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Use of Polyelectrolyte-Enhanced Ultrafiltration to Remove Chromate from Water

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ABSTRACT

Polyelectrolyte-enhanced ultrafiltration (PEUF) is a process which can be used to remove multivalent ions from water. In PEUF a polyelectrolyte of opposite charge to the target ion is added to the water to bind the ion to be removed. The solution is then treated using ultrafiltration with membrane pore sizes small enough to reject the polymer and bound ion. In this study, chromate (CrO_4^{2-}) is removed from water using poly(diallyldimethyl ammonium chloride) with an average molecular weight of 240K as the polyelectrolyte. 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. A study of the flux of the

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system yielded a gel concentration of 0.55 M cationic polyelectrolyte. This high gel concentration and high rejection mean that the ultrafiltration can produce a concentrated, low-volume waste stream, and a purified stream containing chromate at low concentration.

INTRODUCTION

Chromium as chromate is one of the most serious environmental problems in Thailand and in other countries. It is used as an alloying and plating element on metal and plastic substrates for corrosion resistance. Chromium is also one of the base components in stainless steel and inorganic pigments. Hexavalent chromium compounds are considered to be carcinogenic and corrosive to tissue. When accumulated in the human body, skin sensitization and kidney damage may occur.

Ion exchange and chemical precipitation are commonly used current technologies to remove toxic heavy metals from water (1). Chemical precipitation is induced by adding lime and precipitating these metals as hydroxides. In the case of chromate (CrO_4^{2-}), a prior step to reduce the hexavalent chromium, presenting as chromate, to the trivalent form (Cr^{3+}) must be done before using this precipitation technique. The reduction step may use either a ferrous sulfate or an acidic sulfite reduction process, followed by lime addition. The whole treatment process requires the use of large quantities of chemicals. Furthermore, this process produces a large volume of sludge of low solid content which must be disposed of. Costs of chemicals and sludge removal can be high.

Ultrafiltration (UF) processes are well known in industrial separation technology to remove and recover solute species with molecular weights of 1000 daltons or more. One attractive feature of ultrafiltration processes is the fact that high fluxes can be obtained at relatively low pressures. Unfortunately, ordinary ultrafiltration methods are not effective in removing solutes having molecular weights less than about 300 daltons (2).

Polyelectrolyte-enhanced ultrafiltration (PEUF) is a process in which a water-soluble polymer or polyelectrolyte is added to the polluted aqueous stream. The polymer has an opposite valence to that of the target ion (ion to be removed). The target ion binds to or adsorbs onto the polyelectrolyte, and the stream is subsequently treated by ultrafiltration with pore sizes small enough to reject the polymer, as shown in Fig. 1.

Past studies of PEUF have demonstrated that high rejections can be attained when removing a divalent cationic heavy metal (e.g., copper) using an anionic polyelectrolyte, or removing a multivalent anion (e.g., chromate) using a cationic polyelectrolyte (3–11). Our previous studies on removal of chromate by PEUF using poly(diallyldimethyl ammonium

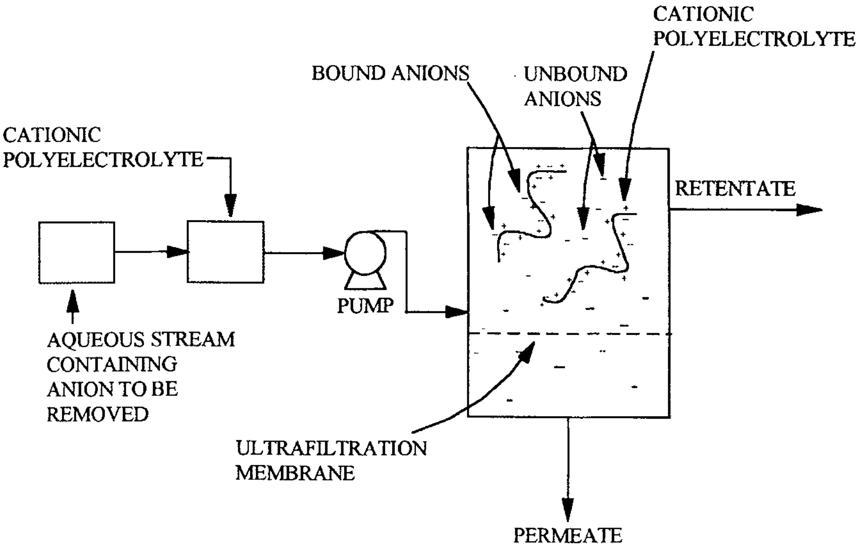

FIG. 1 Schematic diagram of polyelectrolyte-enhanced ultrafiltration to remove multivalent anions from water.

