รายงานวิจัยฉบับสมบูรณ์

โครงการ

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

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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

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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 (2.1×10^{-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.

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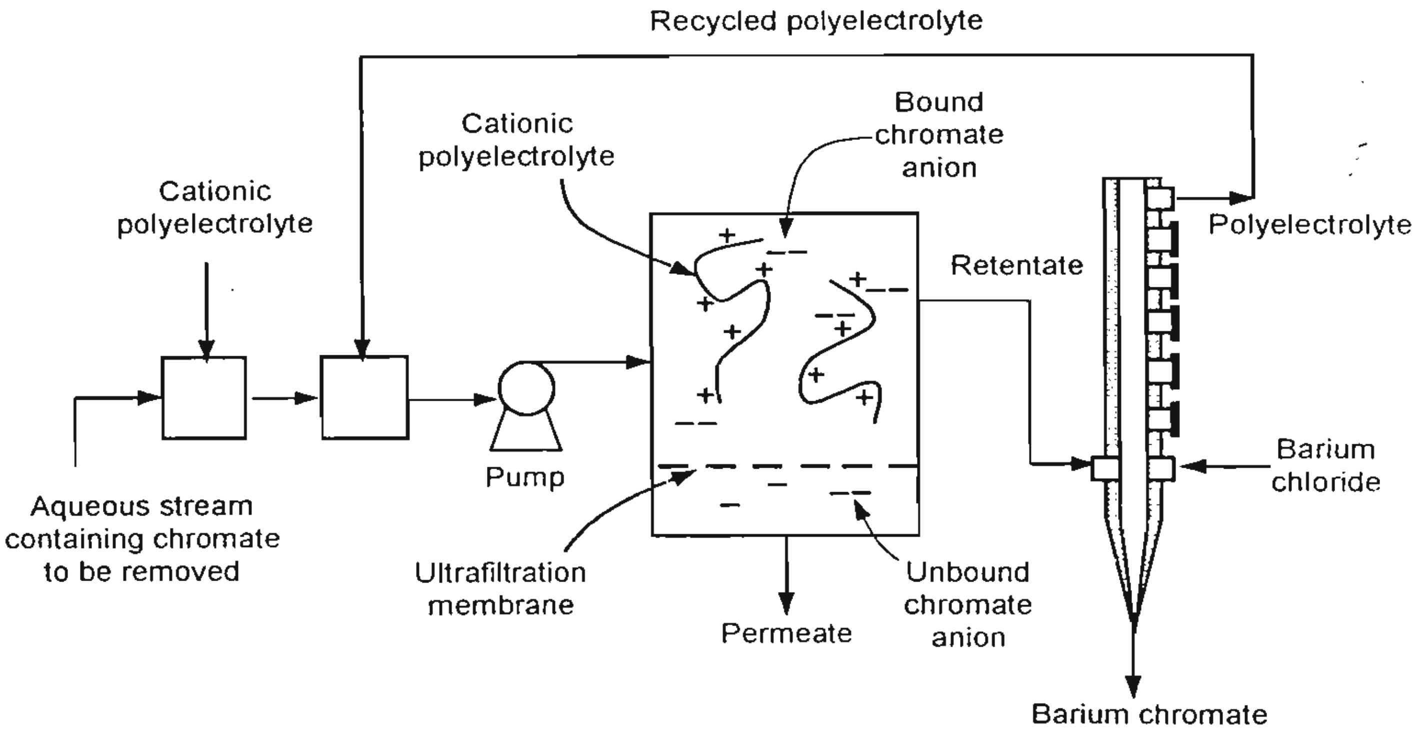

Figure 1. Schematic diagram of PEUF and polyelectrolyte regeneration processes to remove chromate from water.

