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 2.4×10^5 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.

ACKNOWLEDGMENTS

Financial support for this work was provided by the Thailand Research Fund in two sources, the Royal Golden Jubilee Ph.D. Program and the Basic Research Grant for the Royal Golden Jubilee Program. In addition, support was received from the industrial sponsors of the Institute for Applied Surfactant Research including Akzo Nobel Chemicals Incoparated, Albemarle Corporation, Amway Corporation, Clorox Company, Colgate-Palmolive, Dial Corporation, Dow Chemical Company, DowElanco, E. I. DuPont de Nemours & Company, Halliburton Services Corporation, Henkel Corporation, Huntsman Corporation, ICI Americas Incoporated, Kerr-McGee Corporation, Lubrizol Corporation, Nikko Chemicals, Phillips Petroleum Company, Pilot Chemical Company, Procter & Gamble Company, Reckitt Benckiser North America, Schlumberger Technology Corporation, Shell Chemical Company, Sun Chemical Corporation, Unilever Incoporated, and Witco Corporation. John Scamehorn holds the Asahi Glass Chair in chemical engineering at the University of Oklahoma.

REFERENCES

(1) Sriratana, S.; Scamehorn, J. F.; Chavadej, S.; Saiwan, C.; Haller, K. J.; Christian, S. D.; Tucker, E. E. *Sep. Sci. Technol.* **1996**, *31*, 2493.

(2) Tangvijitsri, S.; Saiwan, C.; Soponvuttikul, C.; Scamehorn, J. F. *Sep. Sci. Technol.* **2002**, *37*, 993.

(3) Christian, S. D.; Tucker, E. E.; Scamehorn, J. F. *Spec. Chem.* **1995**, *13*, 148.

(4) Sabatini, D. A.; Knox, R. C.; Tucker, E. E.; Puls, R. W. *Innovative Measures for Subsurface Chromium Remediation: Source Zone, Concentrated Plume, and Diluted Plume (EPA/600/S-97/005)*; U.S. Government Printing Office: Washington, D.C., 1997.

(5) Tucker, E. E.; Christian, S. D.; Scamehorn, J. F.; Uchiyama, H.; Guo, W. In *Transport and Remediation of Subsurface Contaminants*; Sabatini, D. A., Knox, R. C., Eds.; American Chemical Society: Washington, D.C., 1992; Chapter 7.

(6) Soponvuttikul, C.; Saiwan, C.; Scamehorn, J. F. *222nd ACS National Meeting*; Chicago, 2001.

(7) Balastre, M.; Persello, J.; Foissy, A.; Argillier, J.-F. *J. Colloid Interface Sci.* **1999**, *219*, 155.

(8) van der Leeden, M. C.; van Rosmalen, G. M. *J. Colloid Interface Sci.* **1995**, *171*, 142.

(9) Williams, P. A.; Harrop, R.; Robb, I. D. *J. Chem. Soc., Faraday Trans. 1* **1984**, *80*, 403.

(10) Amjad, Z. *Colloids Surf.* **1990**, *48*, 95.

(11) Bauer, D.; Killmann, E.; Jaeger, W. *Colloid Polym. Sci.* **1998**, *276*, 698.

(12) Ter[illegible], H.; Okumura, K.; Sakai, K.; Torigoe, K.; Esumi, K. *Colloids Surf., B* **2001**, [illegible] 73.

(13) B[illegible]r, D.; Killmann, E.; Jaeger, W. *Prog. Colloid Polym. Sci.* **1998**, *109*, 161.

(14) Killmann, E.; Bauer, D.; Fuchs, A.; Portenlanger, O.; Rehmet, R.; Rustemeier, O. *Prog. Colloid Polym. Sci.* **1998**, *111*, 135.

(15) van der Leeden, M. C.; van Rosmalen, G. M. In *Mineral Scale Formation Inhibition*; Amjad, Z., Ed.; Plenum Press: New York, 1995; Chapter 9.

(16) Thompson, R. G. In *Colloid-Polymer Interactions: Particulate, Amphiphilic, and Biological Surfaces*; Dubin, P. L., Tong, P., Eds.; American Chemical Society:

Washington, D.C., 1993; Chapter 15.

(17) Kretzschmar, R.; Robarge, W. P.; Weed, S. B. *Soil Sci. Soc. Am. J.* **1993**, *57*, 1277.

(18) Lagaly, G. In *Coagulation and Flocculation: Theory and Application*; Dobias, B., Ed.; Marcel Dekker, Inc.: New York, 1993; Chapter 10.

(19) Dickinson, E.; Eriksson, L. *Adv. Colloid Interface Sci.* **1991**, *34*, 1.

(20) Antonious, M. S.; Ramsis, M. N.; Youssef, A. O. *Monatsh. Chem.* **1996**, *127*, 15.

(21) Ramsis, M. N.; Antonious, M. S.; Rizkalla, E. N.; Youssef, A. O. *Monatsh. Chem.* **1996**, *127*, 1099.

(22) Foust, A. S.; Wenzel, L. A.; Clump, C. W.; Maus, L.; Andersen, L. B. *Principles of Unit Operations*; 2nd ed.; John Wiley & Sons: Singapore, 1980; Chapter 22.

(23) McCabe, A. S.; Smith, J. C.; Harriott, P. *Unit Operations of Chemical Engineering*; 5th ed.; McGraw-Hill Book Company: Singapore, 1985; Chapter 30.

(24) Rushton, A.; Ward, A. S.; Holdich, R. G. *Solid-Liquid Filtration and Separation Technology*; 2nd ed.; WILEY-VCH: Darmstadt, 2000; Chapter 3.

(25) Wright, J. A.; Harrop, R.; Williams, P. A.; Pass, G.; Robb, I. D. *Colloids Surf.* **1984**, *24*, 249.

(26) Wilkes, G. L. In *Concise Encyclopedia of Polymer Science and Engineering*; Kroschwitz, J. I., Ed.; John Wiley & Sons: New York, 1990; p 994.

(27) Kawatra, S. K.; Bakshi, A. K.; Rusesky, M. T. *Miner. Eng.* **1996**, *9*, 881.

(28) Bakshi, A. K.; Kawatra, S. K. *Miner. Metall. Process.* **1996**, *13*, 165.

(29) Packter, A.; Alleem, A. *Cryst. Res. Technol.* **1981**, *16*, 33.

(30) Soponvuttikul, C. Ph.D. Dissertation, The Petroleum and Petrochemical College, Thailand, 2003.

(31) Sonntag, H. In *Coagulation and Flocculation: Theory and Application*; Dobias, B., Ed.; Marcel Dekker, Inc.: New York, 1993; Chapter 3.

(32) Everett, D. H. *Basic Principles of Colloid Science*; Royal Society of Chemistry: London, 1992; Chapter 9.

(33) Hunter, R. J. *Foundations of Colloid Science I*; The Universities Press (Belfast) Ltd.: Belfast, 1991; Chapter 8.

(34) YI, L. *J. Hydraul. Res* **1994**, *32*, 41.

(35) Zaman, A. A. In *Polymers in Particulate Systems: Properties and Application*;

Hackley, V. A., Somasundaran, P., Lewis, J. A., Eds.; Marcel Dekker, Inc.: New York, 2001; Chapter 7.

(36) Sato, T.; Ruch, R. *Stabilization of Colloidal Dispersions by Polymer Adsorption*, Marcel Dekker, Inc.: New York, 1980; Chapter 2.

(37) Fleer, G. J.; Scheutjens, J. M. H. M. In *Coagulation and Flocculation: Theory and Application*; Dobias, B., Ed.; Marcel Dekker, Inc.: New York, 1993; Chapter 5.

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

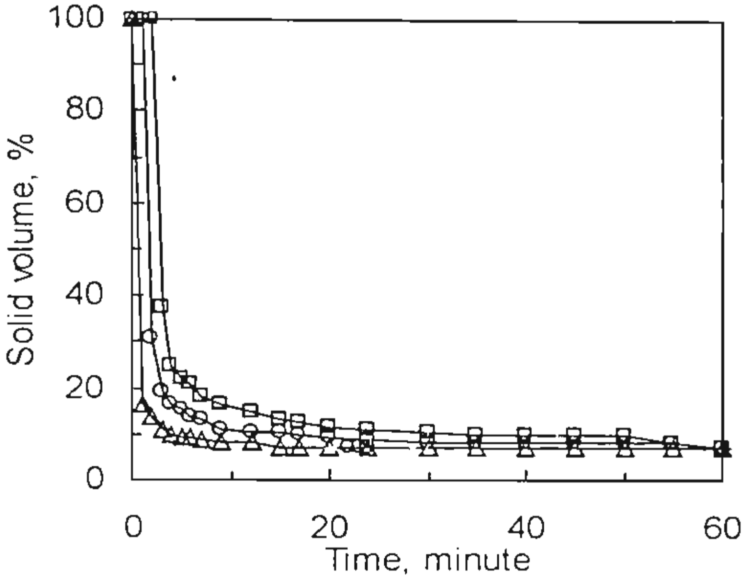

Figure 1. Rate of barium chromate sedimentation in the absence of QUAT at various temperatures. (□) 10°C, (○) 25°C, (△) 50°C

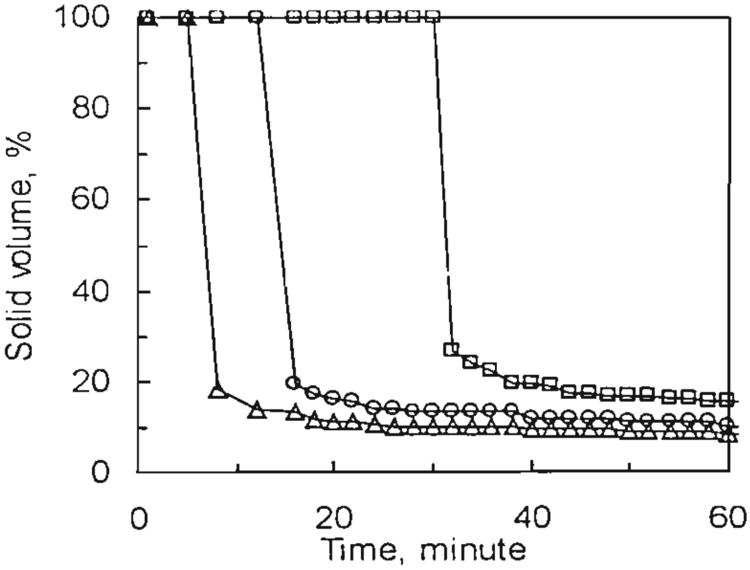

Figure 2. Rate of barium chromate sedimentation in the presence of 0.1 M QUAT at various temperatures. (□) 10°C, (○) 25°C, (△) 50°C.

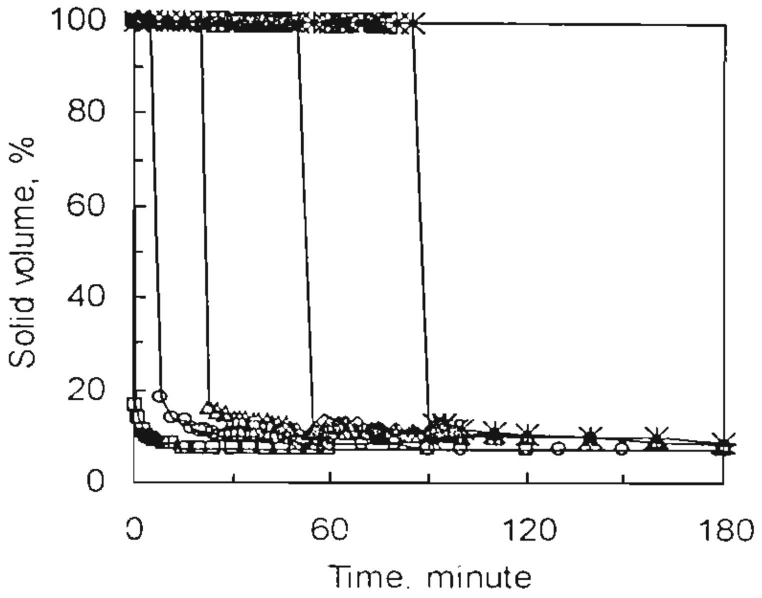

Figure 3. Rate of barium chromate sedimentation at 50°C at various QUAT concentrations. (□) 0 M, (○) 0.1 M, (△) 0.2 M, (◇) 0.3 M, (✳) 0.4 M.

