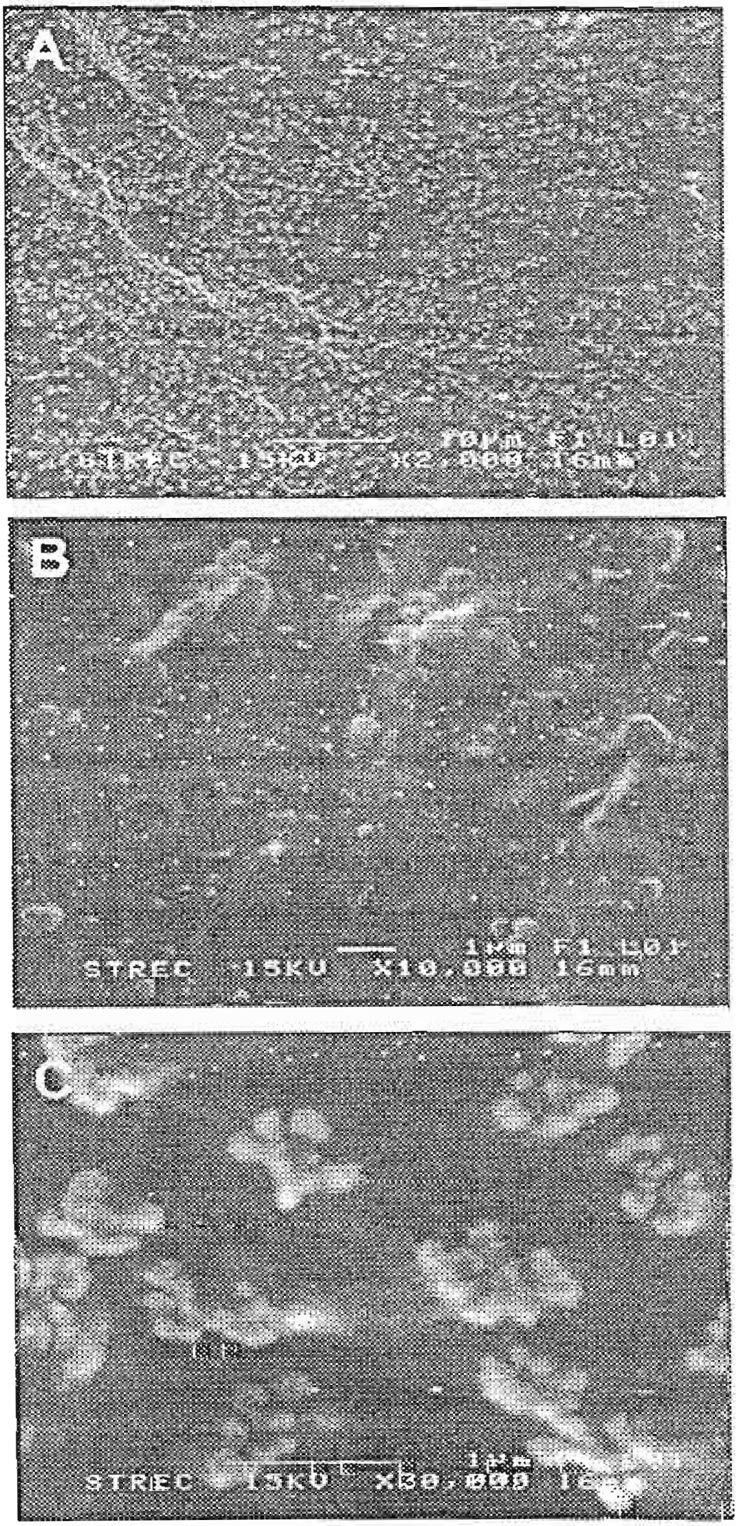

Figure 20. SEM views of barium chromate crystals in the presence of 0.2 M QUAT. Magnification (A) 2000X, (B) 10000X, (C) 30000X.

# CHAPTER V

# OUTPUTS

Output จากโครงการวิจัยที่ได้รับทุนจาก สกว.

1. ผลงานตีพิมพ์ในสารสารวิชาการนานาชาติ :

1.1 Soponvuttikul, C.; Scamehorn, J. F.; Saiwan, C. Aqueous Dispersion Behavior of Barium Chromate Crystals: Effect of Cationic Polyelectrolyte. *Langmuir*. (in press)

1.2 Tangvijitsri, S.; Saiwan, C.; Soponvuttikul, C.; Scamehorn, J. F. Polyelectrolyte-Enhanced Ultrafiltration of Chromate, Sulfate, and Nitrate. *Sep. Sci. Technol.*, **2002** *37*, 993-1007.

2. ผลงานตีพิมพ์ในงานประชุมวิชาการนานาชาติ :

2.1 Chalothorn Soponvuttikul, Chintana Saiwan, John F. Scamehorn. *Recovery of Polyelectrolyte from Polyelectrolyte-Ehanced Ultrafiltration (PEUF) by a Crystallization Process.* Proceeding of Chemical and Process Engineering Conference (CPEC 2000), in conjunction with Regional Symposium on Chemical Engineering (RSCE 2000), Singapore, December 11-13, 2000.

2.2 Chalothorn Soponvuttikul, Chintana Saiwan, John F. Scamehorn. *A Polymer Recovery Process in Polyelectrolyte-Enhanced Ultrafiltration (PEUF) for Chromate Wastewater Treatment.* Proceeding of First International Symposium on Process Intensification and Miniaturisation, Newcastle, England, August 18-21, 2003. (Accepted)

3. การนำเสนอผลงานวิจัยในงานประชุมวิชาการนานาชาติ :

3.1 Chalothorn Soponvuttikul, Chintana Saiwan, John F. Scamehorn. *Use of Polyelectrolyte-Enhanced Ultrafiltration to Remove Chromate from Water: Polymer Recycle by Precipitation.* 222nd ACS National Meeting. Chicago, U.S.A., August 26-30, 2001.

3.2 Chalothorn Soponvuttikul, Chintana Saiwan, John F. Scamehorn. *Recovery of Polyelectrolyte from Polyelectrolyte-Enhanced Ultrafiltration by a Precipitation Process.* 91st AOCS Annual Meeting & Expo. San Diego, U.S.A., April 25-28, 2000.

3.3 Chalothorn Soponvuttikul, Chintana Saiwan, John F. Scamehorn. *Recovery of Polyelectrolyte from Polyelectrolyte-Enhanced Ultrfiltration by a Precipitation Process. I. Equilibrium Precipitation.* The Fourth Princess Chulabhon International Science Congress. Bangkok, Thailand, November 28-December 2, 1999.

4. การนำเสนอผลงานวิจัยในงานประชุมวิชาการในประเทศ :

4.1 Chalothorn Soponvuttikul, Chintana Saiwan, John F. Scamehorn. *Use of Polyelectrolyte-Enhanced Ultrafiltration (PEUF) to Remove Chromate from Water II. Polyelectrolyte Recovery by a Continuous Crystallizer.* RGJ-Ph.D. Congress III. Pattaya, Thailand, April 25-27, 2002.

4.2 Chalothorn Soponvuttikul, Chintana Saiwan, John F. Scamehorn. *Recovery of Polyelectrolyte from Polyelectrolyte-Enhanced Ultrafiltration (PEUF) by a Crystallization Process.* RGJ-Ph.D. Congress II. Pattaya, Thailand, April 26-30, 2001.

# CHAPTER VI

# CONCLUSIONS

# CONCLUSIONS

This work demonstrates for the first time that the polyelectrolyte recovery from polyelectrolyte-enhanced ultrafiltration (PEUF) can be scaled up from batch experiments in a laboratory scale to batch and continuous operations in a pilot scale, steady state crystallizer. In batch experiments, the precipitation of barium chromate was carried out at equilibrium condition in a laboratory scale. It was found that an increase in barium to chromate concentration ratio and added electrolyte (NaCl) concentration could enhance the polymer recovery, whereas the polymer recovery decreases with increasing polyelectrolyte to chromate concentration ratio. At stoichiometric ratio of barium chromate, the percentage of polymer recovered are 93.1, 88.5, 84.5, and 81.5 % at QUAT to chromate ratios of 5, 10, 15, and 20, respectively.