chloride) or QUAT utilized a spiral-wound ultrafiltration device and investigated QUAT concentrations substantially below the gel concentration (5). It has been shown that the chromate can be removed from the stream not passing through the membrane (retentate) by precipitation with barium to produce solid barium chromate, permitting the concentrated polyelectrolyte solution to be reused (5). This process then results in a solid waste as the only emission. This regeneration step was not further investigated here. In this study the gel concentration and chromate rejection at high QUAT concentration is determined using a stirred cell device.

EXPERIMENTAL

Materials

Poly(diallyldimethyl ammonium chloride) (QUAT), having an average molecular weight of approximately 240K, was supplied by Calgon Corp. and has the trade name MERQUAT-100. Elemental analysis showed that the QUAT monomer has the empirical formula

$$(H_2C{=}CHCH_2)_2N(CH_3)_2Cl.$$

This polyelectrolyte was purified 3 times by using a 10K molecular weight cut-off (MWCO) spiral-wound membrane in order to remove the lower molecular weight components to the point where only a trace concentration of polyelectrolyte was detected in the permeate. Analytical reagent-grade sodium chromate (Fisher Co. Ltd.) was used without further purification. Water was deionized twice, passed through a carbon adsorption bed, and filtered before use.

Methods

Ultrafiltration was studied by using a 400-mL stirred cell from Spectrum (as shown in Fig. 2). The solution temperature was controlled at 30°C by submerging the cell into a clear water bath at constant temperature. The solution was stirred with a stirrer bar next to the membrane at a speed of 250 rpm with a pressure drop of 60 psi (414 kPa) across the membrane. A 76-mm diameter Spectrum cellulose acetate membrane with a MWCO of 10K was soaked overnight in deionized water, then in a very low concentration of purified QUAT. In each experiment, 300 mL of deionized water was used to measure the pure water flux rate for each membrane. Subsequently, a 300-mL feed solution containing polyelectrolyte, chromate, and sodium chloride was used, and each run was terminated when 200 mL had passed through the membrane as permeate (the solution pass-

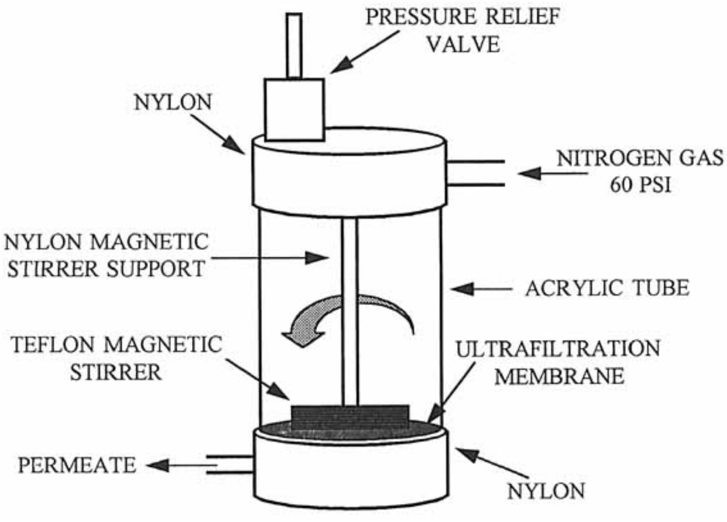

FIG. 2 Illustration of stirred cell (ultrafiltration device).

ing through the membrane). Fluxes were determined by timing and weighing samples of the permeate, and the concentration of chromate or polyelectrolyte in the permeate was measured at frequent intervals throughout a run. For each run the permeate composition, retentate composition, and rejection are reported as the point in the run where 100 mL of permeate has passed through the membrane (midpoint), so only one rejection datum is reported per run, although multiple flux data are reported per run. By knowing the permeate concentrations during the run, one can calculate the retentate (the solution not passing through the membrane) concentration at any point in the run from a material balance. The chromate concentrations were measured as chromium by using a Varian SpectrAA-20 atomic absorption spectrophotometer. The QUAT concentration in the permeate was measured by using a Rosemount Analytical DC-180 total organic carbon analyzer.