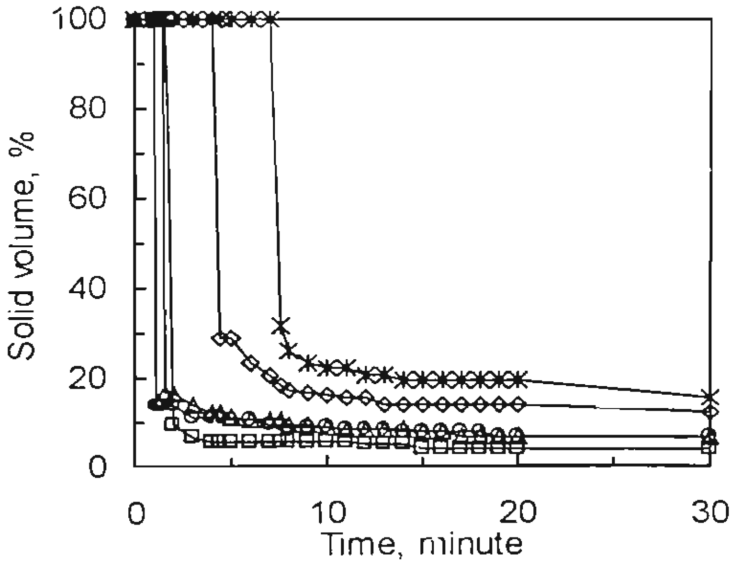

Figure 4. Rate of barium chromate sedimentation in the absence of QUAT at 50°C at various [barium] to [chromate] ratios. (□) 0.5, (○) 1.0, (△) 2.0, (◇) 5.0, (✳) 10.0.

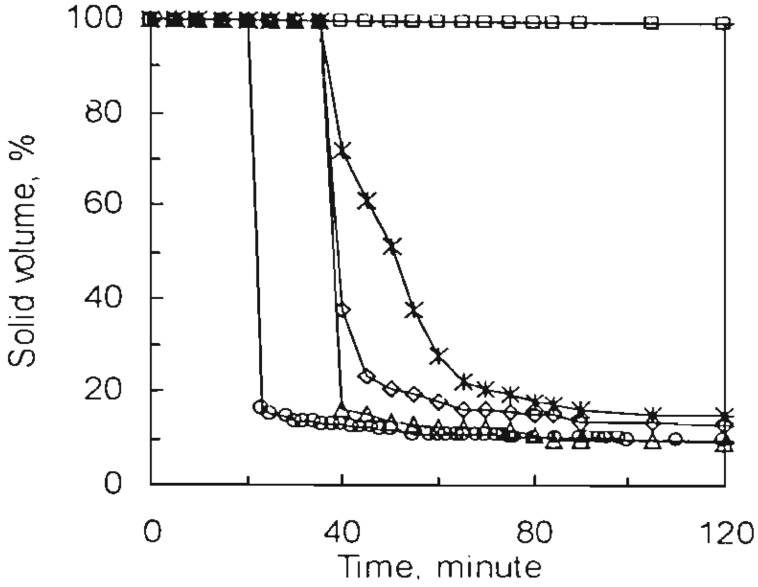

Figure 5. Rate of barium chromate sedimentation in the presence of 0.2 M QUAT at 50°C at various [barium] to [chromate] ratios. (□) 0.5, (○) 1.0, (△) 2.0, (◇) 5.0, (✳) 10.0

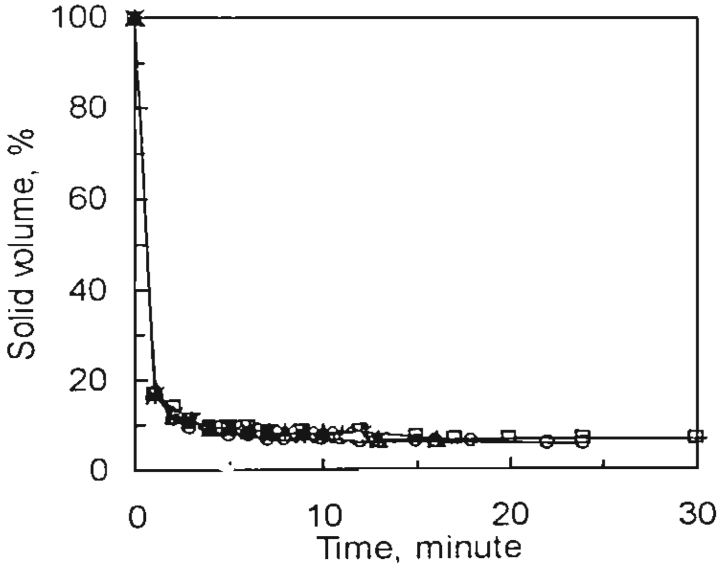

Figure 6. Rate of barium chromate sedimentation in the absence of QUAT at 50°C at various NaCl concentrations. (□) 0 M, (○) 0.01 M, (△) 0.05 M, (✳) 0.10 M NaCl.

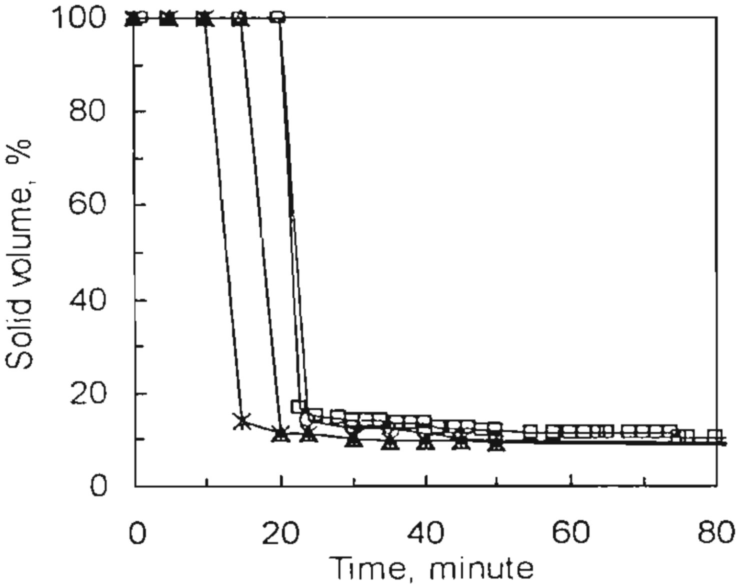

Figure 7. Rate of barium chromate sedimentation in the presence of 0.2 M QUAT at 50°C at various NaCl concentrations. (□) 0 M, (○) 0.01 M, (△) 0.05 M, (✱) 0.10 M NaCl.

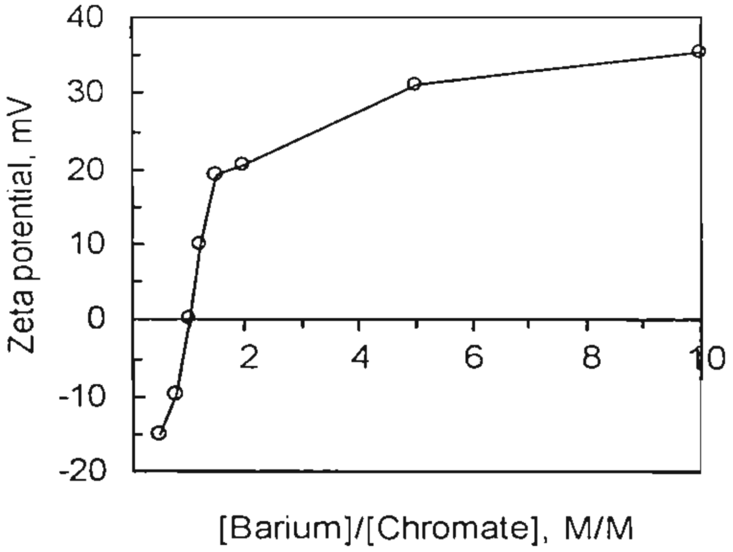

Figure 8. Effect of [barium] to [chromate] ratio on zeta potential of barium chromate particles.

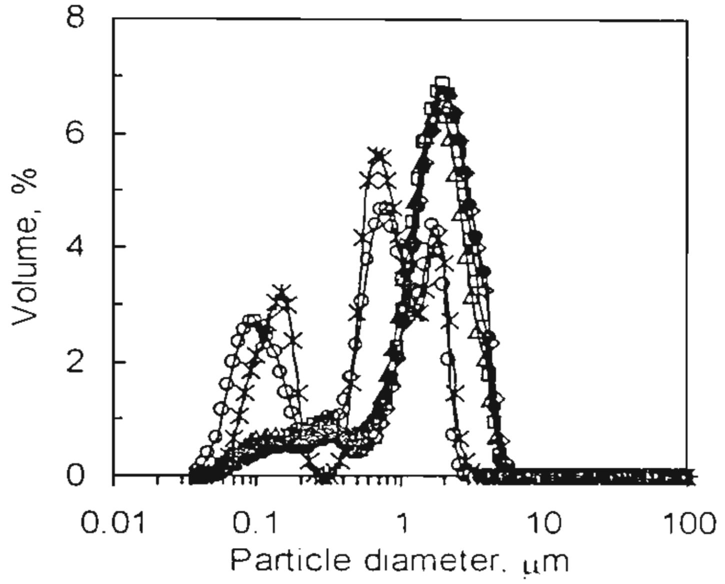

Figure 9. Barium chromate particle size distribution at 50°C at a low QUAT concentration range. (●) 0 mM, (◇) 1 mM, (□) 5mM, (△) 10 mM, (○) 50 mM, (✱) 100 mM.

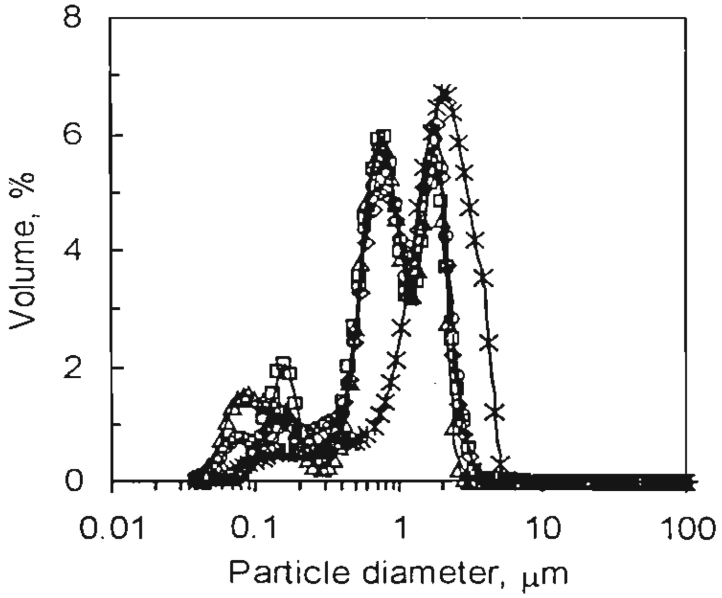

Figure 10. Barium chromate particle size distribution at 50°C at a high QUAT concentration range. (✱) 0 M, (◇) 0.1 M, (□) 0.2 M, (△) 0.3 M, (○) 0.4 M.