The polymer regeneration unit was subsequently scaled up to operate in both batch and continuous crystallizers. In the continuous system, the polymer recovery decreases with increasing QUAT to chromate ratio, increasing drainage flow rate, and decreasing feed flow rate. The fraction of carry-over barium chromate solid increases as feed flow rate and QUAT to chromate ratio increase. It can be concluded that the dispersion of barium chromate particles in the presence of the cationic polyelectrolyte leads to poor separation efficiency in the continuous crystallizer. However, the longer residence time can enhance the solid settling in the batch system. 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.

The dispersion of barium chromate particles in the presence of polymer is due to the polymer adsorption, which leads to a decrease in particle size, as well as an increase in solution viscosity. This phenomenon causes the sedimentation rate to decrease with increasing QUAT concentration. Above 0.05 M QUAT, polymer adsorption and particle size level off, so the reductions in sedimentation rate are primarily due to continuing viscosity increase with QUAT concentration.

This study shows the feasibility in substituting conventional processes with the PEUF process with a polymer regeneration unit in chromate wastewater treatment.

# CHAPTER VII

# RECOMMENDATIONS

# RECOMMENDATIONS

In order to improve the polyelectrolyte regeneration unit, a longer mixing zone and a lower supersaturation ratio might be required to produce larger particles, which can be settled at a higher rate. Therefore, a batch scale experiment to investigate the particle size distribution at the lower supersaturation ratio ($S < 135$) might be useful before operating in a settler.

It has been proved that a residence time is one of significant parameters affecting solid/polyelectrolyte separation. A batch settler seems to be the best choice; however; it is not applicable for industries. Thus, a semi-continuous operation might be an alternative way to integrate PEUF and recovery processes. The PEUF operation can be carried out continuously via a spiral wound ultrafiltration membrane, while the recovery step can be operated in multi-batch setters (swing- settler). Therefore, the entire operation would be continuous, which is suitable for industries.

It is interesting for further investigation to study other cationic polyelectrolytes (molecular weight < 240,000 Daltons), which have lower affinity to bind with barium chromate particles. With lower MW polyelectrolyte, poorer polymer adsorption and lower viscosity of the polyelectrolyte solution would be obtained, resulting in larger particle size and higher sedimentation rate.

The XRD, SEM, and EDX measurements might be useful to explain the barium chromate sedimentation and bimodal in particle size distribution.

In addition, the PEUF and regeneration processes should be applied to various types of contaminants and mixed-contaminant systems. For example, the mixture of chromate and sulfate, which present in groundwater.

Furthermore, the recovery of polyelectrolyte from a ligand-modified polyelectrolyte-enhanced ultrafiltration might be investigated based on this research work.

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# APPENDIX

SEPARATION SCIENCE AND TECHNOLOGY, 37(5), 993-1007 (2002)

# POLYELECTROLYTE-ENHANCED ULTRAFILTRATION OF CHROMATE, SULFATE, AND NITRATE

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**Chalothorn Soponvuttikul,[1] and John F. Scamehorn[2,*]**

## ABSTRACT

Polyelectrolyte-enhanced ultrafiltration (PEUF) involves addition of a polyelectrolyte of opposite charge to that of the multivalent ions to be removed to the contaminated water. In this study, a water soluble polyelectrolyte, poly(diallyldimethylammonium chloride) or QUAT is added to the aqueous solutions containing divalent anions chromate or sulfate. Removal of monovalent anion nitrate is also studied to probe the effect of valence. The water is then passed through an ultrafiltration membrane with pore size small enough to reject the polyelectrolyte with bound target ions. The rejection of anions increases with increasing concentration ratio of QUAT to anion. A high QUAT concentration in the retentate decreases relative flux due to accumulation of polyelectrolyte near the membrane surface (hydrodynamic boundary layer). Rejections of chromate and sulfate are similar and > 98% at reasonable operating conditions. Rejection of nitrate is substantially below that of the divalent anions, but can be as high as 97% under feasible operating conditions. The gel concentration (where flux approaches zero) of the QUAT varied from 5.1 to 8.1 wt%.

## INTRODUCTION

Polyelectrolyte-enhanced ultrafiltration (PEUF) (1-17), sometimes called polymer-assisted ultrafiltration or polymer filtration, is a specific colloid-enhanced ultrafiltration method (11) which is useful in removing multivalent ions from water. In PEUF, a water soluble polymer of opposite charge to the target ion is added to the contaminated water. For example, anionic polyelectrolyte has been used to treat water containing divalent cation copper (1, 3). The water is then treated by an ultrafiltration membrane with pore sizes small enough to block the polymer with the bound target ion from passing through. The purified water passing through the membrane is called the permeate and that retained by the membrane is the retentate, as illustrated in Figure 1. In a modification of PEUF, ligands can be attached to the polymer, giving selectivity on a

basis other than charge to the separation (e.g., $Cu^{2+}$ vs. $Ca^{2+}$) in a method called ligand-modified PEUF (18, 19).

A target ion of particular interest in this study is chromate ($CrO_4^{2-}$). Chromate contamination of water can come from a number of industrial sources, including electroplating. The cationic polymer used is poly (diallyldimethyl ammonium chloride) or QUAT. In a previous study of this system by our group, high rejections and the substantial reduction in rejection with added NaCl were observed (2). However, QUAT concentrations well below the gel concentration (at which flux approaches zero) were used (2). For high water recovery (permeate/feed ratio), the retentate must have a high QUAT concentration (approximately $^1/_3$ to $^1/_2$ of the gel concentration) and these conditions were studied here. Another reason to study chromate is that an efficient method has been developed to recover the QUAT for reuse involving precipitating the chromate from the retentate using barium (11-13).

In this study, divalent sulfate and monovalent nitrate were removed from water using PEUF under the same conditions as the chromate. Comparison of these systems indicates the effect of divalent anion structure and valence on separation efficiency. Although not of as much interest as chromate, removal of sulfate and nitrate from water is of some concern. For example, a combined reverse osmosis/nano-filtration process has been investigated for nitrate removal from tap water (20). Biological desulfurization of wastewater has been considered (21).

## EXPERIMENTAL

### Materials

Poly(diallyldimethyl ammonium chloride) or QUAT having an average molecular weight of approximately 240,000 Daltons, was supplied by Calgon Corporation and has the trade name MERQUAT®. The repeating unit of the polymer is $(H_2C{=}CHCH_2)_2N(CH_3)_2Cl$. The polyelectrolyte was purified using a 10,000 molecular weight cut -off, spiral wound membrane in order to remove the lower molecular weight components to the point only trace amounts of polyelectrolyte was detected in the permeate. Sodium chromate was analytical grade (purity of 99%) supplied by Reidel-deHaen. Sodium sulfate (AR grade) and sodium nitrate (purity of 99.5%) were obtained from Carlo Erba. *p* - Hydroxybenzoic acid (99%) and sym-diphenylcarbazide were manufactured by Fluka. Gracial acetic acid (99.9%) was obtained from J.T. Baker. All chemicals were used as received. Deionized and distilled water was used to prepare solutions.

### Methods

Ultrafiltration experiments were carried out in a 400 mL stirred cell. Spectrum™ cellulose acetate (type C) ultrafiltration membranes from Spectrum Medical Company were used in these experiments with molecular weight cut-off equal to 10,000 Daltons. A 300 mL solution of polyelectrolyte, chromate, sulfate or nitrate ions was placed in the

basis other than charge to the separation (e.g., $Cu^{2+}$ vs. $Ca^{2+}$) in a method called ligand-modified PEUF (18, 19).

