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Ion-Expulsion Ultrafiltration to Remove Chromate from Wastewater

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Abstract

In ion-expulsion ultrafiltration, a water-soluble colloid with the same charge as the target ion to be removed is added to water. This stream is then treated by ultrafiltration with membrane pores small enough to reject the colloid. In this study, chromate was removed from water using polystyrene sulfonate as the colloid in both batch-stirred cell and spiral-wound ultrafiltration devices. At very low pressures, Donnan equilibrium could be used to describe the permeate chromate concentration. As the pressure increased, diffusional effects caused the separation to become poorer. A spiral-wound unit resulted in a much higher separation efficiency than a stirred cell in this process.

INTRODUCTION

Chromate is an extremely toxic substance which has many industrial uses, such as in the metal plating industry and aircraft maintenance. Because of its widespread use, chromate is often found in contaminated wastewater, groundwater, and soil.

Colloid-enhanced ultrafiltration methods have been shown to be extremely effective at removing contaminants from wastewater streams (*1–13*). Ion-expulsion ultrafiltration (IEUF), the newest of the colloid-enhanced ultrafiltration techniques, has recently been reported by our laboratory (*13*). It is known that ionic colloids (micelles and polyelectrolytes) in aqueous solutions bind a less than stoichiometric fraction of dissolved counterions (*14–19*). IEUF is based on the fact that the fraction of charges on the colloid which are neutralized by counterion binding is nearly a constant throughout large concentration ranges (*14–16*).

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IEUF uses the charge characteristics of a colloid to expel a like-charged target species across a membrane in an ultrafiltration process. The membrane has pores which are small enough to prohibit the movement of the colloid while allowing free movement of the target species. Figure 1 is a general schematic of the IEUF process. If the unassociated co-ion and counterion are in equilibrium across the membrane between retentate and permeate, the ion activity product for all neutral electrolytes will be the same across the membrane. Note that this does not mean that the activity of each individual ion is the same across the membrane at equilibrium, only that of each neutral electrolyte pair present. The resulting equilibrium concentration of each ion in solution in the permeate can be computed by a Donnan equilibrium calculation (*13*, *20*, *21*). Figure 2 shows a numerical calculation using the Donnan assumptions to illustrate the equilibrium

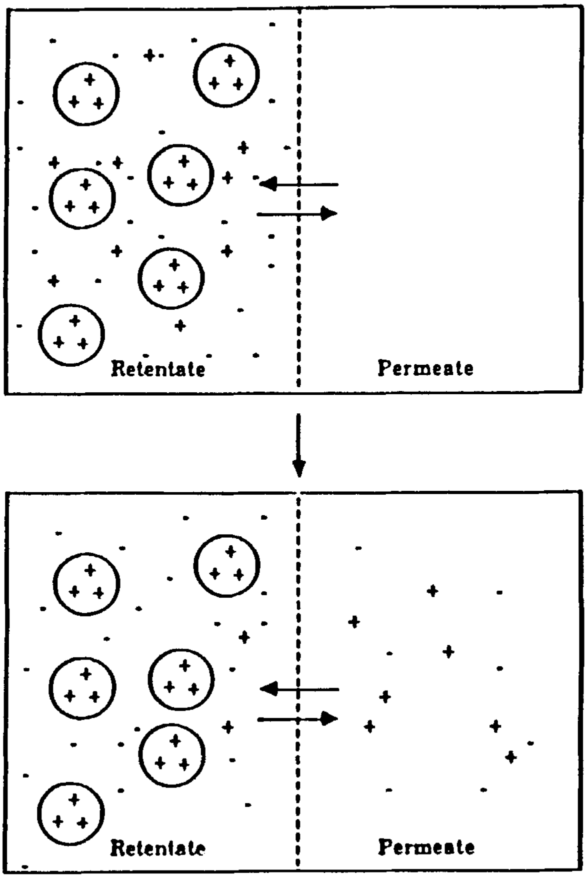

FIG. 1. Schematic of IEUF.

retentate solution

concentration of PSS $[PSS] = 0.100\ M$

initial chromate concentration $[CrO_4^{-2}] = 1.00 \times 10^{-4}\ M$

initial sodium concentration $[Na^+]=0.2 \times 0.10 = 0.02\ M$

ion product constant $[CrO_4^{-2}][Na^+]^2 = 4.0 \times 10^{-8}\ M^3$

ultrafiltration membrane ------------------------------

by electrical neutrality $2[CrO_4^{-2}] = [Na^+]$

ion product constant $[CrO_4^{-2}][Na^+]^2 = 4[CrO_4^{-2}]^3$

$= 4.0 \times 10^{-8}$

permeate chromate concentration $[CrO_4^{-2}] = 2.15 \times 10^{-3}\ M$

permeate solution

FIG. 2. Example of Donnan equilibrium calculation.

separation which could occur using the ion-expulsion technique to expel sodium chromate using sodium polystyrene sulfonate (PSS) as the colloid. Two assumptions are made in Fig. 2: the species activities can be approximated by their concentrations and the PSS has 80% counterion binding. The calculations show that if Donnan equilibrium is satisfied, the chromate is 21.5 times more concentrated in the permeate than in the retentate.