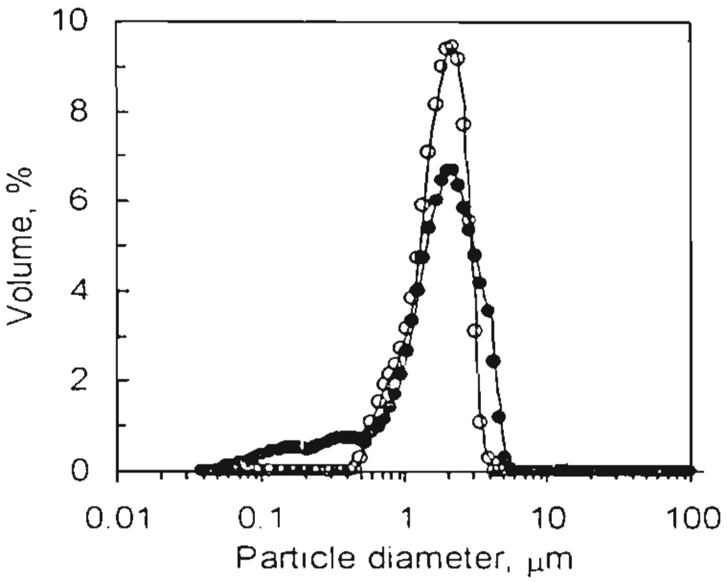

Figure 11. Barium chromate particle size distribution in the absence of QUAT at various temperatures. (○) 10°C, (●) 50°C.

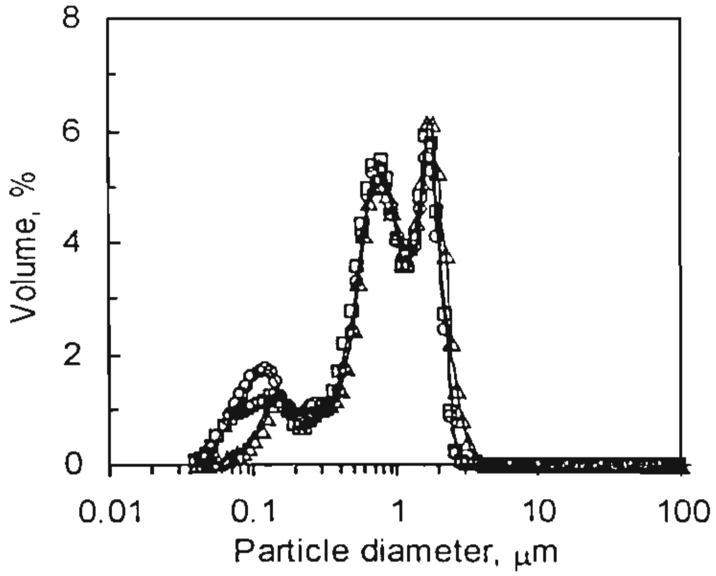

Figure 12. Barium chromate particle size distribution in the presence of 0.1 M QUAT at various temperatures. (□) 10°C, (○) 25°C, (△) 50°C.

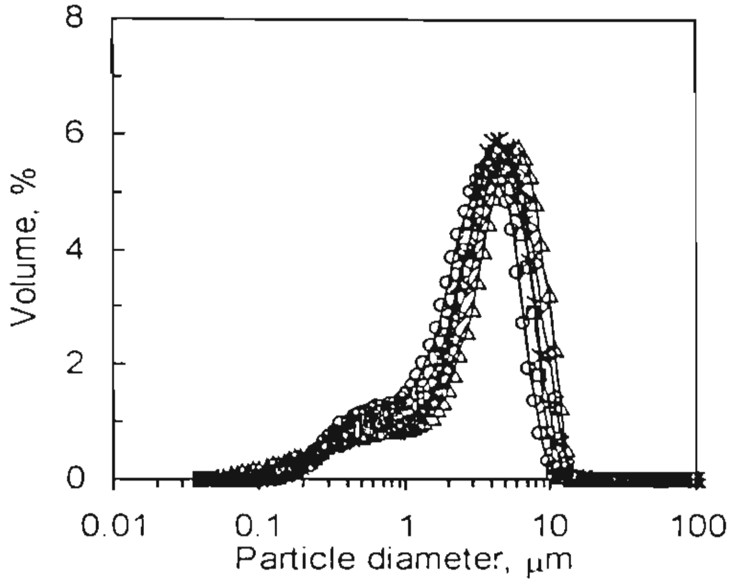

Figure 13. Barium chromate particle size distribution in the absence of QUAT at 50°C at various [barium] to [chromate] ratios (○) 0.5, (△) 1.0, (◇) 2.0, (✳) 5.0, (□) 10.0.

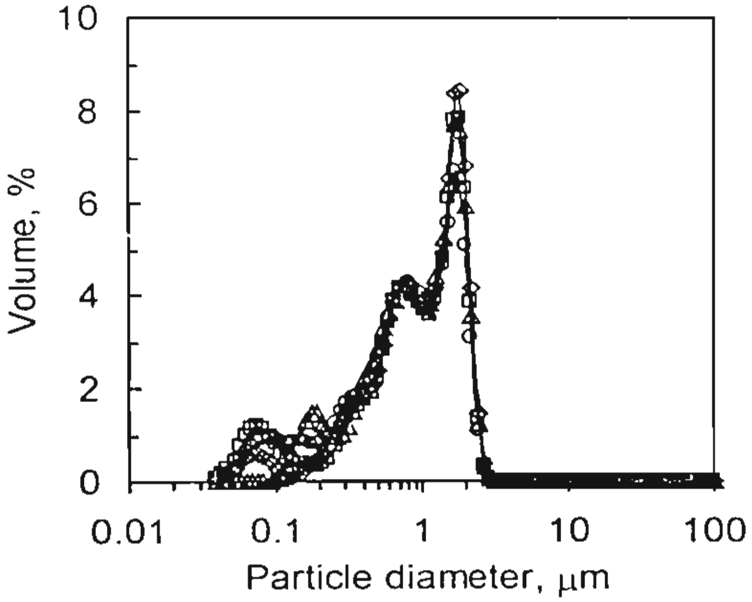

Figure 14. Barium chromate particle size distribution in the presence of 0.2 M QUAT at 50°C at various [barium] to [chromate] ratios. (◇) 0.5, (□) 2.0, (△) 5.0, (○) 10.0.

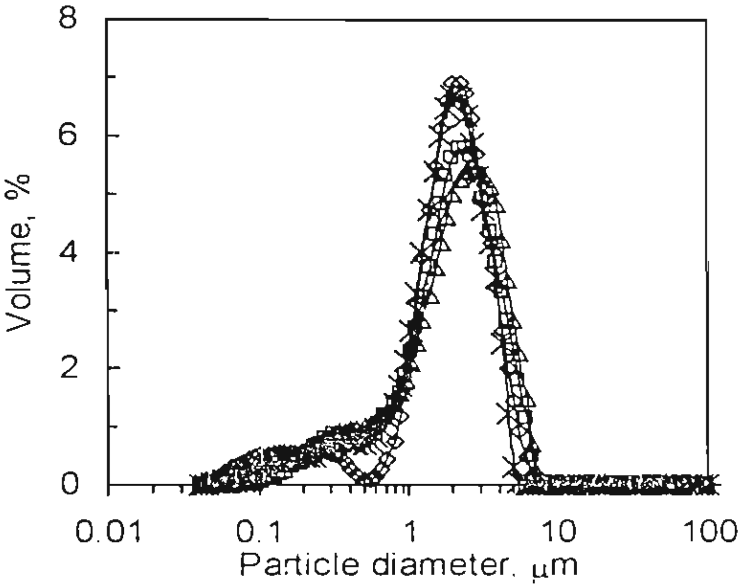

Figure 15. Barium chromate particle size distribution in the absence of QUAT at 50°C at various NaCl concentrations. (✱) 0 M, (◇) 0.01 M, (□) 0.05 M, (△) 0.10 M NaCl.

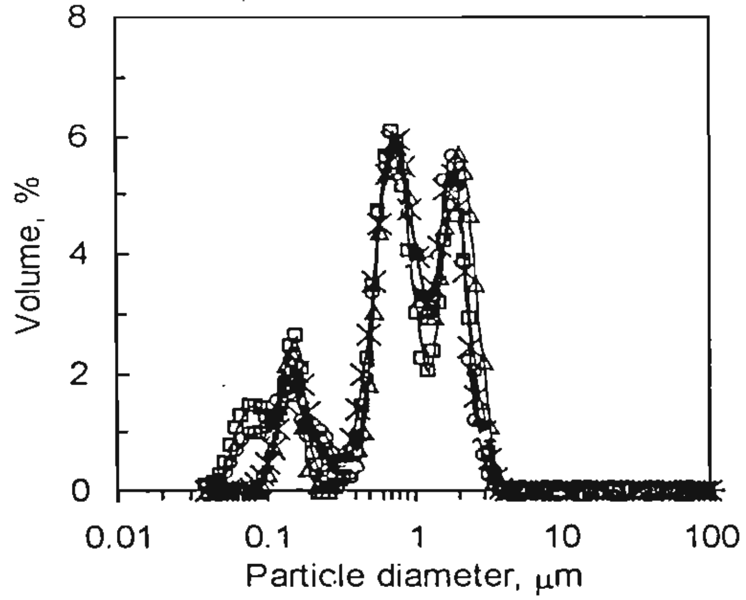

Figure 16. Barium chromate particle size distribution in the presence of 0.2 M QUAT at 50°C at various NaCl concentrations. (✱) 0 M, (□) 0.01 M, (△) 0.05 M, (○) 0.10 M NaCl.

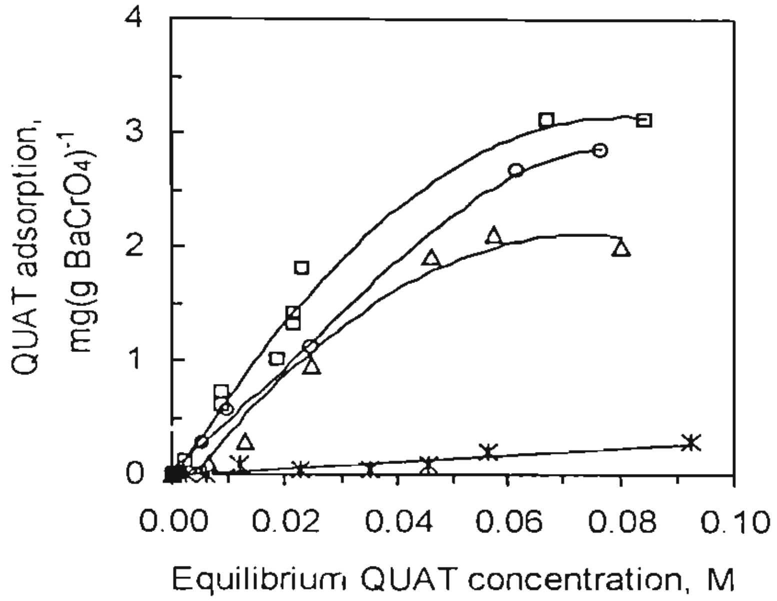

Figure 17. Adsorption isotherm of QUAT on barium chromate in water and in 0.1 M NaCl at various [barium] to [chromate] ratios. (□) 0.5 in water, (△) 1.0 in water, (✳) 1.5 in water, (○) 1.0 in 0.1 M NaCl.

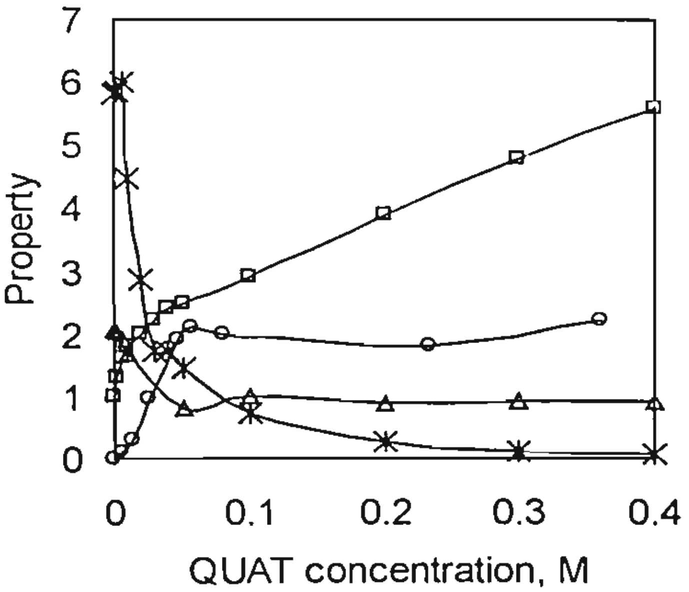

Figure 18. Effect of QUAT concentration on barium chromate sedimentation, barium chromate particle size, polymer adsorption, and relative viscosity of polymer solution. (✳) sedimentation rate (cm/min), (△) average particle diameter (μm), (○) QUAT adsorption ($mg(gBaCrO_4)^{-1}$), (□) relative viscosity.