A target ion of particular interest in this study is chromate ($CrO_4^{2-}$). Chromate contamination of water can come from a number of industrial sources, including electroplating. The cationic polymer used is poly (diallyldimethyl ammonium chloride) or QUAT. In a previous study of this system by our group, high rejections and the substantial reduction in rejection with added NaCl were observed (2). However, QUAT concentrations well below the gel concentration (at which flux approaches zero) were used (2). For high water recovery (permeate/feed ratio), the retentate must have a high QUAT concentration (approximately $^1/_3$ to $^1/_2$ of the gel concentration) and these conditions were studied here. Another reason to study chromate is that an efficient method has been developed to recover the QUAT for reuse involving precipitating the chromate from the retentate using barium (11-13).

In this study, divalent sulfate and monovalent nitrate were removed from water using PEUF under the same conditions as the chromate. Comparison of these systems indicates the effect of divalent anion structure and valence on separation efficiency. Although not of as much interest as chromate, removal of sulfate and nitrate from water is of some concern. For example, a combined reverse osmosis/nano-filtration process has been investigated for nitrate removal from tap water (20). Biological desulfurization of wastewater has been considered (21).

## EXPERIMENTAL

### Materials

Poly(diallyldimethyl ammonium chloride) or QUAT having an average molecular weight of approximately 240,000 Daltons, was supplied by Calgon Corporation and has the trade name MERQUAT®. The repeating unit of the polymer is $(H_2C{=}CHCH_2)_2N(CH_3)_2Cl$. The polyelectrolyte was purified using a 10,000 molecular weight cut -off, spiral wound membrane in order to remove the lower molecular weight components to the point only trace amounts of polyelectrolyte was detected in the permeate. Sodium chromate was analytical grade (purity of 99%) supplied by Reidel-deHaen. Sodium sulfate (AR grade) and sodium nitrate (purity of 99.5%) were obtained from Carlo Erba. *p* - Hydroxybenzoic acid (99%) and sym-diphenylcarbazide were manufactured by Fluka. Gracial acetic acid (99.9%) was obtained from J.T. Baker. All chemicals were used as received. Deionized and distilled water was used to prepare solutions.

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stirred cell which was submerging into an acrylic plexi-glass plastic box containing circulating water to control the solution temperature. The experiments were run at 30 °C and a natural pH of approximately 8. The solution was stirred at a speed of 250 rpm with a pressure drop of 60 psi (414 kPa) across the membrane using nitrogen gas. Approximately 200 mL of the solution was filtered through the membrane as permeate to produce eight samples of 25 mL each. Fluxes were determined during the run by timing and weighing samples of permeate. The permeate samples were analyzed for concentrations of polyelectrolyte, chromate, sulfate and nitrate. The rejection of chromate, sulfate, or nitrate was determined at the midpoint of the run where 100 mL of permeate has passed through the membrane. By knowing permeate concentrations during the run, the retentate concentrations at any point in the run were calculated from a material balance. In this work, initial ratios of QUAT to the anions were fixed. It is this ratio which is reported. Since rejection of the QUAT is essentially 100%, if rejection of the target anion is high (as in most experiment here), this ratio varies little throughout the experiments.

### Analysis

The chromate concentrations were measured by using a UV/VIS spectrophotometer (Perkin Elmer, Lamda 16) 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 the solution of 10% acetic acid in distilled water.

The concentrations of sulfate and nitrate ions in permeate and retentate solutions were analyzed by a Hewlett Packard Series 1050 ion chromatography with a Alltech Anion/R column (1 μm, 150 mm X 4.6 mm) and conductivity detector (Alltech 350). The mobile phase was 5 mM p- hydroxybenzoic acid and operated at a flow rate of 1.0 mL/min. Retention time of sulfate and nitrate were 10.7 and 7.0 minutes respectively.

The concentrations of QUAT in the permeate and retentate solutions were determined by a Shimadzu TOC-5000A total organic carbon (TOC) analyzer. This measurement was used to determine when pretreatment of the polymer was complete.

## RESULTS AND DISCUSSION

### Rejection of anions

The removal efficiency of the chromate, sulfate, and nitrate are represented by the rejection, R in percent as defined by

$$R \quad = \quad 100\,[1 - (C_P/C_R)]$$

where $C_P$ is permeate concentration of anion and $C_R$ is retentate concentration of the anion. The QUAT concentrations are based on the moles/liter of the repeating units, not the total molecular weight. Since the repeating unit has a charge of +1, the stoichiometric ratio of [QUAT]/[$CrO_4^{2-}$] is 2.

The anion rejection is shown in Figures 2-4 as a function of retentate [QUAT] for chromate, sulfate and nitrate, respectively. The low [QUAT] data from the previous PEUF work (2) have been combined with the high [QUAT] data from this work in fig. 2 for chromate. For all three anions, as the initial [QUAT]/[anion] ratio increases, the rejection increases since the increased polyelectrolyte in solution provides more binding sites for the target anion. When the initial [QUAT] or [anion] increases at constant [QUAT]/[anion], the rejection decreases. This trend is expected and at low initial [QUAT] or [anion], a modified Oosawa two-state binding model successfully described these results quantitatively (1, 4, 10). While this dilute solution model did not successfully model the high concentration data shown here, this trend at constant initial [QUAT]/[anion] is qualitatively predicted. For chromate and sulfate, rejections of greater than 98% are observed until high retentate [QUAT] levels are reached. However, even at the high retentate [QUAT] levels expected in a PEUF operation with high water recovery (ca. 0.3 M), if a high enough [QUAT]/[divalent anion] is used, high rejections are still attainable. For example, at a [QUAT]/[$CrO_4^{2-}$] of 20 and retentate [QUAT] = 300 mM, chromate rejection = 99.4 %.

The anion rejection is plotted in Figures 5-7 at initial [QUAT]/[anion] ratios of 5, 10, and 20, respectively. Chromate and sulfate rejections are similar under all conditions. The rejection of nitrate is much lower than the chromate or sulfate. For example, at an initial [QUAT]/[anion] ratio of 20 and retentate [QUAT] = 200 mM, chromate and sulfate rejections are >99.5% while nitrate rejection = 96.3%.

Anions commonly form species of different valance in water and the concentration of each ion depends on pH (22). For chromium (VI) present here, the predominant species between pH 1.5 and 4.0 is $HCrO_4^-$. At pH 6.5, $HCrO_4^-$ and $CrO_4^{2-}$ exist in equal amount and at high pH, $CrO_4^{2-}$ predominates. For sulfate, $SO_4^{2-}$ is present at pH level above 3.0. The sulfate and bisulfate ions exist about equal amount at pH 2.0 and the bisulfate ion predominates at pH 1.0. Nitrate ions from most metal nitrate salts or strong nitric acid are in $NO_3^-$ form at both low and high pH. The pH condition which the PEUF of these anions were operated was about 8.0. Therefore, the ions species present mainly would be $CrO_4^{2-}$, $SO_4^{2-}$ and $NO_3^-$. The divalent chromate and sulfate are removed with approximately the same efficiency, confirming that valence is the predominant variable affecting removal of anion. In a previous study of micellar-enhanced ultrafiltration (similar to PEUF except charged micelles are used instead of polyelectrolyte), a similar conclusion was reached for divalent cations removed by anionic micelles (23).