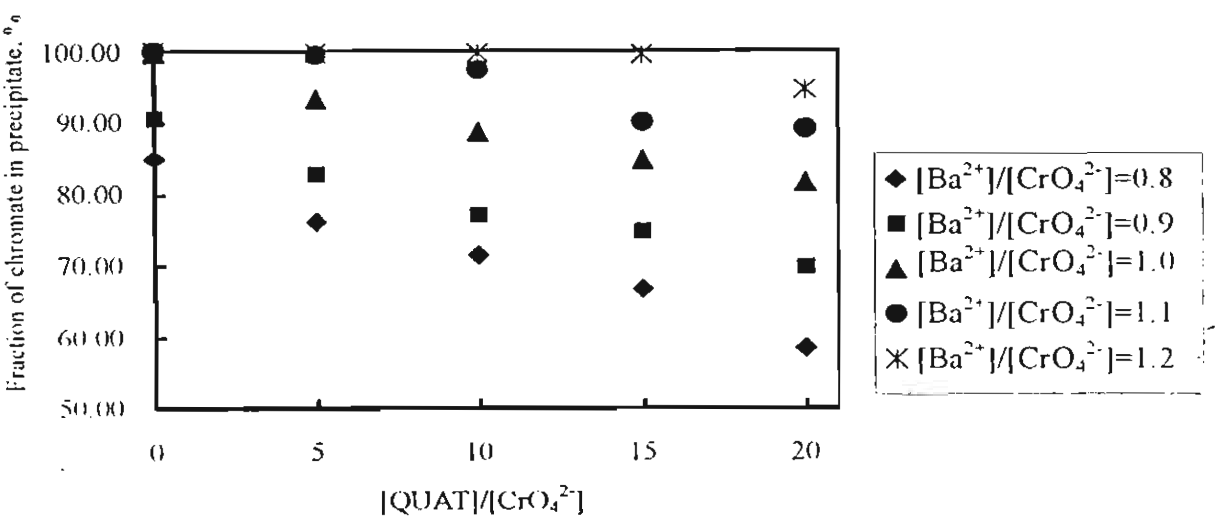

Figure 2. Fraction of chromate in precipitation at different $[QUAT]/[CrO_4^{2-}]$ ratios.

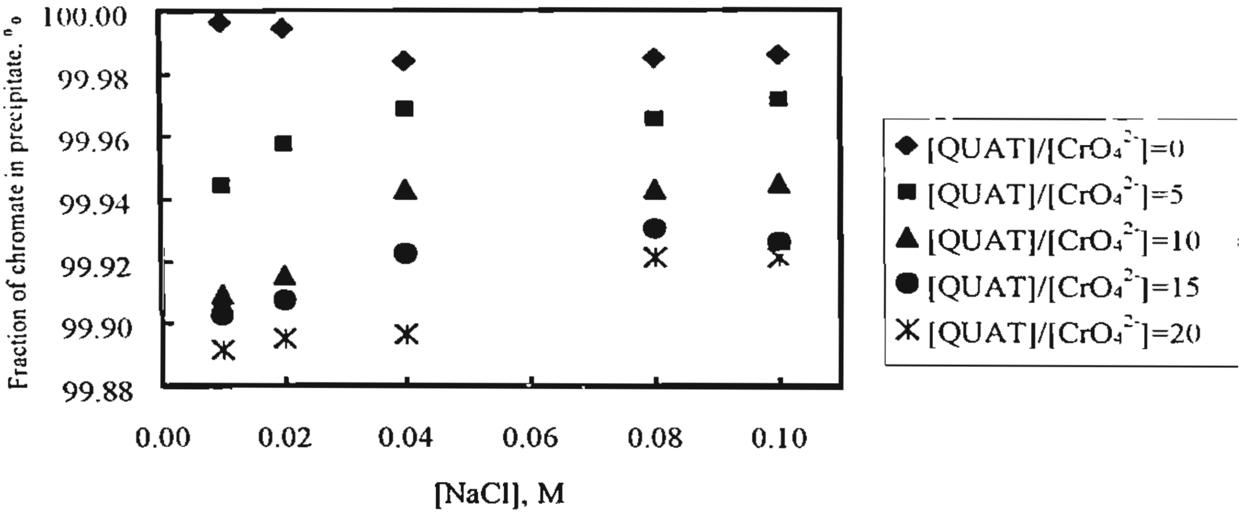

Figure 3. Fraction of chromate in precipitate at different [NaCl].