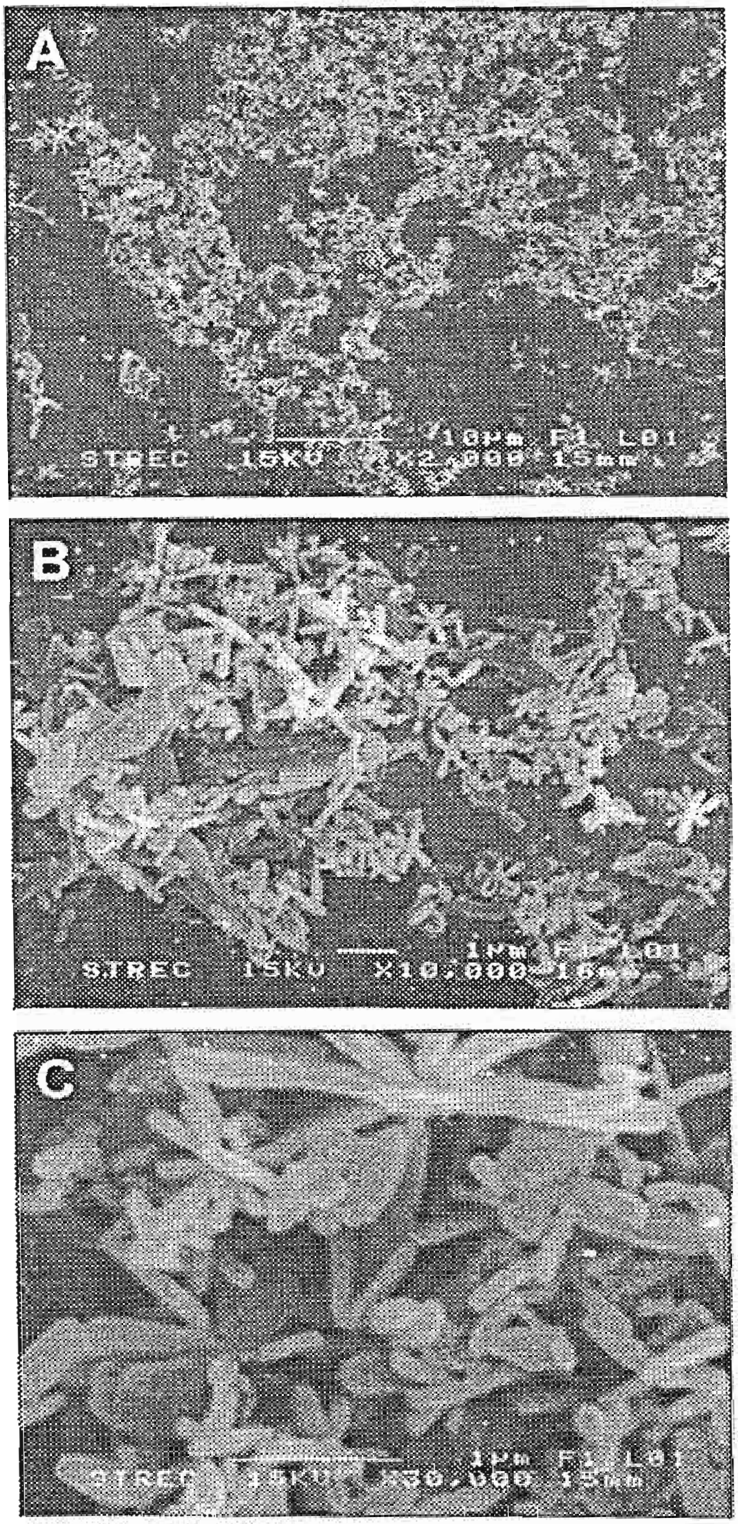

Figure 19. SEM views of barium chromate crystals in the absence of QUAT. Magnification (A) 2000X, (B) 10000X, (C) 30000X.

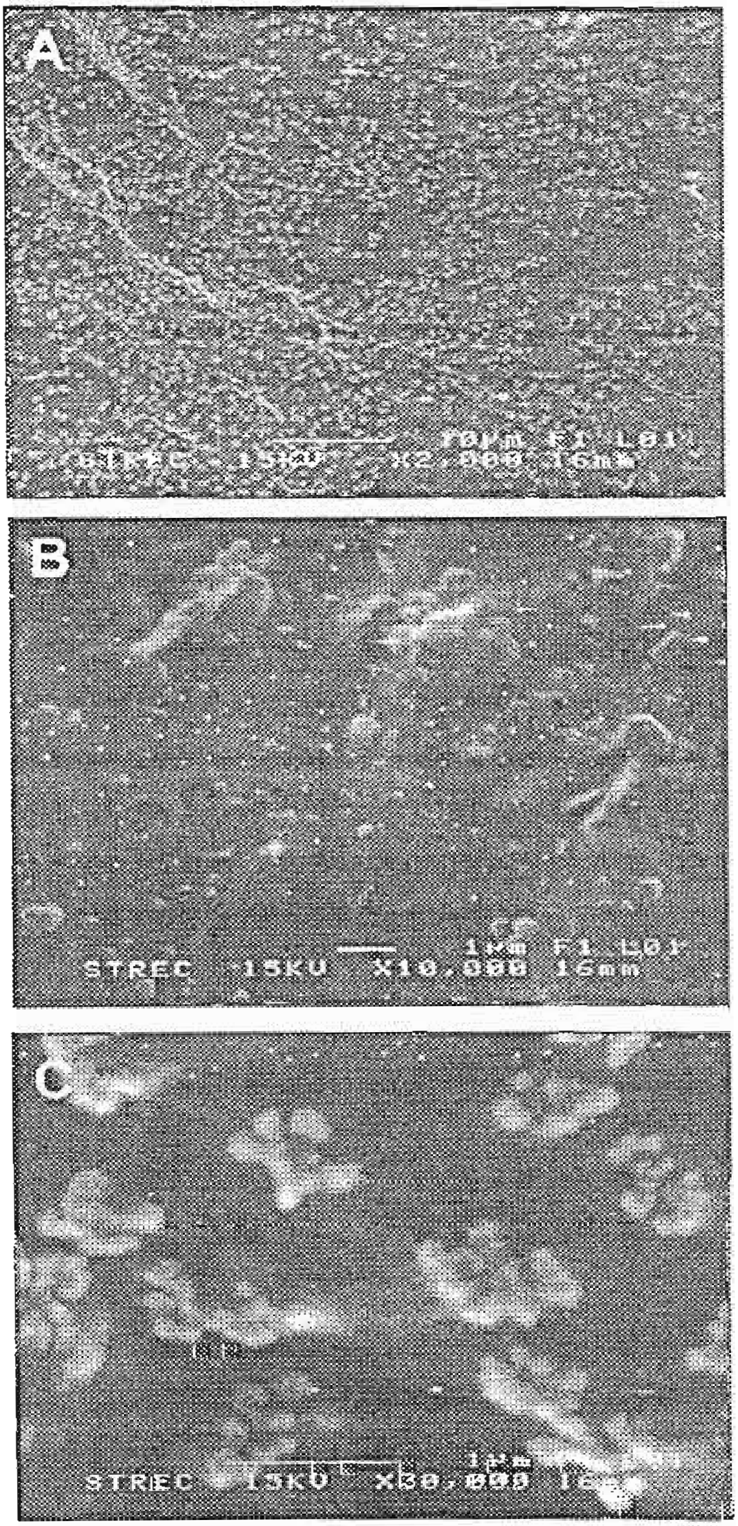

Figure 20. SEM views of barium chromate crystals in the presence of 0.2 M QUAT. Magnification (A) 2000X, (B) 10000X, (C) 30000X.

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.

REFERENCES

Bhat, S.N., Smith, G.A., Tucker, E.E., Christian, S.D., and Scamehorn, J.F. (1987) Solubilization of Cresols by 1-Hexadecylpyridinum Chloride Micelles and Removal of Cresols from Aqueous Stream by Micellar-Enhanced Ultrafiltration. Ind. Eng. Chem. Res., 26 (6), 1217-1222.

Choi, Y., Lee, S.B., Lee, D.J., Ishigami, Y., and Kajiuchi, T. (1998) Micellar Enhanced Ultrafiltration using PEO-PPO-PEO Block Copolymers. J. Membr. Sci., 148 (2), 185-194.

Christian, S.D., Bhat, S.N., Tucker, E.E., Scamehorn, J.F., and El-Sayed, D.A. (1988) Micellar-Enhanced Ultrafiltration of Chromate Anion from Aqueous Streams. AIChE J., 34 (2), 189-194 .

Christian, S.D., Tucker, E.E., Scamehorn, J.F., Lee, B.H., and Sasaki, K.J. (1989) Ion-Expulsion Ultrafiltration-A New Method for Purifying Aqueous Streams Langmuir, 5 (3), 876-879.

Christian, S.D., Tucker, E.E., and Scamehorn, J.F. (1990) Colloid-Enhanced Ultrafiltration Processes for Purifying Aqueous Streams and Reservoirs. Am. Environ. Lab., 2 (1), 13-20.

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

Dunn, R.O., Scamehorn, J.F., and Christian, S.D. (1985) Use of Micellar-Enhanced Ultrafiltration to Remove Dissolved Organics from Aqueous Streams. Sep. Sci. Technol., 20 (4), 257-284.

Dunn, R.O., Scamehorn, J.F., and Christian, S.D. (1987) Concentration Polarization Effects in the Use of Micellar-Enhanced Ultrafiltration to Remove Dissolved Organics Pollutants from Wastewater. Sep. Sci. Technol., 22 (2&3), 763-789.57-284.

Fillipi, B.R., Scamehorn, J.F., Taylor, R.W., and Christian, S.D. (1997)Selective Removal of Copper using Ligand-Modified Micellar-Enhanced Ultrafiltration using an Alkyl-β-diketone Ligand. Sep. Sci. Technol., 32 (15), 2401-2424.

Fillipi, B.R., Scamehorn, J.F., Christian, S.D., and Taylor, R.W. (1998) A Comparative Economic Analysis of Copper Removal from Water by Ligand-Modified

Micellar-Enhanced Ultrafiltration and by Conventional Solvent Extraction, J. membr. Sci., 145 (1), 27-44.

Geckeler, K.E. and Volchek, K. (1996) Removal of Hazardous Substances from Water using Ultrafiltration in conjunction with Soluble Polymers. Envir. Sci. Technol., 30 (3), 725-733.

Guo, W., Uchiyama, H., Tucker, E.E., Christian, S.D., and Scamehorn, J.F. (1997) Use of Polyelectrolyte-Surfactant Complexes in Colloid-Enhanced Ultrafiltration. Colloids Surf., A, 123-124, 695-703.

Gzara, L. and Dhahbi, M. (2001) Removal of Chromate Anions by Micellar-Enhanced Ultrafiltration using Cationic Surfactants. Desalination, 137 (1-3), 241-250.

Juang, R.-S. and Chen, M.-N. (1996) Retention of Copper(II)-EDTA Chelates from Dilute Aqueous Solutions by a Polyelectrolyte-Enhanced Ultrafiltration Process. J. Membr. Sci., 119 (1), 25-37.

Klepac, J., Simmons, D.L., Taylor, R.W., Scamehorn, J.F., and Christian, S.D. (1991) Use of Ligand-Modified Micellar-Enhanced Ultrafiltration in the Selective Removal of Metal Ions from Water. Sep. Sci. Technol., 26 (2), 165-173.