## Flux

Figures 8-16 show the relative flux (flux/flux of pure water) as a function of the logarithm of retentate [QUAT]. As seen in previous studies, this semilogarithmic flux plot is linear at high concentrations. When extrapolated to zero flux, the [QUAT] is called the gel concentration, which are tabulated in Table 1 for these systems. These vary between 559 and 885 mM. A higher [QUAT]/[anion] ratio results in a lower gel concentration for all three target anions. This might be due to the lower bound counterion/repeating polymer unit, causing the polymer to be less coiled, forming a more entangled networks of polymer chains in the gel layer, reducing flux. Bound monovalent may correspond to a less coiled configuration than divalent chromate and sulfate, accounting for the lower gel concentration for the nitrate systems. These explanations are speculative but consistent with the data. The gel concentration is obtained by extrapolation to zero flux on a log scale, so there is substantial opportunity for inaccuracy. Therefore, Table 1 contains the range of gel concentrations corresponding to a 95 % confidence level from a statistical analysis of the curve fit, as well as the best fit value.

The 559 to 885 mM gel concentration observed here compares well to gel concentrations of 550 mM obtained in a previous study of this system at a [QUAT] / [chromate] of 10 (2), 1000 mM for anionic polyelectrolyte (3), 708 mM for anionic surfactant (23), and 530 mM for cationic surfactant (24). These fluxes limit the maximum concentration of the polymer practically attainable in the retentate since unacceptably low fluxes make an operation uneconomical. For example, the arbitrary level of 300 mM as the final retentate concentration used to discuss rejections before, relative fluxes vary from 0.208 to 0.288 from Figures 8-16. However, this retentate polymer concentrations is quite high and indicate that high water recovery levels are attainable in PEUF with high rejections.

As an example to summarize the efficiency of this process, if a feed water has a chromate concentration of 1.0 mM, a [QUAT]/[chromate] feed ratio of 20 is used and, the final retentate [QUAT] = 300 mM, the initial permeate [$CrO_4^{2-}$] will be 0.022 mM and the final will be 0.084 mM (compared to 1.0 mM in the feed). The initial relative flux will be 0.893 and the final relative flux will be 0.208. Water recovery will be 93.3%. If the process were continuous, the relative flux and permeate [$CrO_4^{2-}$] will be between these extremes (an integrated average). However, this example shows that high purification with high water recovery and reasonable flux is attainable using PEUF. A higher final retentate [QUAT] yields a higher water recovery, lower average flux (more membrane area required), a slightly higher [$CrO_4^{2-}$] in the composite permeate, and a higher [$CrO_4^{2-}$] in the final retentate. A higher [QUAT]/[$CrO_4^{2-}$] feed ratio results in a purer composite permeate, lower average flux, lower water recovery, and lower [$CrO_4^{2-}$] in the final retentate. So, the final retentate [QUAT] and the feed [QUAT]/[$CrO_4^{2-}$] are optimization variables.

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DuPont de Nemours & Co., Halliburton Services Corp., Henkel Corporation, Huntsman Corporation, ICI Americas Inc., Kerr-McGee Corporation, Lever Brothers, Lubrizol Corporation, Nikko Chemicals, Phillips Petroleum Company, Pilot Chemical Company, Procter & Gamble Company, Reckitt Benckiser North America, Schlumberger Technology Corp., Shell Chemical Company, Sun Chemical Corporation, Unilever Inc. and Witco Corporation. John Scamehorn holds the Asahi Glass Chair in chemical engineering at the University of Oklahoma.

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Table 1. Gel Concentrations of QUAT (mM), Best fit and range of values within 95% confidence level

| Initial [QUAT]/[ANION] | 5 | 10 | 20 |
|---|---|---|---|
| Chromate | 838 (778-913) | 718 (670-776) | 581 (549-621) |
| Sulfate | 885 (780-1035) | 719 (663-790) | 582 (549-621) |
| Nitrate | 797 (701-938) | 574 (547-604) | 559 (536-586) |

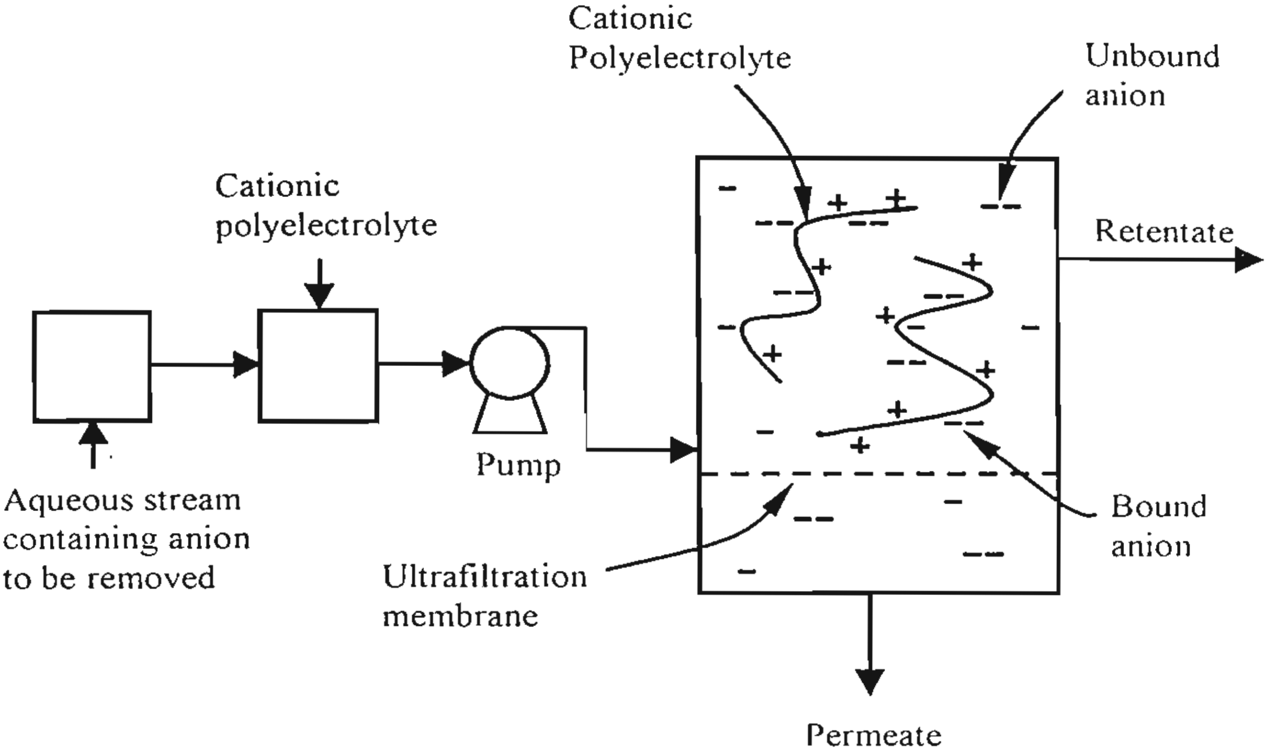

Figure 1. Schematic diagram of PEUF to remove anions from water.

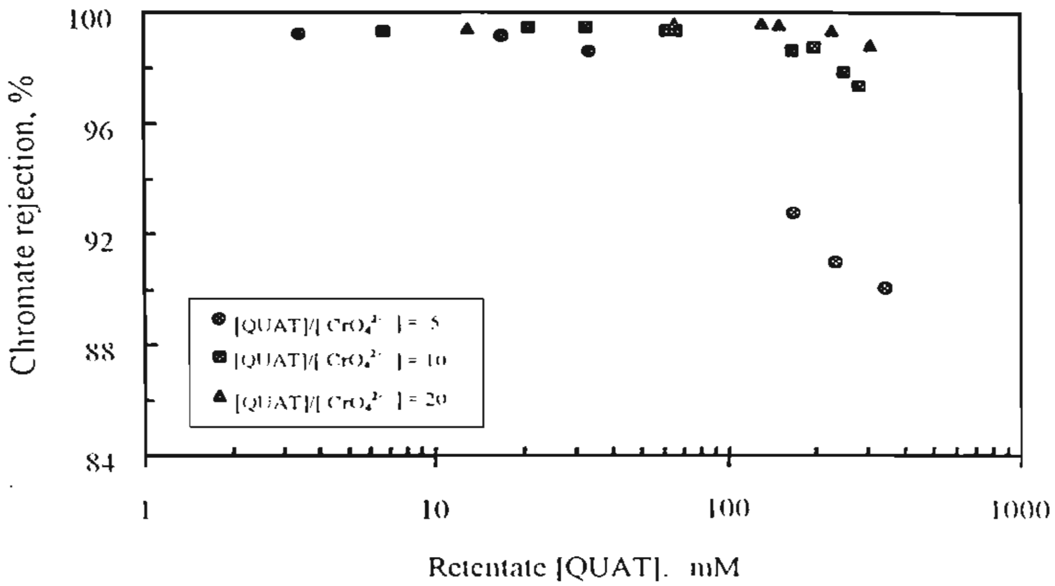

Figure 2. Effect of retentate [QUAT] on chromate rejection.