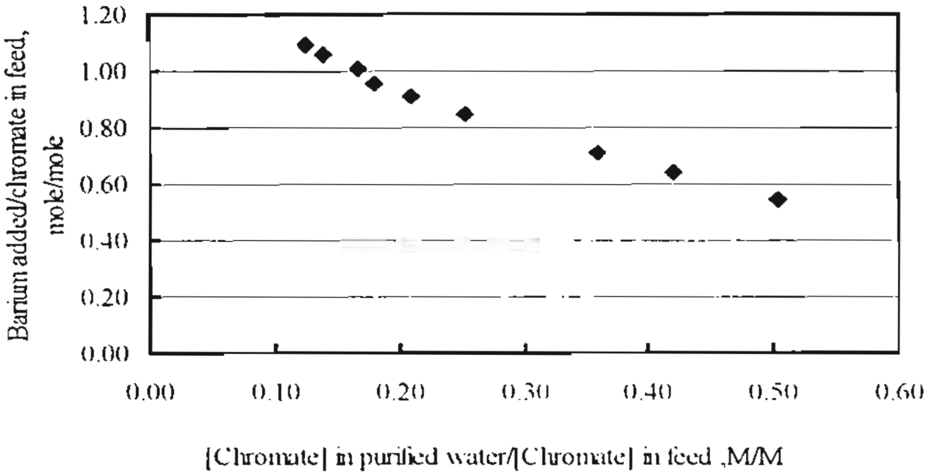

Figure 4. Added barium in crystallizer/chromate in feed at different chromate removal levels.

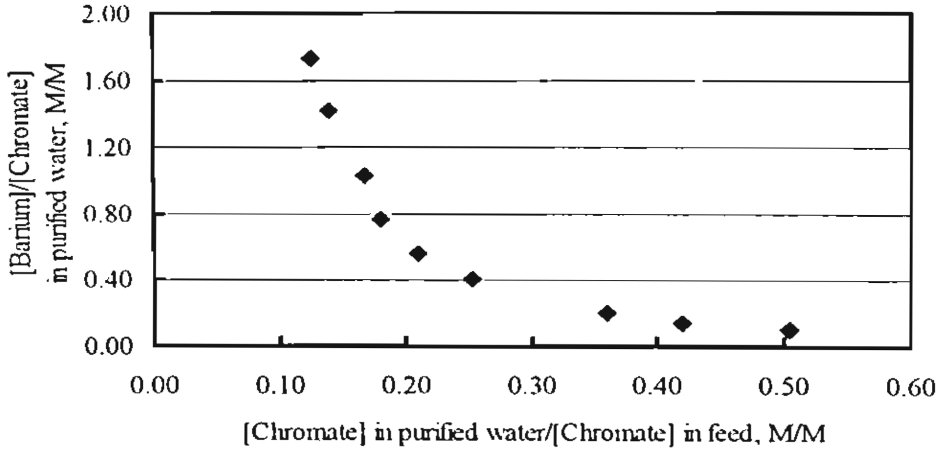

Figure 5. Barium concentration/chromate concentration in purified water at different chromate removal levels.

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 2.4×10^5 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.

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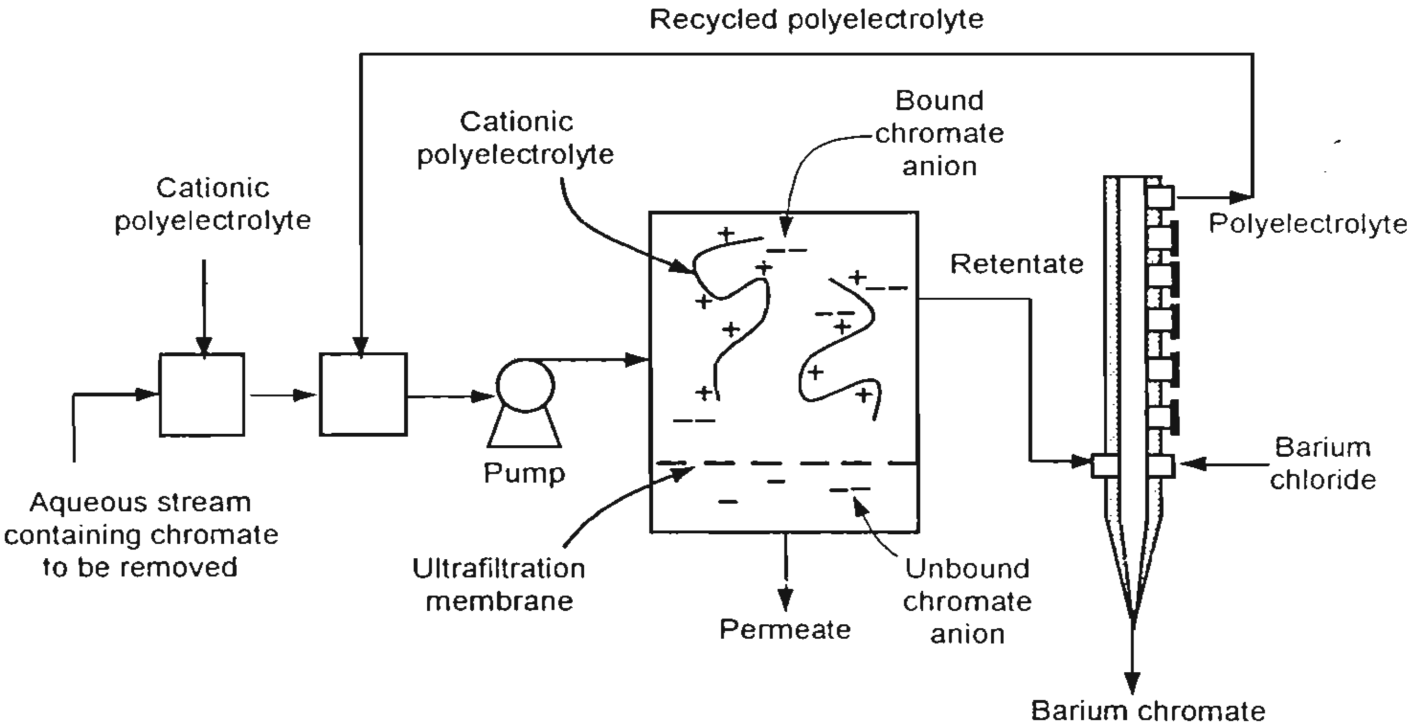