Kongsricharoern, N. and Polprasert, C. (1995) Electrochemical Precipitation of Chromium (Cr^{6+}) from an Electroplating Wastewater. Wat. Sci. Tech. 31 (9), 109-117.

Kongsricharoern, N. and Polprasert, C. (1996) Chromium Removal by a Bipolar Electrochemical Precipitation Process. Wat. Sci. Tech. 34 (9), 109-116.

Krehbiel, D.K., Scamehorn, J.F, Ritter, R., Christian, S.D., and Tucker, E.E. (1992) Ion-Expulsion Ultrafiltration to Remove Chromate from Wastewater. Sep. Sci. Technol., 27 (13), 1775-1787.

Lalvani, S.B., Wiltowski, T., Hübner, A., Weston, A., and Mandich, N. (1998) Removal of Hexavalent Chromium and Metal Cations by a Selective and Novel Carbon Adsorbent. Carbon, 36 (7-8), 1219-1226.

Legault, A.S., Volchek, K., Tremblay, A.Y., and Whittaker, H. (1993) Removal of Arsenic from Groundwater using Reagent Binding/Membrane Separation. Environ. Prog., 12 (2), 157-159.

Mundkur, S.D. and Watters, J.C. (1993) Polyelectrolyte-Enhanced Ultrafiltration of Copper from a Waste Stream. Sep. Sci. Technol., 28 (5), 1157-1168.

Müslehddinoglu, J., Uludag, Y., Özbelge, H.Ö., and Yilmaz, L. (1998) Effect of Operating Parameter on Selective Separation of Heavy Metals from Binary Mixtures via Polymer Enhanced Ultrafiltration. J. Membr. Sci. 140 (2), 251-266.

Nguyen, Q.T., Aptel, P., and Neel, J. (1980) Application of Ultrafiltration to the Concentration and Separation of Solutes of Low Molecular Weight. J. Membr. Sci., 6 (1), 71-82.

Novikov, P.A., Shiknev, V.M., Spivakov, B.Ya., Myasoedov, B.F., Geckeler, K.E., and Bayer, E. (1989) Separation and Concentration of Actinides by a Water Soluble Oxine Polymer Using Membrane Filtration. Radiochim. Acta, 46, 35-45.

Page, B.J., Loar, G.W. (1993) In Encyclopedia of Chemical Technology, John Wiley & Sons: New York, 6, 263.

Sasaki, K.J., Burnett, S.L., Christian, S.D., Tucker, E.E., and Scamehorn, J.F. (1989) Polyelectrolyte Ultrafiltration of Mutivalent Ions. Removal of Cu2+ by Sodium poly(styrenesulfonate). Langmuir, 5 (2), 363-369.

Scamehorn, J.F., Ellington, R.T., Christian, S.D., Penney, B.W., Dunn, R.O., and Bhat, S.N. (1986) Removal of Multivalent Metal Cations from Water using Micellar-Enhanced Ultrafiltration. AIChE Sym. Ser., 82 (250), 48-58.

Scamehorn, J.F., Christian, S.D., El-Sayed, D.A., Uchiyama, H., and Younis, S.S. (1994) Removal of Divalent Metal Cations and Their Mixtures from Aqueous Streams Using Micellar-Enhanced Ultrafiltration. Sep. Sci. Technol., 29 (7), 809-830.

Shkinev, V.M., Vorob'eva, G.A., Spivakov, B.Ya., Geckeler, K., and Bayer, E. (1987) Enrichment of Arsenic and Its Separation from Other Elements by Liquid-Phase Polymer-Based Retention. Sep. Sci. Technol., 22 (11), 2165-2173.

Smith, G.A., Christian, S.D., Tucker, E.E., and Scamehorn, J.F. (1987) Equilibrium Solubilization of Benzene in Micellar Systems and Micellar-Enhanced Ultrafiltration of Aqueous Solutions of Benzene. Ordered Media in Chemical Separations, ACS Symp. Ser., 342, 184-195.

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

Tabatabai, A., Scamehorn, J.F., and Christian, S.D. (1995) Water Softening using Polyelectrolyte-Enhanced Ultrafiltration. Sep. Sci. Technol., 30 (2), 211-224.

Tabatabai, A., Scamehorn, J.F., and Christian, S.D. (1995) Economic Feasibility Study of Polyelectrolyte-Enhanced Ultrafiltration (PEUF) for Water Softening. J. Membr. Sci., 100 (3), 193-207.

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

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

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

Tuncay, M., Christian, S.D., Tucker, E.E., Taylor, R.W., and Scamehorn, J.F. (1994) Ligand-Modified Polyelectrolyte-Enhanced Ultrafiltration with Electrostatic Attachment if Ligands.1. Removal of Cu(II) and Pb(II) with Expulsion of Ca(II). Langmuir, 10 (12), 4688-4692.

Tuncay, M., Christian, S.D., Tucker, E.E., Taylor, R.W., and Scamehorn, J.F. (1994) Ligand-Modified Polyelectrolyte-Enhanced Ultrafiltration with Electrostatic Attachment if Ligands.2. Use of Diethylenetriaminepentaacetic Acid/ Cationic Polyelectrolyte Mixtures to Remove Both Cations and Anions from Aqueous Streams. Langmuir, 10 (12), 4693-4697.

Uludag, Y., Özbelge, H.Ö., and Yilmaz, L. (1997) Removal of Mercury from Aqueous Solutions via Polymer-Enhanced Ultrafiltration. J. Membr. Sci., 129 (1), 93-99.

Volchek, K., Krentsel, E., Zhilin, Y., Shtereva, G., and Dytnersky, Y. (1993) Polymer Binding/Ultrafiltration as a Method for Concentration and Separation of Metals. J. Membr. Sci., 79 (2&3), 253-272.

Westbrook, J.H. (1993) In Encyclopedia of Chemical Technology, John Wiley & Sons: New York, 6, 228.

Zhao, D., SenGupta, A.K., and Stewart, L. (1998) A New Ion-Exchange Process for Chromate Removal, Proceedings of the 30th Mid-Atlantic Industrial Waste Conference, Silver Spring, July.

Zhou, R., Palmer, V., and Geckeler, K.E. (1994) Removal of Inorganic Ions by Polymer-Based Colloid-Enhanced Membrane Filtration in Aqueous Solution. Wat. Res., 28 (5), 1257-1260.

APPENDIX

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

POLYELECTROLYTE-ENHANCED ULTRAFILTRATION OF CHROMATE, SULFATE, AND NITRATE

Surachet Tangvijitsri,[1] Chintana Saiwan,[1] 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.

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.

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

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

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

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.

ACKNOWLEDGEMENTS

Financial support for this work was provided by the Thailand Research Fund under the Golden Jubilee Ph.D. Program. In addition, support was received from the industrial sponsors of the Institute for Applied Surfactant Research including Akzo Nobel Chemicals Inc, Albemarle Corporation, Amway Corporation, Clorox Company, Colgate-Palmolive, Dial Corporation, Dow Chemical Company, DowElanco, E. I.

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.

REFERENCES

1. Sasaki, K.J.; Burnett, S.L.; Christian, S.D.; Tucker, E.E.; Scamehorn, J.F. Polyelectrolyte Ultrafiltration of Multivalent Ions. Removal of Cu^{2+} by Sodium Poly(styrenesulfonate). Langmuir **1989**, *5* (2), 363-369.
2. Sriratana, S.; Scamehorn, J.F.; Chavadej, S.; Saiwan, C.; Haller, K.J.; Christian, S.D.; Tucker, E.E. Use of Polyelectrolyte-Enhanced Ultrafiltration to Remove Chromate from Water. Sep. Sci. Technol. **1996**, *31* (18), 2493-2504.
3. Scamehorn, J.F.; Christian, S.D.; Tucker, E.E.; Tan, B.I. Concentration Polarization in Polyelectrolyte-Enhanced Ultrafiltration. Colloids Surf. **1990**, *49* (3&4), 259-267.
4. Tabatabai, A.; Scamehorn, J.F.; Christian, S.D. Water Softening Using Polyelectrolyte-Enhanced Ultrafiltration. Sep. Sci. Technol. **1995**, *30* (2), 211-224.
5. Tabatabai, A.; Scamehorn, J.F.; Christian, S.D. Economic Feasibility Study of Polyelectrolyte-Enhanced Ultrafiltration (PEUF) for Water Softening. J. Membr. Sci. **1995**, *100* (3), 193-207.
6. Mundkur, S.D.; Watters, J.C. Polyelectrolyte-Enhanced Ultrafiltration of Copper from a Waste stream. Sep. Sci. Technol. **1993**, *28* (5), 1157-1168.
7. Volchek, K.; Krentsel, E.; Zhilin, Y.; Shtereva, G.; Dytnersky, Y. Polymer Binding/Ultrafiltration as a Method for Concentration and Separation of Metals. J. Membr. Sci. **1993**, *79* (2&3), 253-272.
8. Zhou, R.; Palmer, V.; Geckeler, K.E. Removal of Inorganic Ions by Polymer-Based Colloid-Enhanced Membrane Filtration in Aqueous Solution. Wat. Res. **1994**, *28* (5), 1257-1260.
9. Geckeler, K.E.; Volchek, K. Removal of Hazardous Substances from Water Using Ultrafiltration in Conjunction with Soluble Polymers. Envir. Sci. Technol. **1996**, *30* (3), 725-733.
10. Dunaway, C.S.; Christian, S.D.; Tucker, E.E.; Scamehorn, J.F. Study of the Binding of Anions by a Cationic Polyelectrolyte Using Equilibrium Dialysis. 1.Chromate Anions. Langmuir **1998**, *14* (5), 1002-1012.
11. Christian, S.D.; Tucker, E.E.; Scamehorn, J.F. Colloid-Enhanced Ultrafiltration in Remediating Wastewater and Groundwater. Spec. Chem. **1995**, *15* (3), 148-151.

12. Tucker, E.E.; Christian, S.D.; Scamehorn, J.F.; Uchiyama, H.; Guo, W. Removal of Chromate from Aqueous Streams by Ultrafiltration and Precipitation. ACS Symp. Ser. **1992**, *491*, 84-98.
13. Tucker, E.E.; Christian, S.D.; Uchiyama, H.; Guo, W.; Scamehorn, J.F.; Puls, R.W. In *Toxic Anion Removal from Aqueous Streams*, Proceedings of the 3rd Annual Conference on Groundwater Quality Research, Dallas, June, 1992.
14. Smith, B.F.; Robison, T.W.; Jarvinen, G.D. Water-Soluble Metal-Binding Polymers with Ultrafiltration. ACS Symp. Ser. **1999**, *716*, 294-330.
15. Novikov, P.A.; Shiknev, V.M.; Spivakov, B.Ya.; Myasoedov, B.F.; Geckeler, K.E.; Bayer, E. Separation and Concentration of Actinides by a Water Soluble Oxine Polymer Using Membrane Filtration. Radiochim. Acta **1989**, *46*, 35-45.
16. Shkinev, V.M.; Vorob'eva, G.A.; Spivakov, B.Ya., Geckeler, K.; Bayer, E. Enrichment of Arsenic and Its Separation from Other Elements by Liquid-Phase Polymer-Based Retention. Sep Sci. Technol. **1987**, *22* (11), 2165-2173.
17. Nguyen, Q.T.; Aptel, P.; Neel, J. Application of Ultrafiltration to the Concentration and Separation of Solutes of Low Molecular Weight. J. Membr. Sci. **1980**, *6* (1), 71-82.
18. Tuncay, M.; Christian, S.D.; Tucker, E.E.; Taylor, R.W.; Scamehorn, J.F. Ligand-Modified Polyelectrolyte-Enhanced Ultrafiltration with Electrostatic Attachment of Ligands. 1. Removal of Cu(II) and Pb(II) with Expulsion of Ca (II). Langmuir **1994**, *10* (12), 4688-4692
19. Tuncay, M.; Christian, S.D.; Tucker, E.E.; Taylor, R.W.; Scamehorn, J.F. Ligand-Modified Polyelectrolyte-Enhanced Ultrafiltration with Electrostatic Attachment of Ligands. 2. Use of Diethylenetriaminepentaacetic Acid/Cationic Polyelectrolyte Mixtures to Remove Both Cations and Anions from Aqueous Streams. Langmuir **1994**, *10* (12), 4693-4697.
20. Bohdziewicz, J.; Bodzek, M.; Wasik, E. The Application of Reverse Osmosis and Nanofiltration to the Removal of Nitrates from Groundwater. Desalination **1999**, *121* (2), 139-147.
21. Huang, C.P.; Wang, H.W.; Chiu, P.C. Nitrate Reduction by Metallic Iron. Wat. Res. **1998**, *32* (8), 2257-2264.
22. Benefield, J.F.; Judkins, J.F; Weand, B.L. Oxidation-Reduction Equilibrium. In *Process Chemistry for Water and Wastewater Treatment*; Prentice-Hall: London, 1982; 141-163.
23. Scamehorn, J.F.; Christian, S.D.; El-Sayed, D.A.; Uchiyama, H.; Younis, S.S. Removal of Divalent Metal Cations and Their Mixtures from Aqueous Streams Using Micellar-Enhanced Ultrafiltration. Sep. Sci. Technol. **1994**, *29* (7), 809-830.
24. Dunn, R.O.; Scamehorn, J.F.; Christian, S.D. Concentration Polarization Effects in the Use of Micellar-Enhanced Ultrafiltration to Remove Dissolved Organic Pollutants from Wastewater. Sep. Sci. Technol. **1987**, *22* (2&3), 763-789.