RESULTS AND DISCUSSION

Rejection of Chromate

The results of the ultrafiltration experiments are shown in Table 1. The QUAT concentration is based on the concentration of monomer or diallyl-

TABLE 1
Chromate Permeate and Retentate Concentrations from Ultrafiltration Experiments[a]

$[\text{Quat}/\text{CrO}_4^{2-}]_{\text{Feed}}$ ratio	$[\text{NaCl}]_{\text{Feed}}$ (M)	$[\text{CrO}_4^{2-}]_{\text{Per}}$ (M)	$[\text{CrO}_4^{2-}]_{\text{Ret}}$ (M)	Rejection (%)
5	—	4.29E−06	5.73E−04	99.23
5	—	2.67 −05	3.10E−03	99.14
5	—	9.64E−05	5.63E−03	98.29
10	—	4.04E−06	5.92E−04	99.32
10	—	1.44E−05	2.71E−03	99.47
10	—	3.81E−05	6.04E−03	99.37
20	—	3.46E−06	5.73E−04	99.40
20	—	1.12E−05	2.77E−03	99.60
20	—	2.23E−05	5.52E−03	99.60
10	0.05	1.77E−04	4.77E−04	62.88
10	0.05	4.91E−04	2.51E−03	80.42
10	0.05	6.38E−04	5.21E−03	87.77
10	0.01	7.15E−05	2.99E−03	97.61
10	0.10	9.63E−04	2.41E−03	59.99
20	0.01	4.08E−05	2.74E−03	98.51
20	0.05	2.79E−04	2.72E−03	89.76
20	0.10	6.97E−04	2.40E−03	71.01

[a] Subscripts Ret, Per, and Feed refer to retentate, permeate, and feed, respectively.

dimethylammonium chloride molecules. This permits ready comparison of experimental conditions relative to stoichiometric conditions. The removal efficiency of the chromate is represented by rejection, *R* (in %), as defined by

$$\text{Rejection } (R) = 100(1 - ([\mathrm{CrO_4^{2-}}]_{\mathrm{Per}}/[\mathrm{CrO_4^{2-}}]_{\mathrm{Ret}}))$$

where subscripts Per refers to permeate and Ret to retentate.

A general observation from the data is that PEUF can achieve high separation factors, with chromate rejections reaching as high as 99.60% for the conditions used here. These rejections are approximately the same as those from previously obtained data on the system studied here using a spiral wound ultrafiltration device (5) at low retentate QUAT concentrations, and for divalent cationic heavy metal removed using an anionic polyelectrolyte (3, 4, 11).

The rejections obtained at feed [QUAT] to [$\mathrm{CrO_4^{2-}}$] ratios of 5, 10, and 20 in the absence of added salt are shown in Fig. 3 as a function of retentate [QUAT]. Since the pretreated QUAT was completely rejected within detection limits and the chromate rejections are very high except when high concentrations of NaCl are present, except in this latter case, the [QUAT]/[$\mathrm{CrO_4^{2-}}$] ratio in the retentate at the reported midpoint value is very nearly the same as the [QUAT/$\mathrm{CrO_4^{2-}}$] in the feed. As the feed ratio of [QUAT] to [$\mathrm{CrO_4^{2-}}$] increases, the rejection increases because of the increase in the number of positively charged sites on the QUAT per unit volume, increasing the fraction of chromate bound to the polymer. As the retentate [QUAT] or [$\mathrm{CrO_4^{2-}}$] increases at constant feed [QUAT] to [$\mathrm{CrO_4^{2-}}$] ratios, the rejection does not vary substantially, except at the lowest feed [QUAT] to [$\mathrm{CrO_4^{2-}}$] ratio studied, where a mild decrease in rejection was observed at higher retentate [QUAT]. It is important to have established that rejections remain high as the retentate becomes concentrated for practical application of PEUF where a concentrated retentate is necessary to produce a low volume retentate stream for further treatment or disposal.