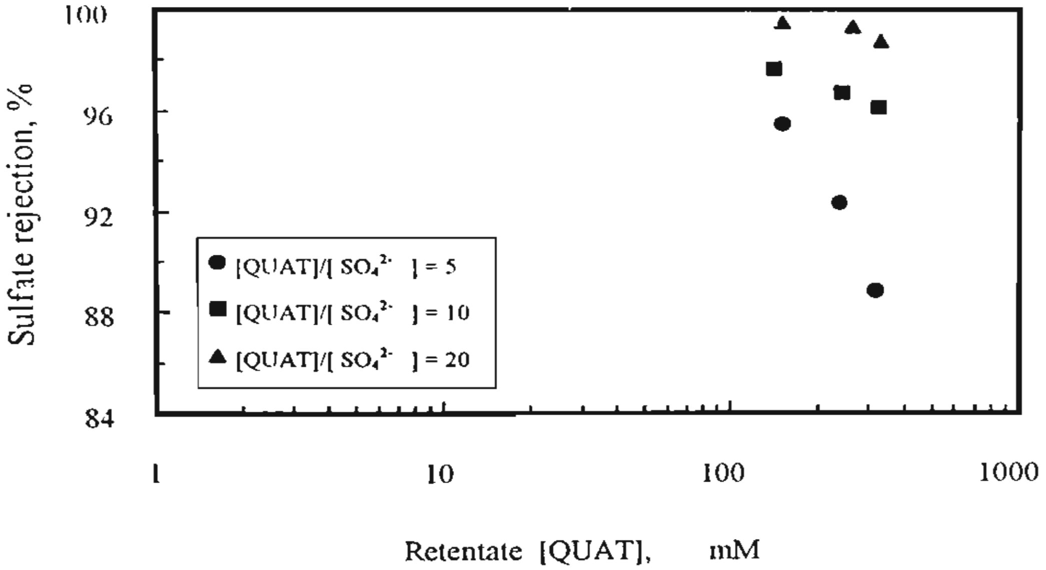

Figure 3. Effect of retentate [QUAT] on sulfate rejection.

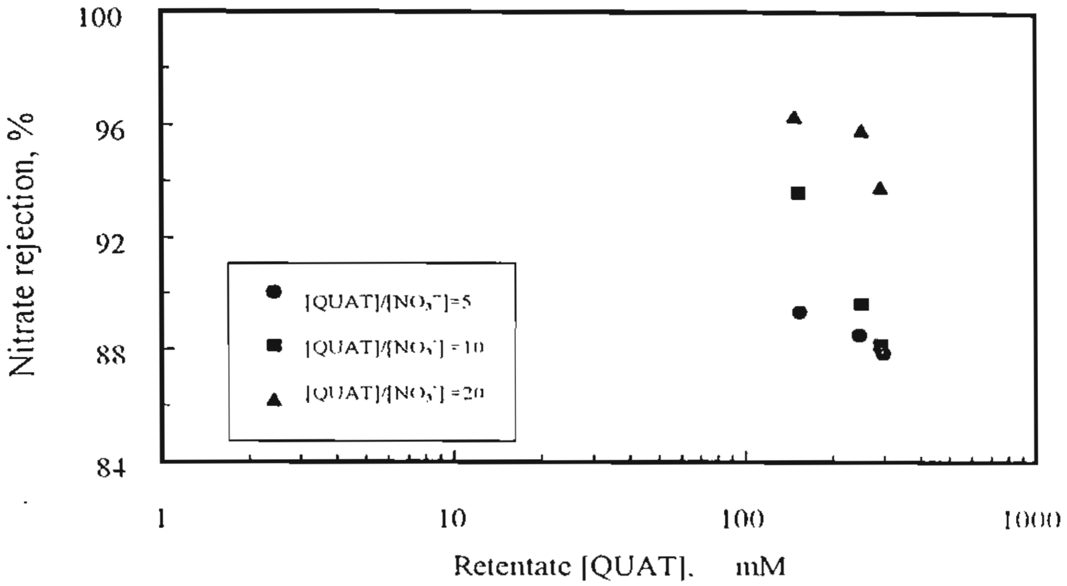

Figure 4. Effect of retentate [QUAT] on nitrate rejection.

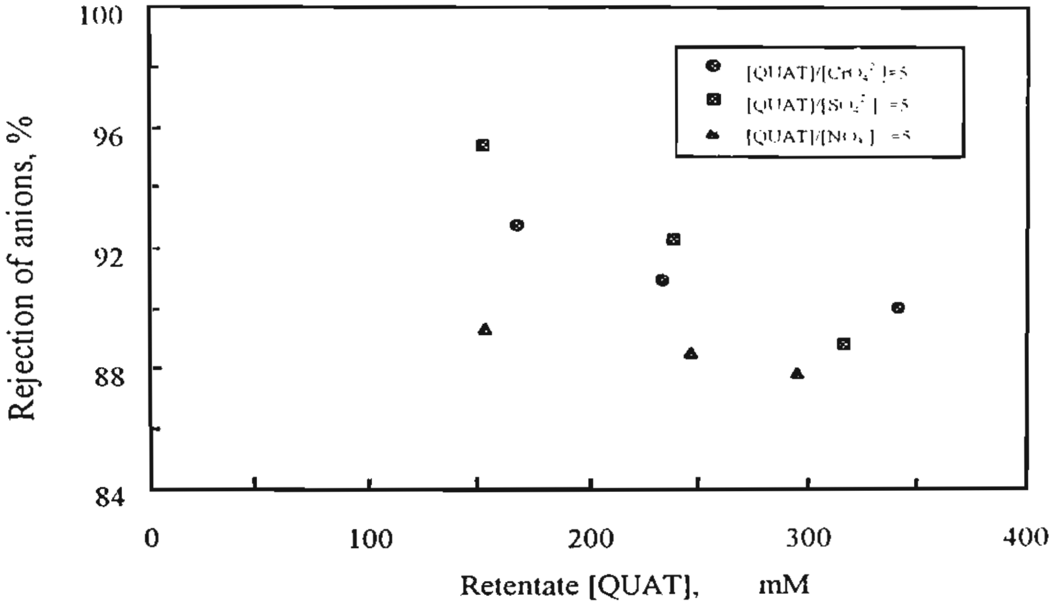

Figure 5. Effect of retentate [QUAT] on chromate, sulfate, and nitrate rejections at a[QUAT]/[anion] of 5.