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)

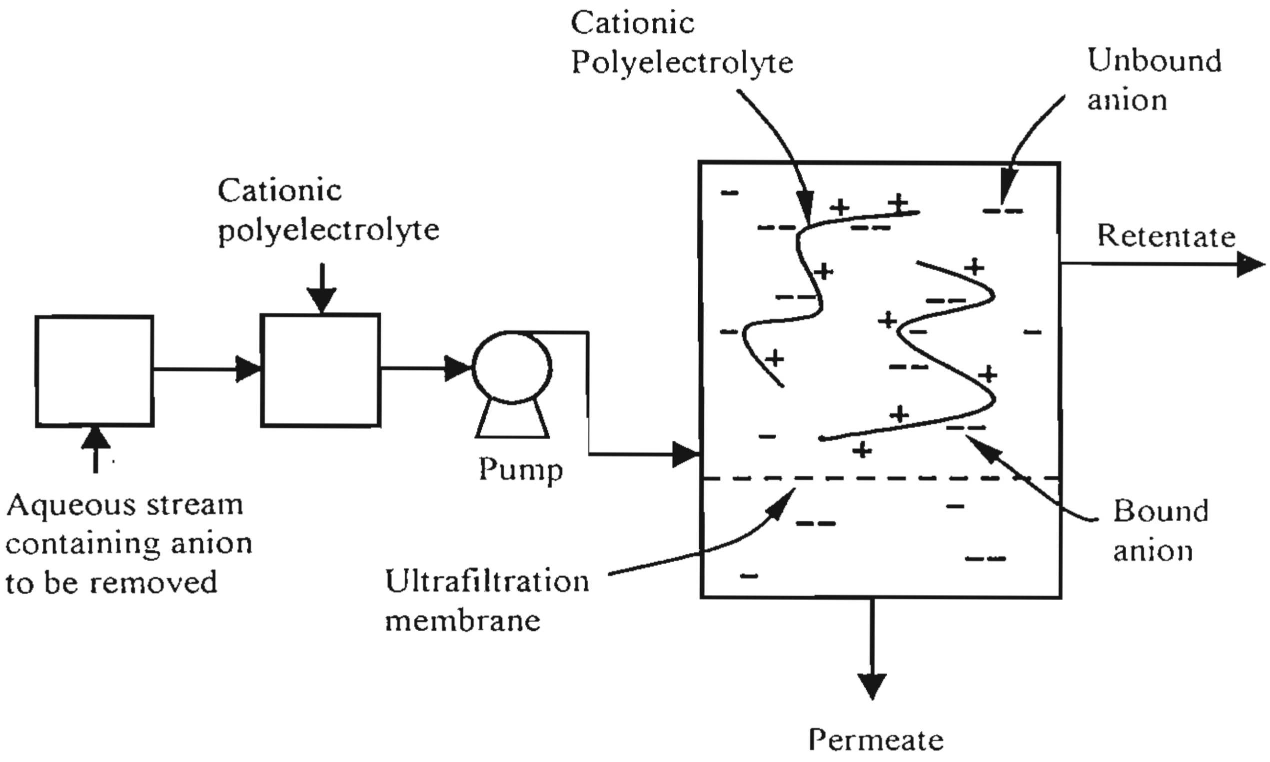

Figure 1. Schematic diagram of PEUF to remove anions from water.

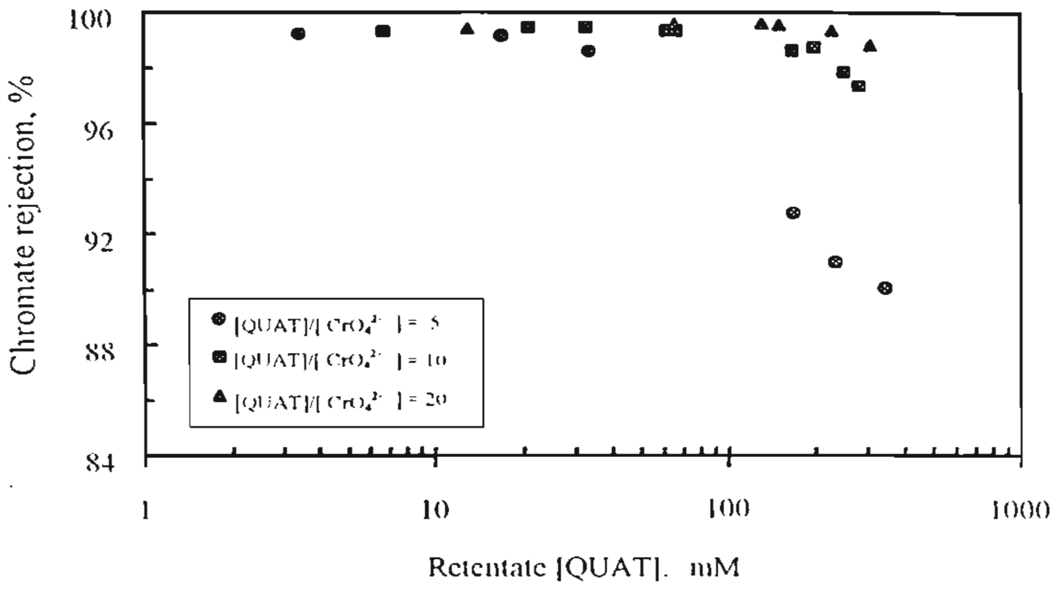

Figure 2. Effect of retentate [QUAT] on chromate rejection.

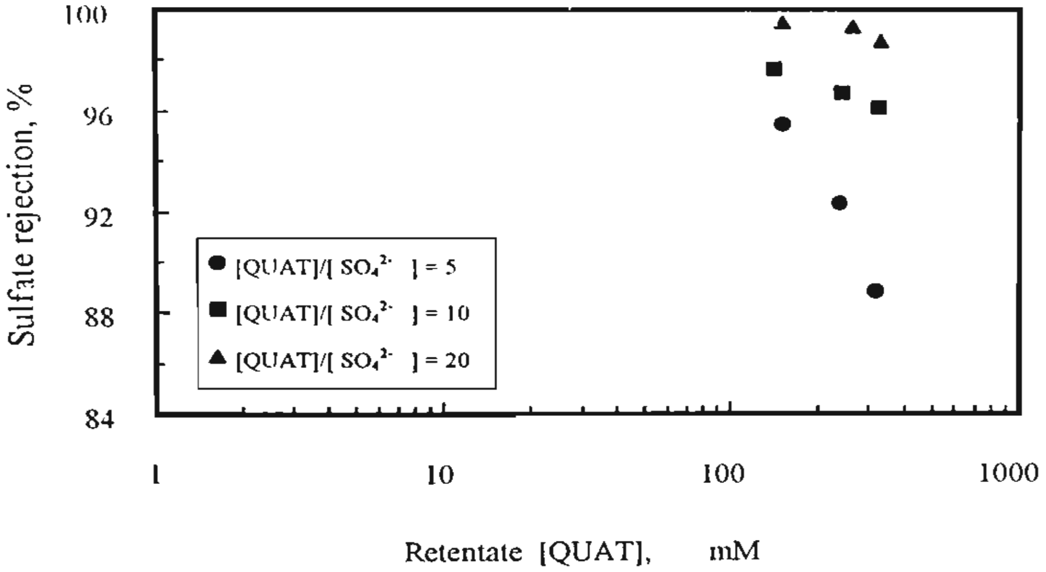

Figure 3. Effect of retentate [QUAT] on sulfate rejection.

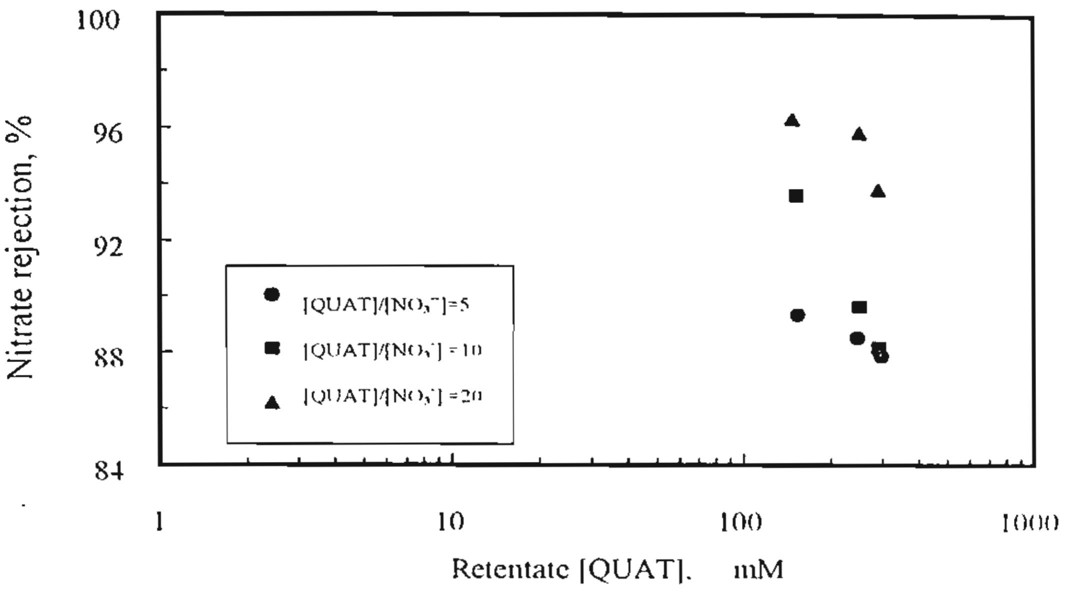

Figure 4. Effect of retentate [QUAT] on nitrate rejection.