Figure 1. Schematic diagram of PEUF and polyelectrolyte regeneration processes to remove chromate from water.

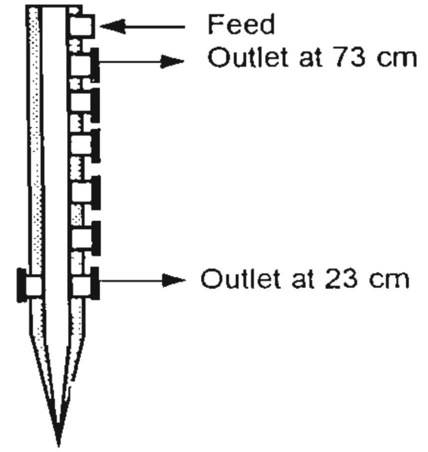

Figure 2. Experimental setup of the batch crystallizer

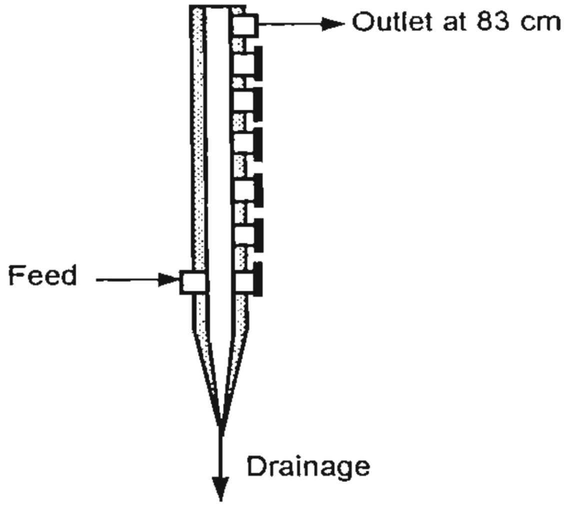

Figure 3. Experimental setup of the continuous crystallizer

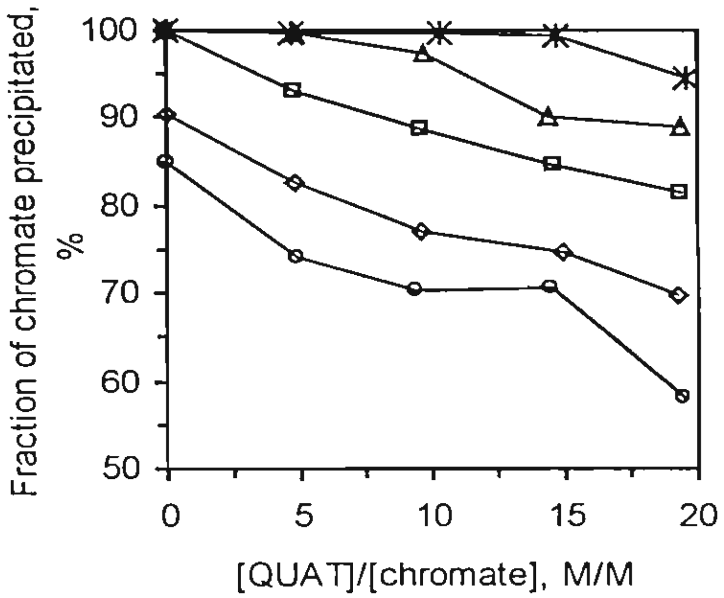

Figure 4. Fraction of chromate in precipitate at different QUAT to chromate ratios and at various barium to chromate ratios. (○) 0.8, (◇) 0.9, (□) 1.0, (△) 1.1, (✳) 1.2.