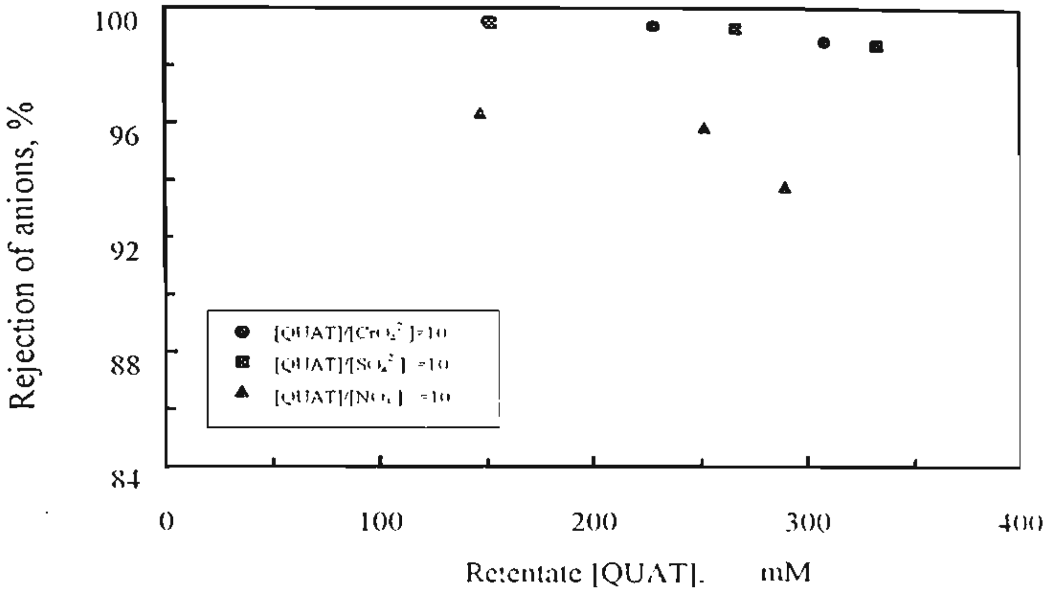

Figure 6. Effect of retentate [QUAT] on chromate, sulfate, and nitrate rejections at a [QUAT]/[anion] of 10.

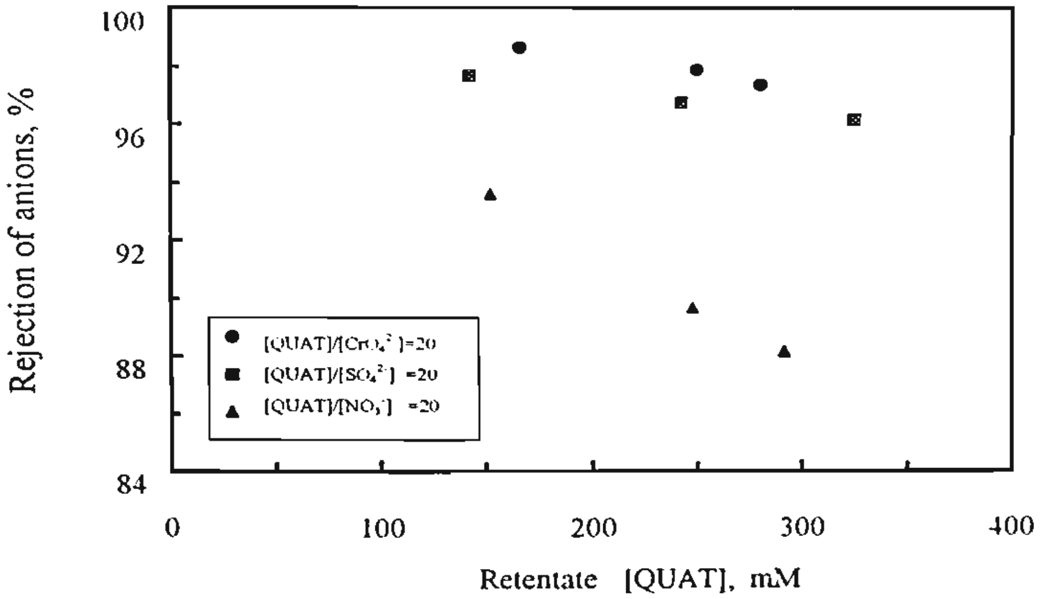

Figure 7. Effect of retentate [QUAT] on chromate, sulfate, and nitrate rejections at a [QUAT]/[anion] of 20.

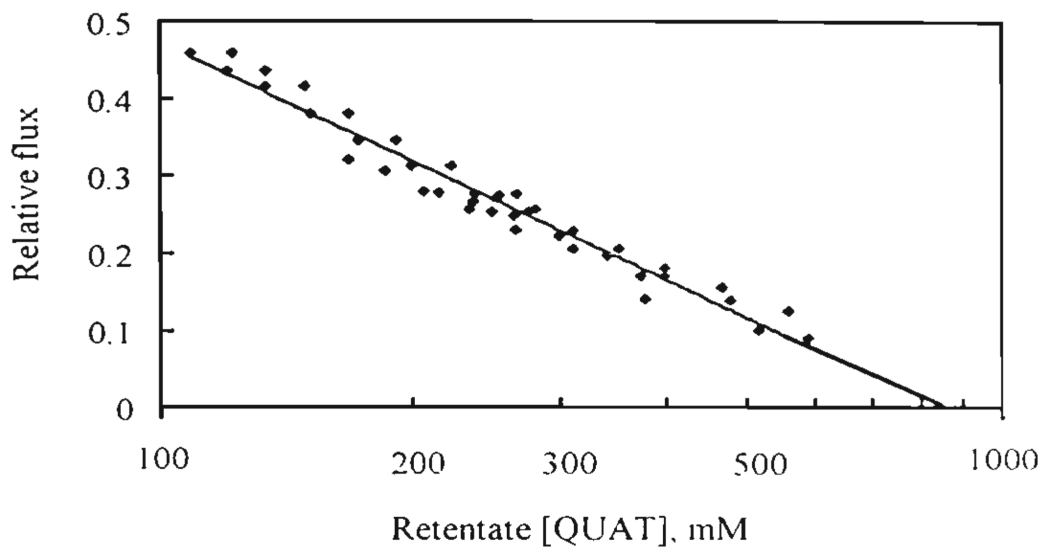

Figure 8. Relative flux of QUAT/chromate system in PEUF at a [QUAT]/[chromate] of 5.

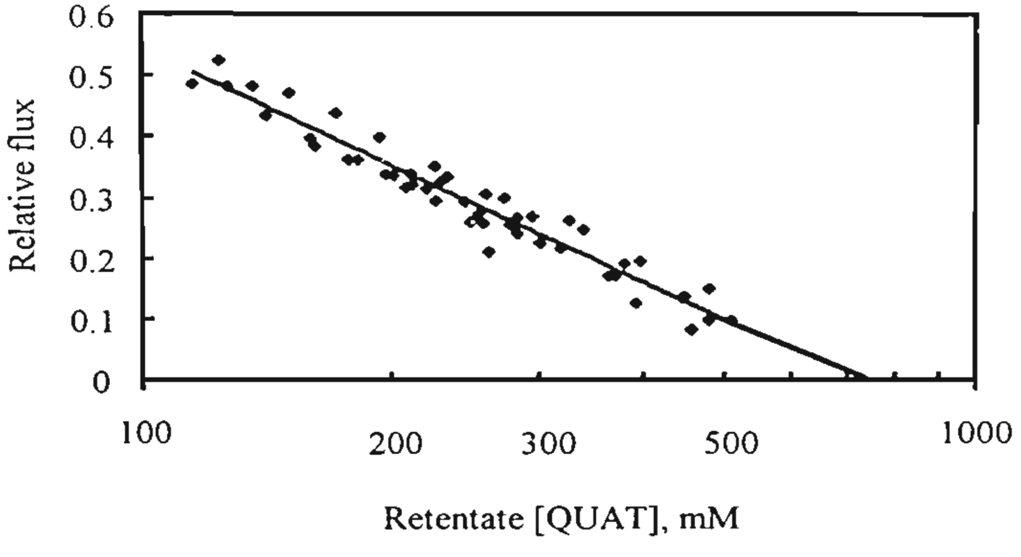

Figure 9. Relative flux of QUAT/chromate system in PEUF at a [QUAT]/[chromate] of 10.