Figure 4 presents the effect of added feed [NaCl] on the chromate rejection. As the salt concentration is increased, the rejection of chromate also decreases or the concentration of chromate in permeate increases, in qualitative agreement with previous work (5). Increasing the NaCl concentration of the solution leads to competition for positively charged binding sites on the polyelectrolyte between the chloride and the chromate, resulting in a decrease in chromate binding per charged group on the QUAT and a decrease in chromate rejection. Figure 5 shows the effect of retentate [QUAT] on chromate rejection with and without added NaCl at a constant feed [QUAT]/[$\mathrm{CrO_4^{2-}}$] ratio. The low rejection which is observed with added salt can be increased at higher retentate [QUAT] unlike

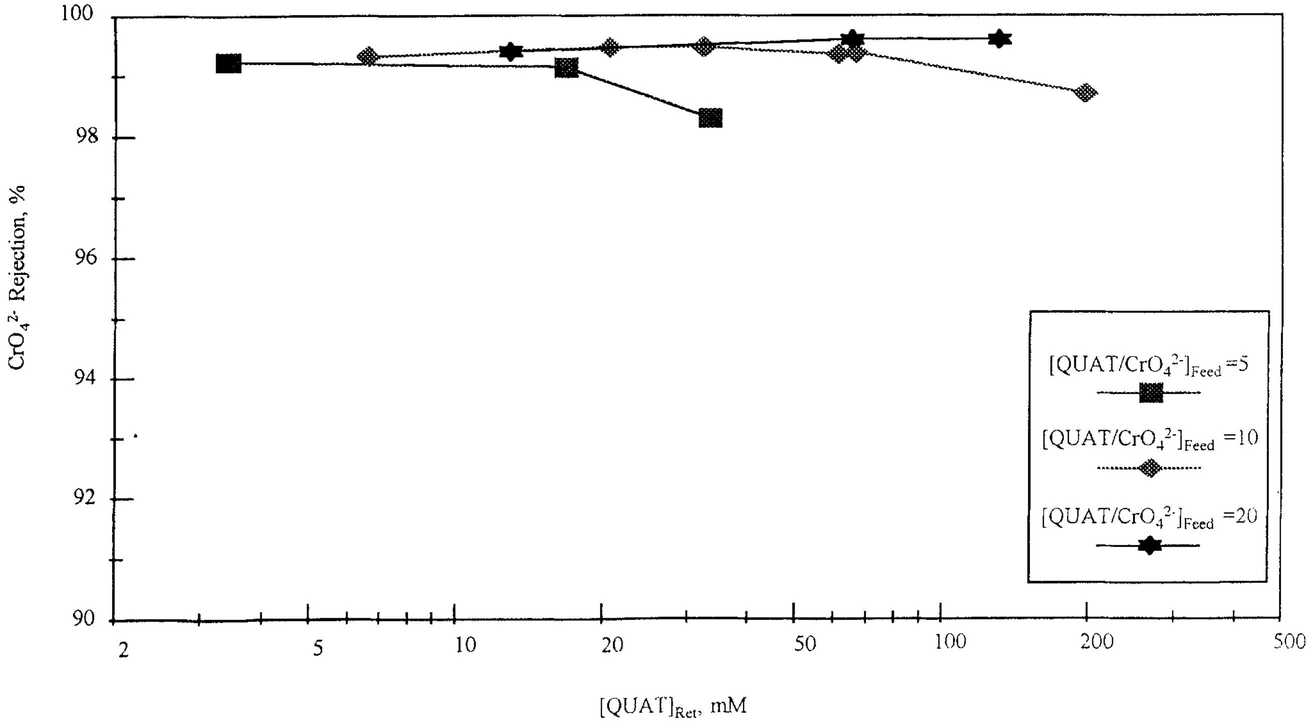

FIG. 3 Effect of $[QUAT]_{Ret}$ on CrO_4^{2-} rejection in the absence of added NaCl.