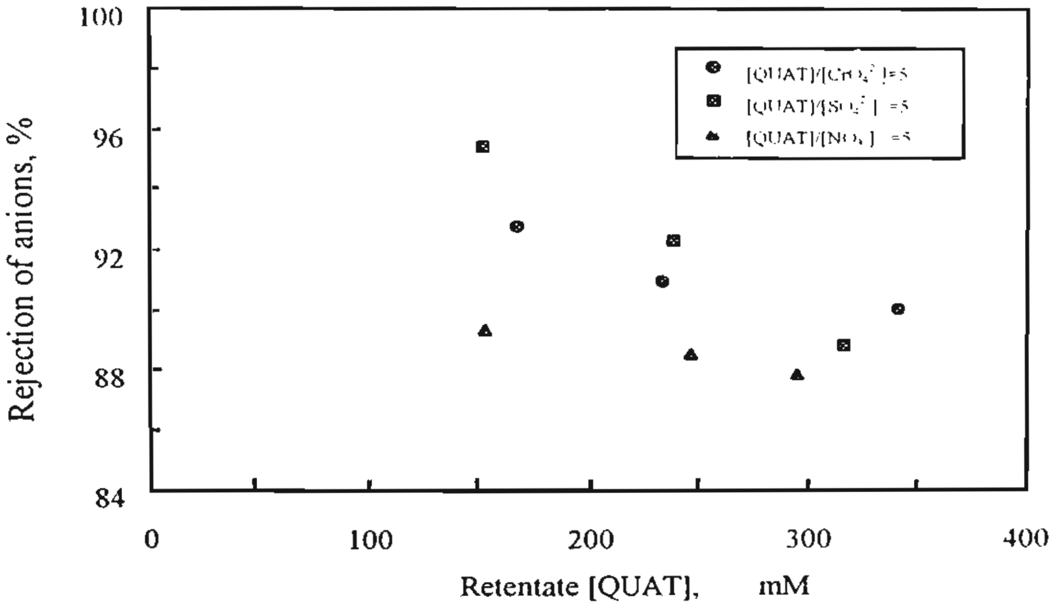

Figure 5. Effect of retentate [QUAT] on chromate, sulfate, and nitrate rejections at a[QUAT]/[anion] of 5.

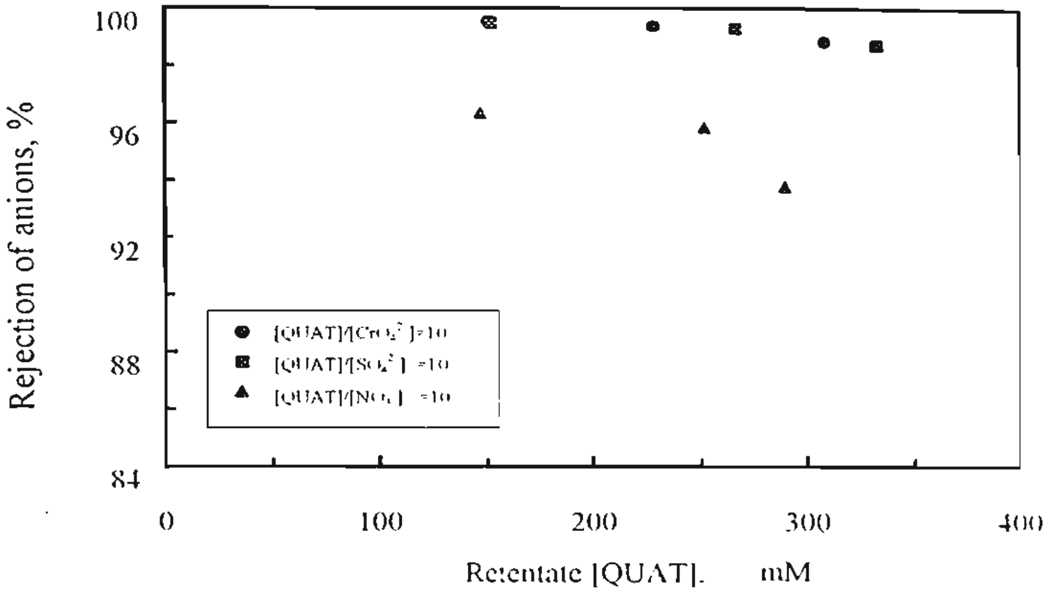

Figure 6. Effect of retentate [QUAT] on chromate, sulfate, and nitrate rejections at a [QUAT]/[anion] of 10.

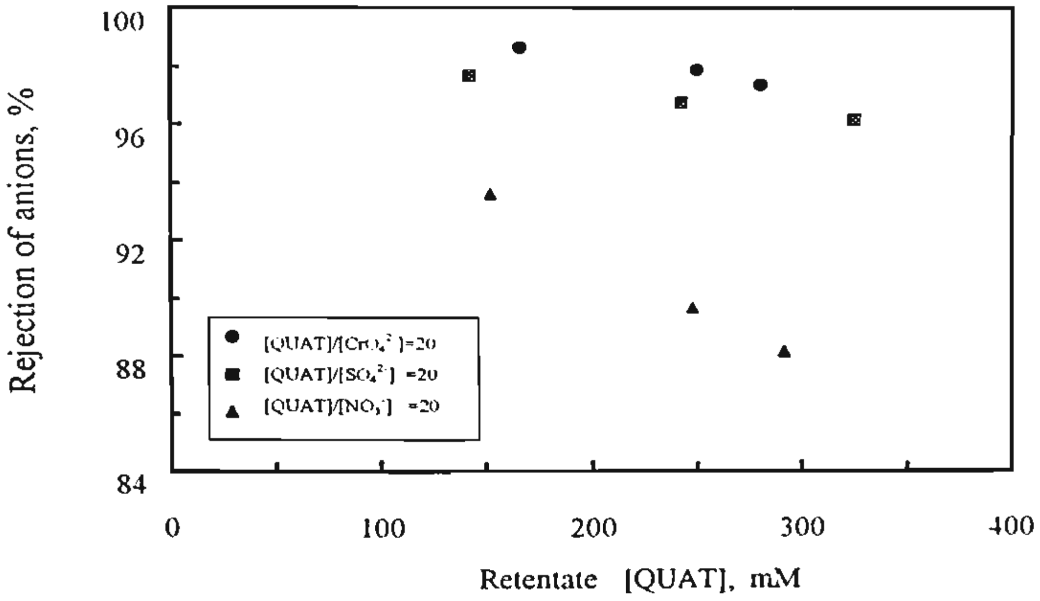

Figure 7. Effect of retentate [QUAT] on chromate, sulfate, and nitrate rejections at a [QUAT]/[anion] of 20.

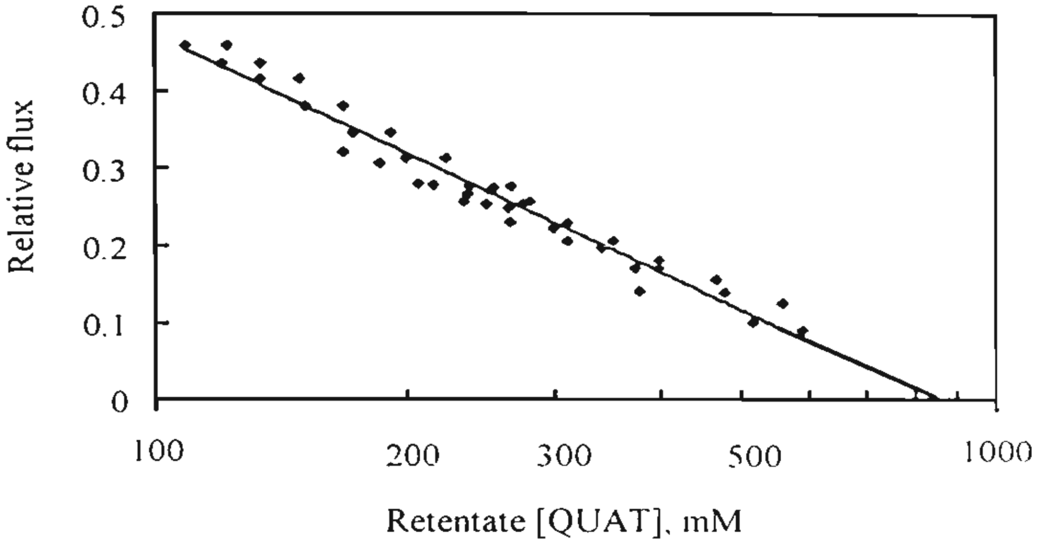

Figure 8. Relative flux of QUAT/chromate system in PEUF at a [QUAT]/[chromate] of 5.

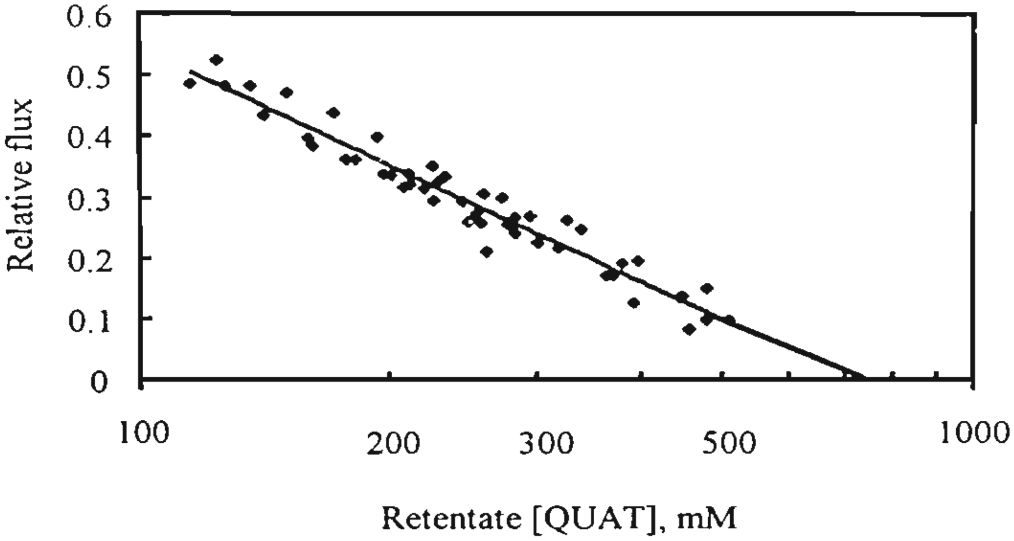

Figure 9. Relative flux of QUAT/chromate system in PEUF at a [QUAT]/[chromate] of 10.

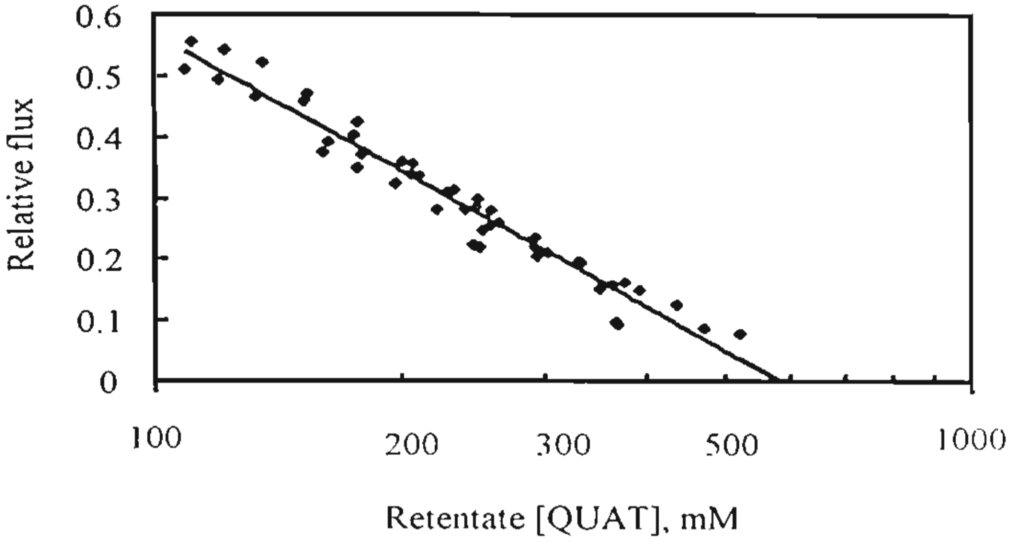

Figure 10. Relative flux of QUAT/chromate system in PEUF at a [QUAT]/[chromate] of 20.