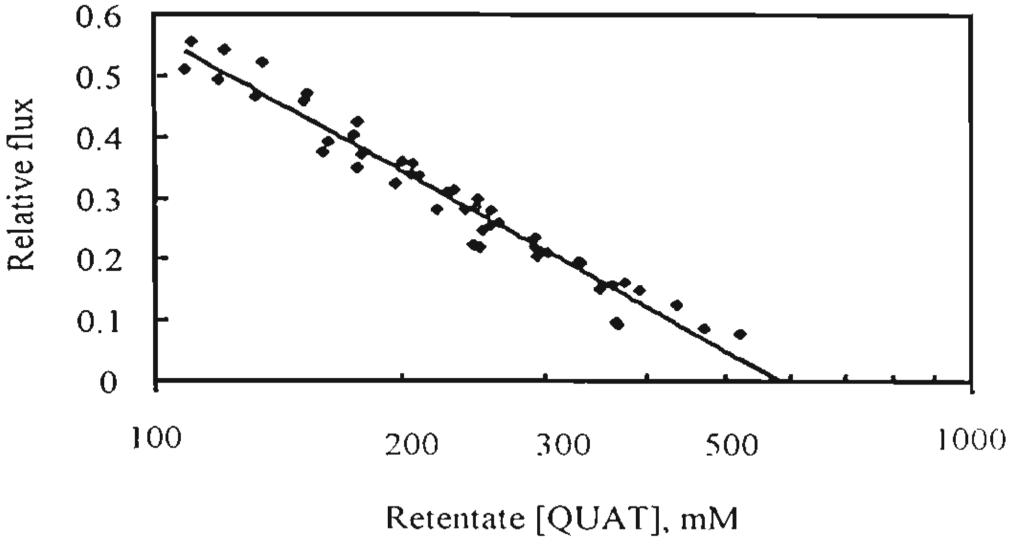

Figure 10. Relative flux of QUAT/chromate system in PEUF at a [QUAT]/[chromate] of 20.

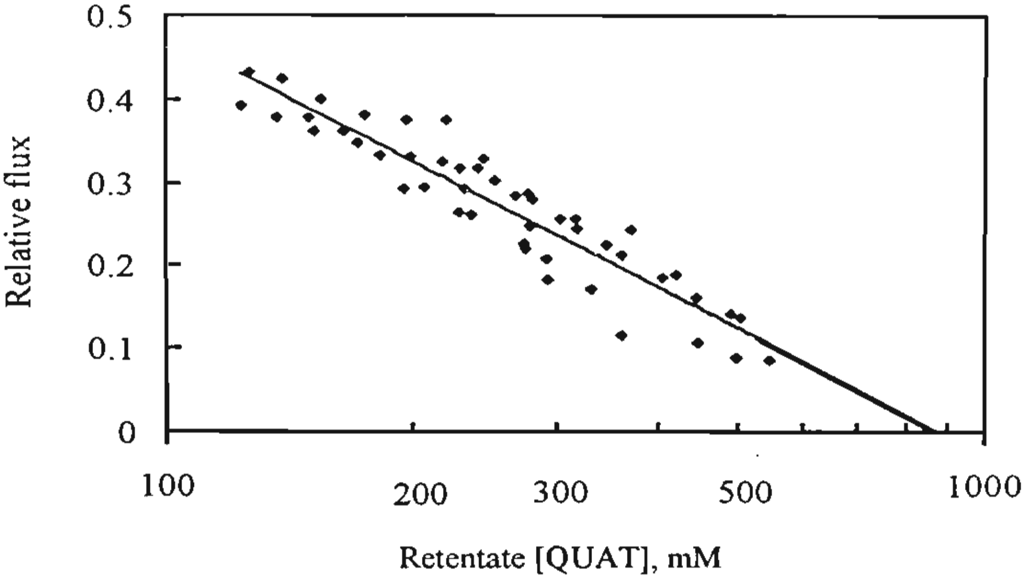

Figure 11. Relative flux of QUAT/sulfate system in PEUF at a [QUAT]/[sulfate] of 5.

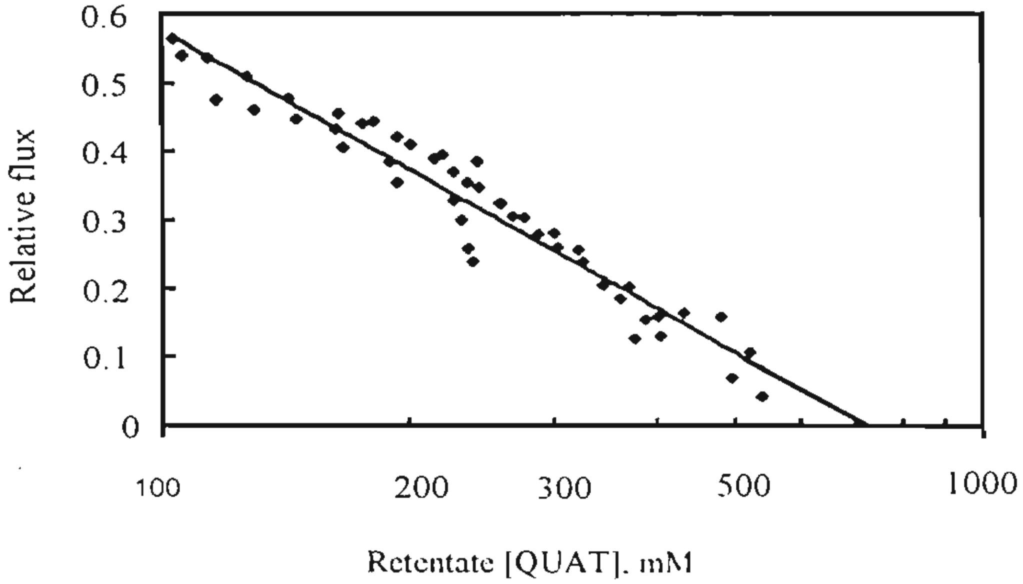

Figure 12. Relative flux of QUAT/sulfate system in PEUF at a [QUAT]/[sulfate] of 10.

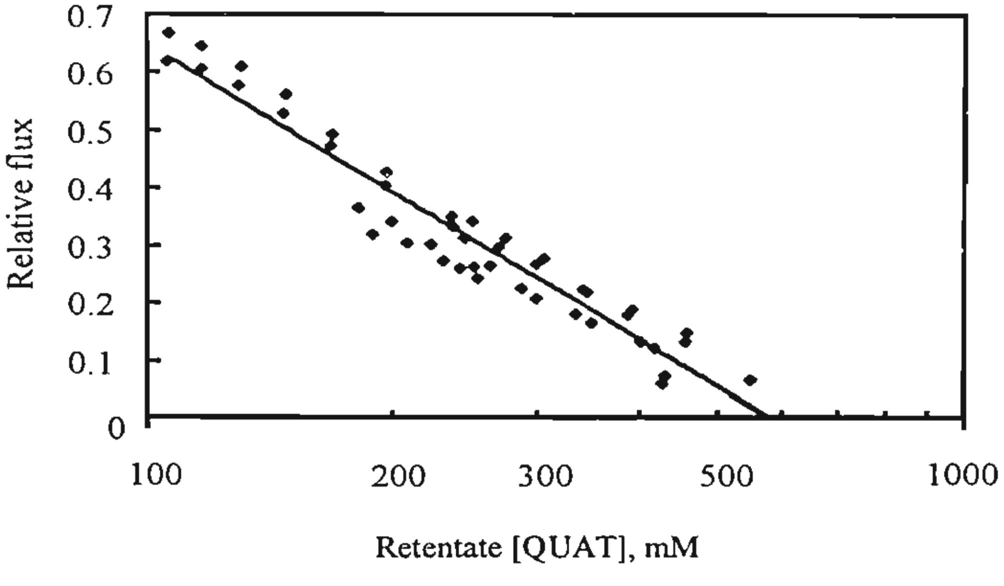

Figure 13. Relative flux of QUAT/sulfate system in PEUF at a [QUAT]/[sulfate] of 20.