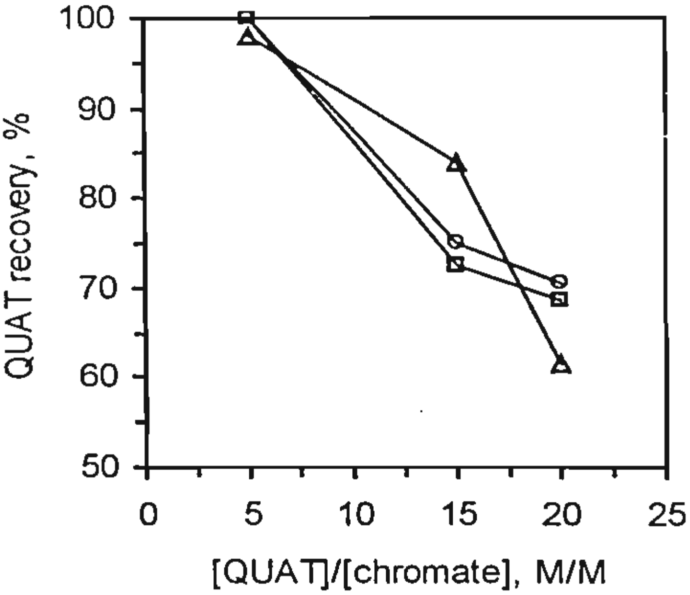

Figure 5. Fraction of QUAT in solution at different QUAT to chromate ratios at various residence times. (○) 30 min, (□) 60 min, (△) 120 min.

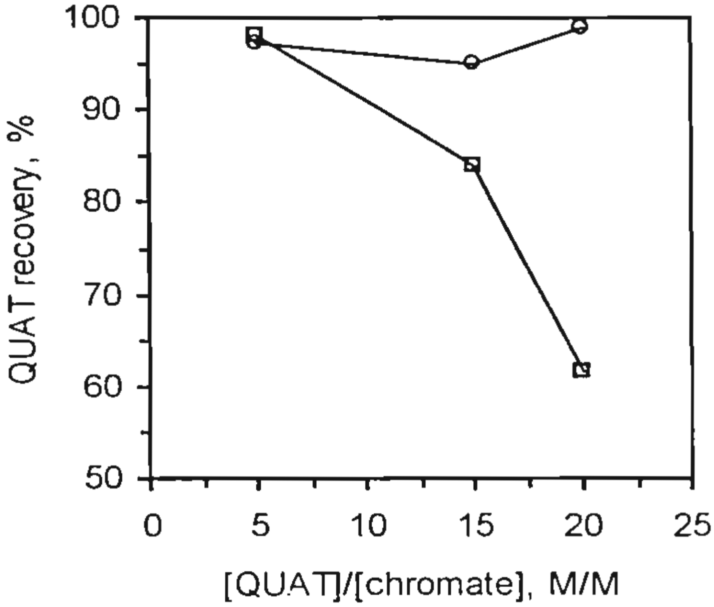

Figure 6. Fraction of QUAT in solution at different QUAT to chromate ratios at various outlet heights. (○) 23 cm, (□) 73 cm.