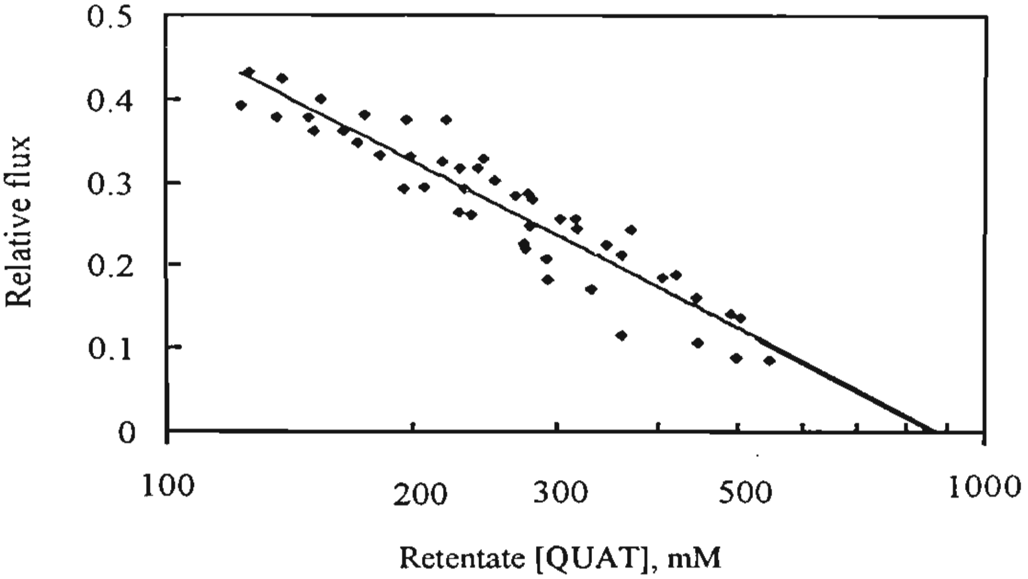

Figure 11. Relative flux of QUAT/sulfate system in PEUF at a [QUAT]/[sulfate] of 5.

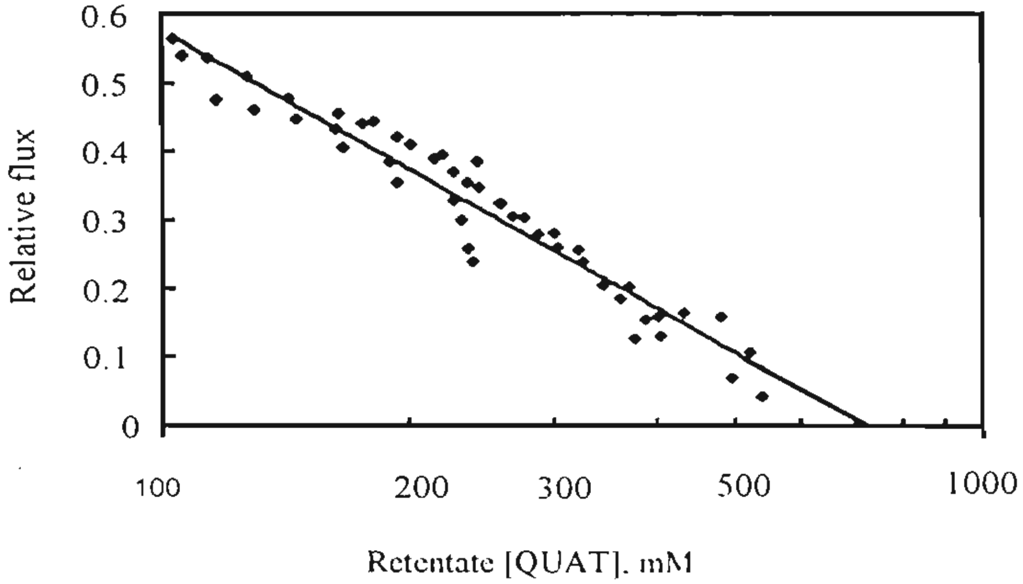

Figure 12. Relative flux of QUAT/sulfate system in PEUF at a [QUAT]/[sulfate] of 10.

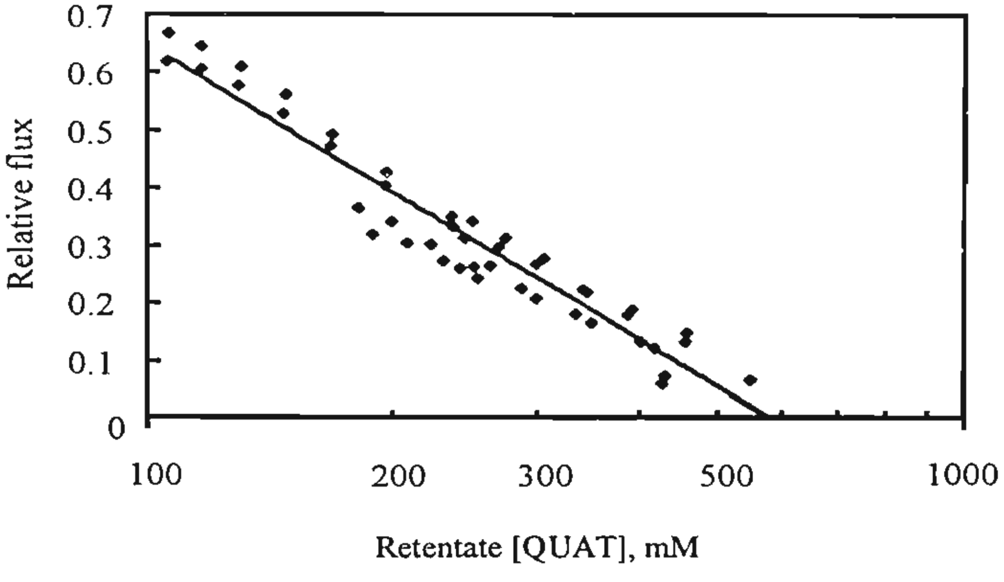

Figure 13. Relative flux of QUAT/sulfate system in PEUF at a [QUAT]/[sulfate] of 20.

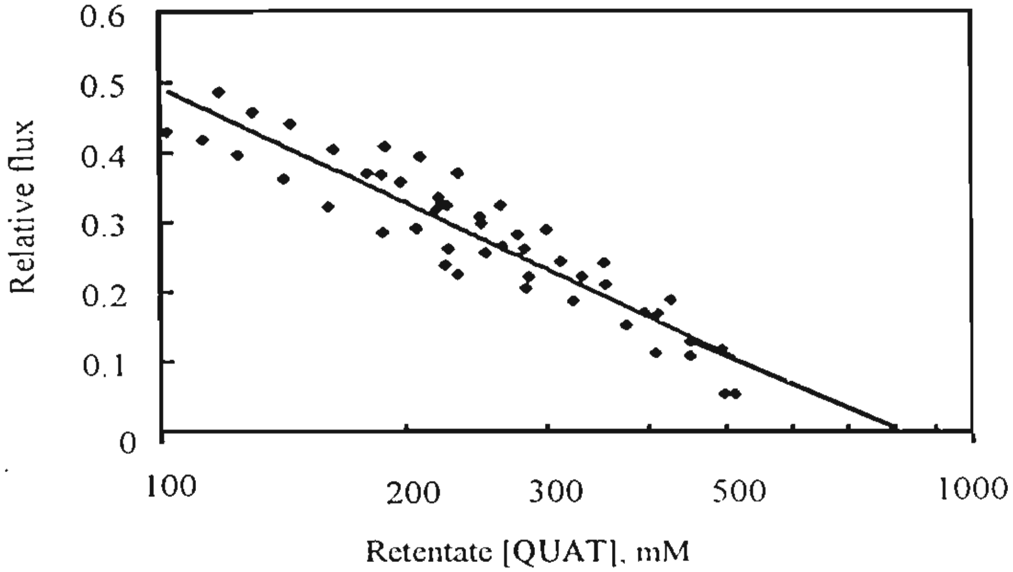

Figure 14. Relative flux of QUAT/nitrate system in PEUF at a [QUAT]/[nitrate] of 5.

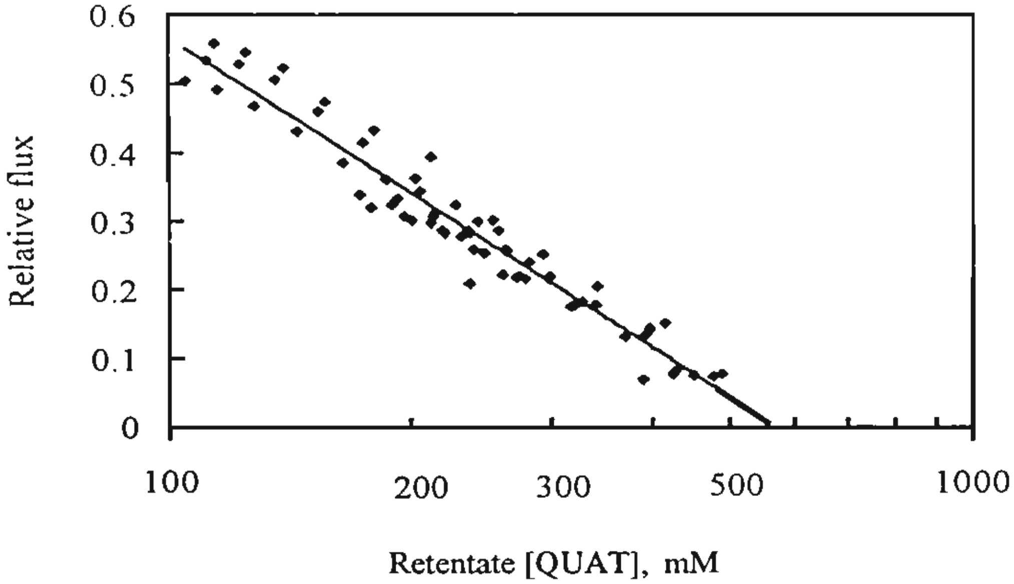

Figure 15. Relative flux of QUAT/nitrate system in PEUF at a [QUAT]/[nitrate] of 10.

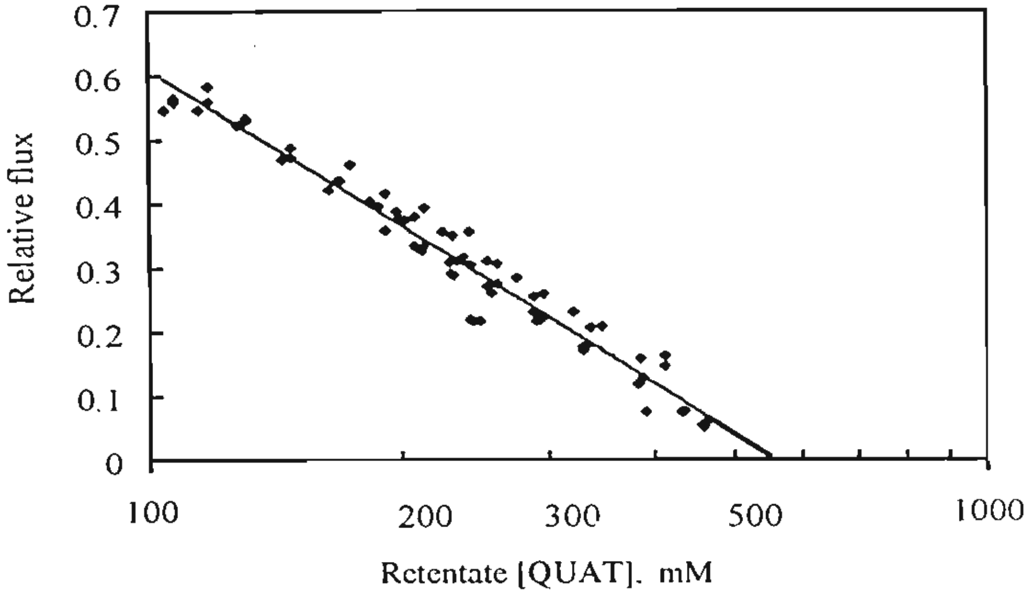

Figure 16. Relative flux of QUAT/nitrate system in PEUF at a [QUAT]/[nitrate] of 20.

CURRICULUM VITAE

Name: Ms. Chalothorn Soponvuttikul

Date of Birth: September 2, 1975

Nationality: Thai

University Education:

1994-1998 B. Eng. in Chemical Engineering, Faculty of Engineering, Srinakharinwirot University, Bangkok, Thailand

Publications:

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

Proceedings:

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. 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)

Presentations:

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.
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.
4. 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.
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.