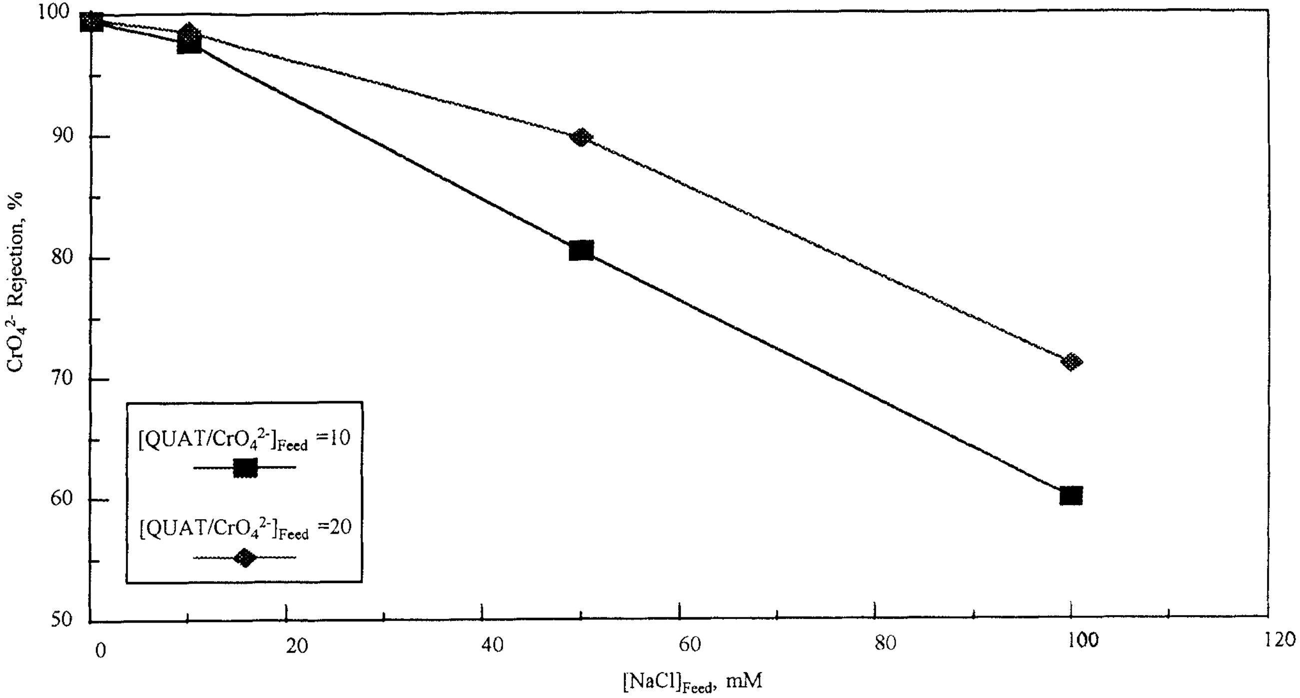

FIG. 4 Effect of $[NaCl]_{Feed}$ on CrO_4^{2-} rejection.

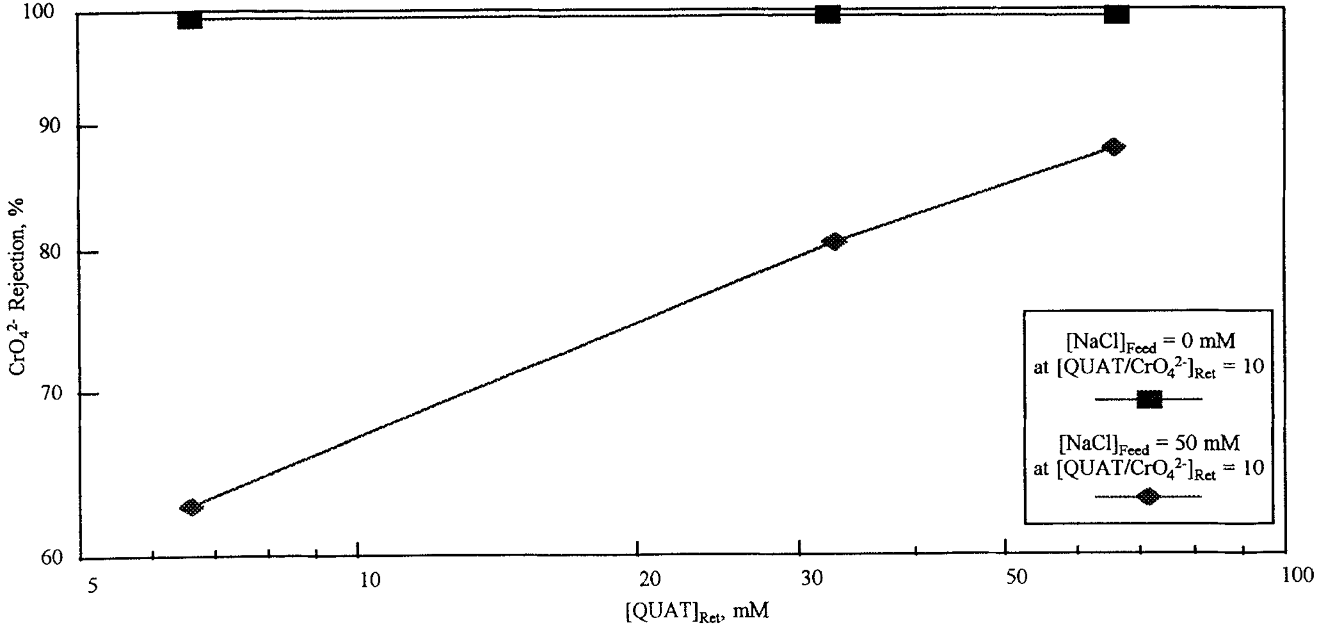

FIG. 5 Effect of $[QUAT]_{Ret}$ on CrO_4^{2-} rejection at two added $[NaCl]_{Feed}$ levels.

the case of no added salt, where this variable has little effect. In other words, the deleterious effect of added salt on rejection can be offset by a higher initial polymer concentration.