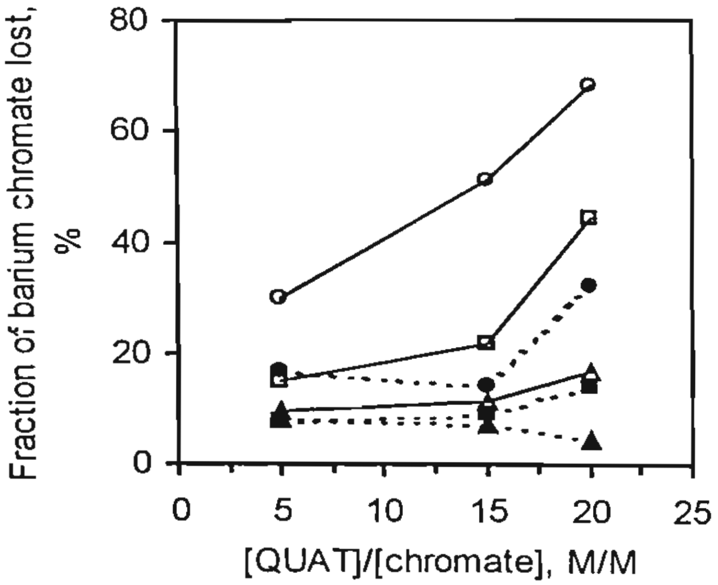

Figure 7. Fraction of barium chromate in solution at different QUAT to chromate ratios at various outlet heights and residence times. (○) 23 cm/30 min, (□) 23 cm/60 min, (△) 23 cm/120 min, (●) 73 cm/30 min, (■) 73 cm/60 min, (▲) 73 cm/120 min.

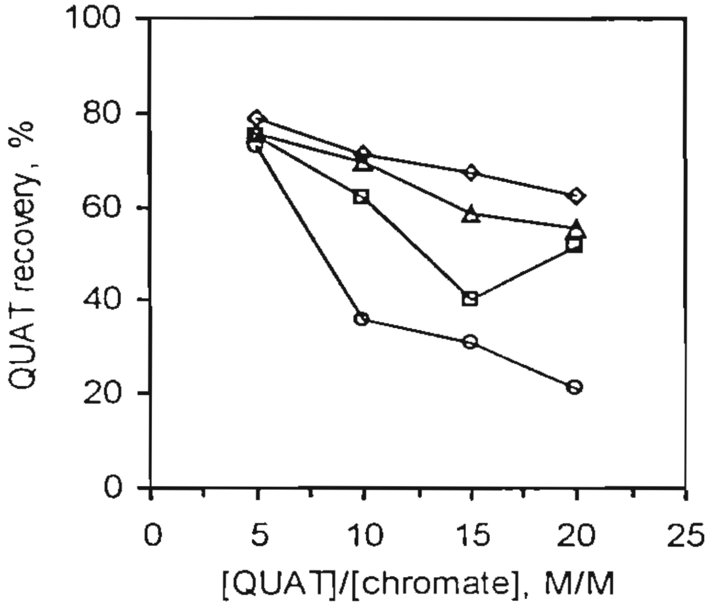

Figure 8. Fraction of QUAT in solution at different QUAT to chromate ratios at various feed flow rates. (○) 4 mL/min, (□) 8 mL/min, (△) 12 mL/min, (◇) 16 mL/min.

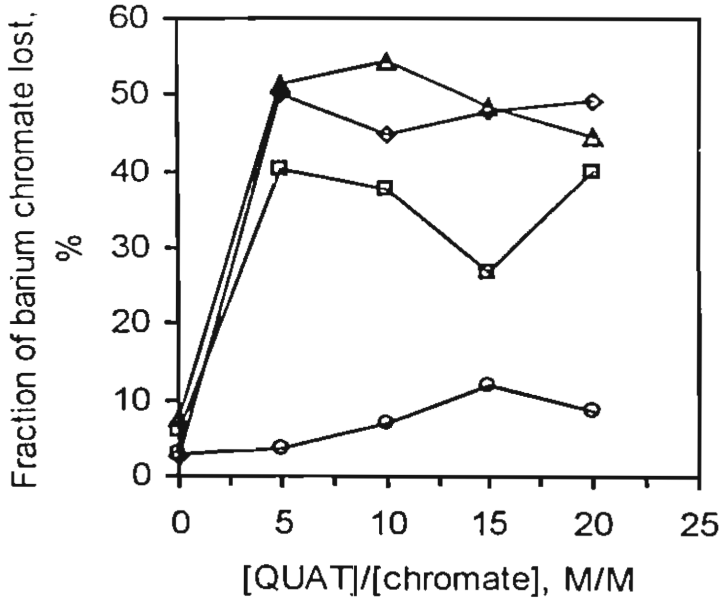

Figure 9. Fraction of barium chromate solid in solution at different QUAT to chromate ratios and at various feed flow rates. (○) 4 mL/min, (□) 8 mL/min, (△) 12 mL/min, (◇) 16 mL/min.

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]