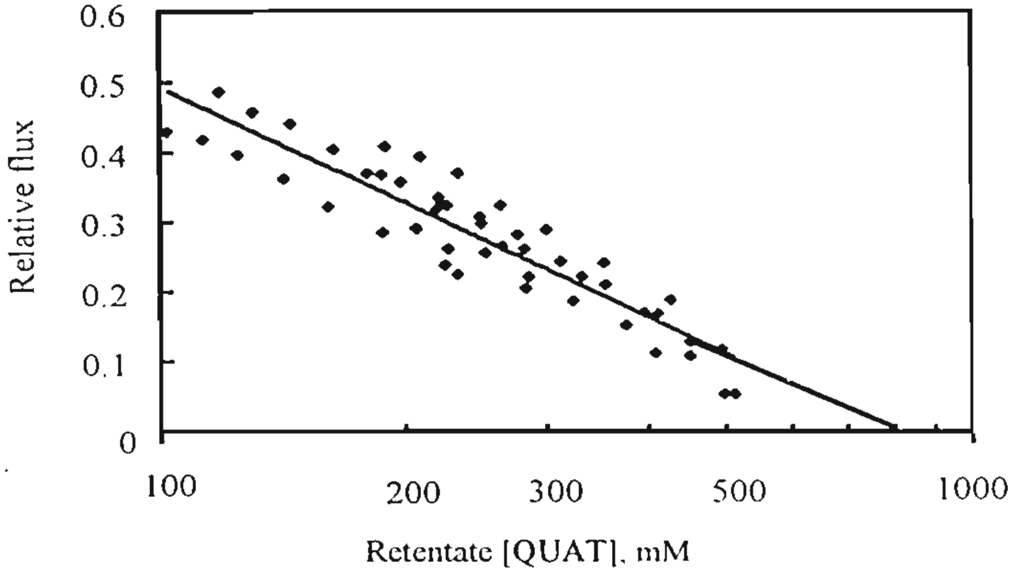

Figure 14. Relative flux of QUAT/nitrate system in PEUF at a [QUAT]/[nitrate] of 5.

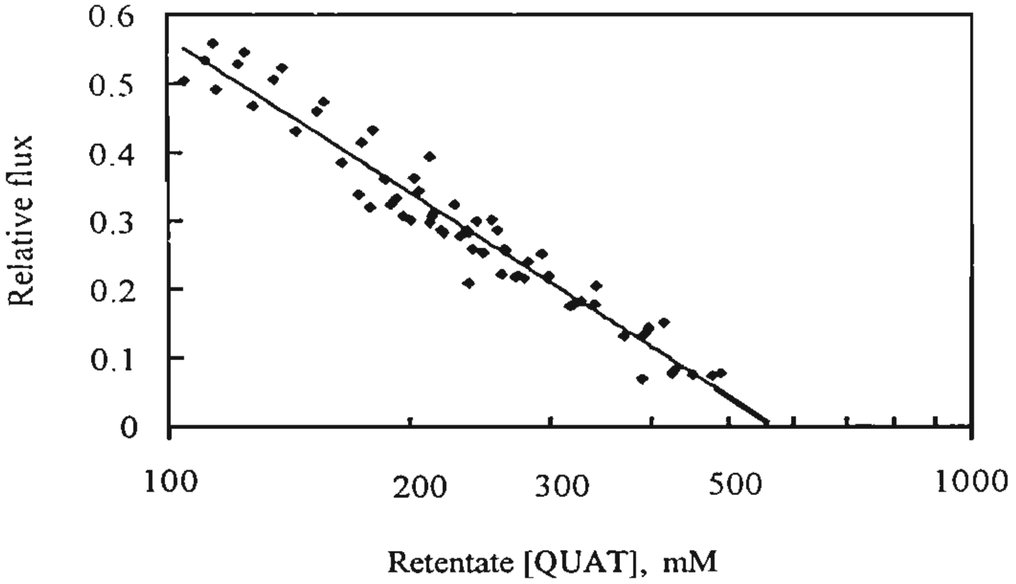

Figure 15. Relative flux of QUAT/nitrate system in PEUF at a [QUAT]/[nitrate] of 10.

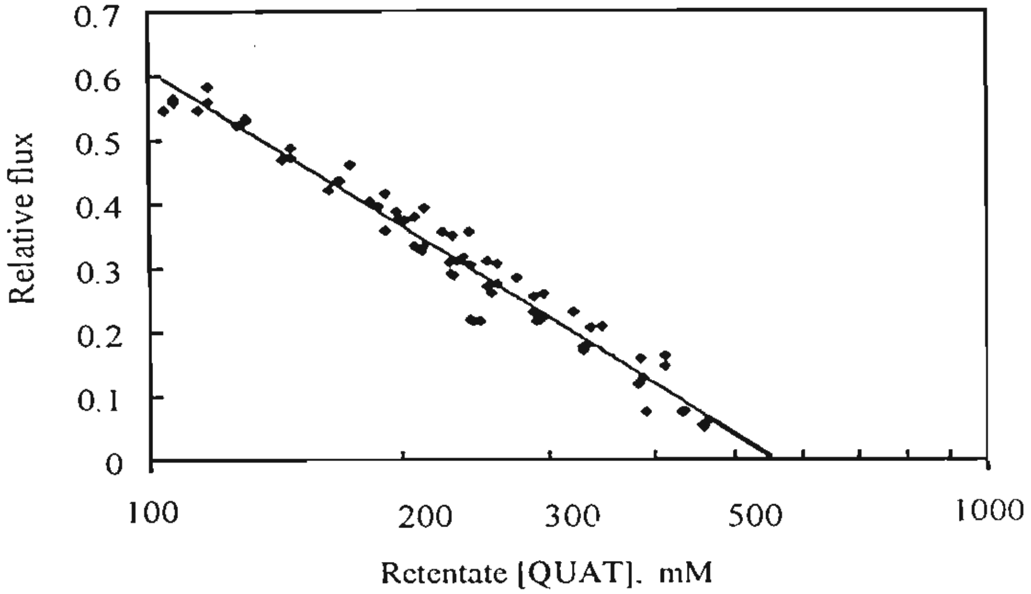

Figure 16. Relative flux of QUAT/nitrate system in PEUF at a [QUAT]/[nitrate] of 20.

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**Proceedings:**

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2. Chalothorn Soponvuttikul, Chintana Saiwan, John F. Scamehorn. *Use of Polyelectrolyte-Enhanced Ultrafiltration to Remove Chromate from Water: Polymer Recycle by Precipitation.* 222nd ACS National Meeting. Chicago. U.S.A., August 26-30, 2001.
3. Chalothorn Soponvuttikul, Chintana Saiwan, John F. Scamehorn. *Recovery of Polyelectrolyte from Polyelectrolyte-Enhanced Ultrafiltration (PEUF) by a Crystallization Process.* RGJ-Ph.D. Congress II. Pattaya, Thailand, April 26-30. 2001.
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5. Chalothorn Soponvuttikul, Chintana Saiwan, John F. Scamehorn. *Recovery of Polyelectrolyte from Polyelectrolyte-Enhanced Ultrfiltration by a Precipitation Process. I. Equilibrium Precipitation.* The Fourth Princess Chulabhon International Science Congress. Bangkok, Thailand, November 28-December 2. 1999.

**Awards:**

1. Outstanding Paper Presentation at the RGJ-Ph.D. Congress III, Pattaya. Thailand, April 25-27, 2002.
2. Outstanding Paper Presentation at the RGJ-Ph.D. Congress II, Pattaya, Thailand, April 26-30, 2001.