Flux

Gel polarization effects can cause flux to be substantially less than that of pure water in PEUF at high polyelectrolyte concentration (4). The relative flux during PEUF for the QUAT/chromate system is shown in Fig. 6 as a function of retentate [QUAT] (relative flux is flux/flux of pure water). Traditional concentration polarization behavior is observed, with

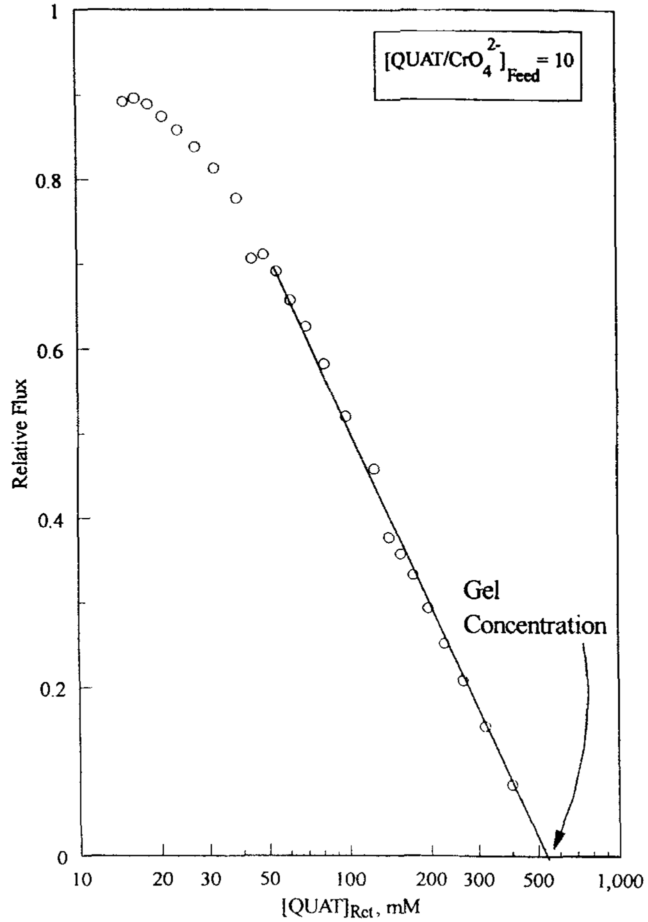

FIG. 6 Relative flux used to obtain gel concentration in the absence of added NaCl.

the flux declining linearly with the logarithm of retentate [QUAT] above a certain retentate [QUAT]. An extrapolation of these data yields a gel concentration (where flux equals 0) of approximately 0.55 M. Other colloidal systems for which gel concentrations have been determined are polystyrene sulfonate (anionic polyelectrolyte), 1.0 M; surfactant micelles of sodium dodecyl sulfonate (anionic surfactant), 0.53 M; and surfactant micelles of *n*-hexadecyl pyridinium chloride (cationic surfactant), 0.53 M (4). The latter two surfactant gel concentrations are based on total surfactant concentrations, not concentration of micelles. It may be concluded that the cationic polyelectrolyte has a gel polarization behavior similar to these other charged colloidal systems.

In practical applications, a region of low relative flux would be avoided, so the important conclusion from Fig. 6 is that the relative flux remains high until high retentate concentrations are achieved. The gel concentration doesn't depend on membrane pore size for polyelectrolyte systems as long as the pores are small enough to reject the polymer (4). For the system studied here, it requires approximately 100 mM QUAT in the retentate to reduce the relative flux to 0.5. Therefore, as long as the product retentate [QUAT] does not exceed approximately 100–150 mM, the flux is not substantially below that of pure water (particularly considering that the overall flux is an integral average between the feed [QUAT] and the final retentate [QUAT] during operation). The maintenance of high rejections at these retentate concentrations (in the absence of high levels of added salt) has already been discussed. Therefore, concentration polarization is not a severe problem in this PEUF application.

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