This paper discusses the results of IEUF experiments which have utilized PSS to remove chromate from water. Experiments were conducted in batch-stirred cell and spiral-wound ultrafiltration devices. The separations are compared to those measured at equilibrium.

EXPERIMENTAL MATERIALS

Anhydrous sodium chromate (Na_2CrO_4) was obtained from Fisher Scientific. Poly(sodium 4-styrenesulfonate) $[—CH_2CH(C_6H_4SO_3Na)—]_n$, average molecular weight 70,000 daltons, was obtained from Aldrich Chemical Company. Chemicals were used as received. Deionized water was used in all experiments.

METHODS

The use of semiequilibrium dialysis (SED) cells to investigate equilibrium ultrafiltration separations has been studied extensively in our laboratory (*3*, *5–7*, *9*, *11*, *13*). Experimental equipment and procedures employed in the SED studies were the same as those previously reported. Membranes employed in the dialysis and ultrafiltration investigations were all of a cellulose ester type. Dialysis membranes had a molecular weight cutoff of approximately 6000 daltons. Dialysis cells were loaded with PSS and chromate solutions, thermostated at 25°C, and equilibrated for approximately 24 h before analysis.

Stirred cells have been widely utilized in batch ultrafiltration studies (*1–13*). Experiments were conducted in a Nuclepore 400 mL batch-stirred cell maintained at 30°C via a water jacket and initially charged with 300 mL of feed solution. The experiment proceeded until approximately 200 mL had passed through the membrane. Pressure was applied by nitrogen gas, and the stirrer speed, held constant at 840 rpm, was determined by a

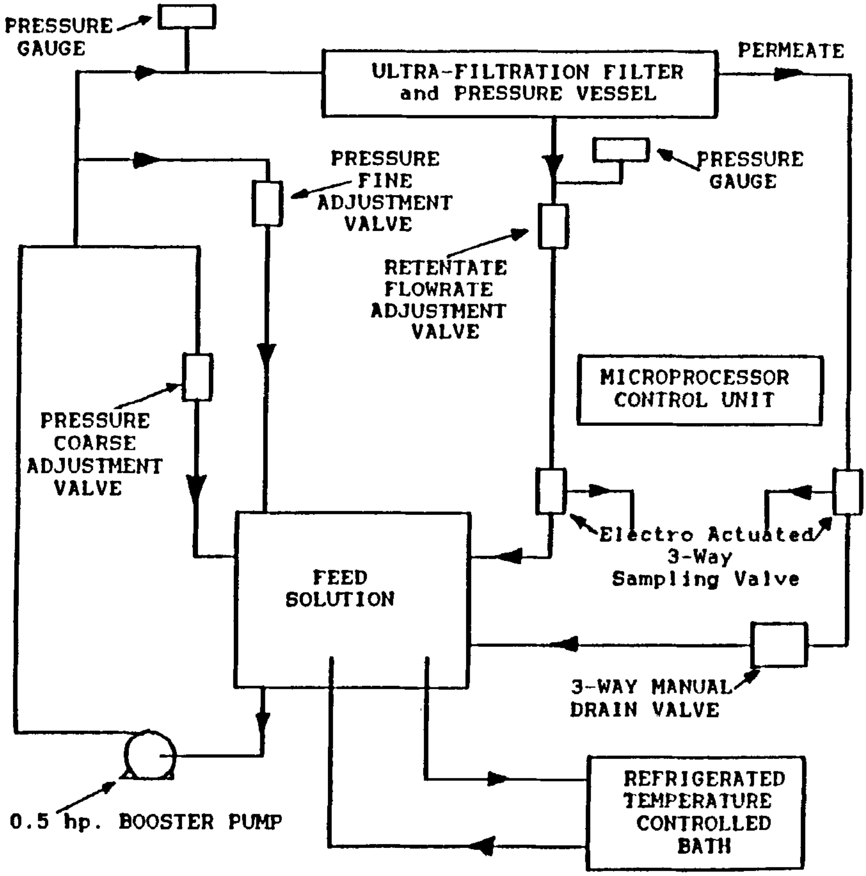

FIG. 3. Diagram of spiral-wound apparatus.

strobe light. The pressure was held constant throughout a run, and samples of approximately 20 mL were collected.

Figure 3 is a process flow diagram of the spiral-wound membrane apparatus used in the ultrafiltration experiments. Spectra/Por Type C membranes with an area of 5 ft^2 and a molecular weight cutoff of 5000 daltons were used for the spiral-wound experiments. The feed tank was loaded with the solution of interest. The amount of solution which moved across the membrane as well as the pressure drop across the membrane was fixed by the recycle rate and the retentate flow rate. The pressure drop, recycle rate, and retentate flow rate were controlled by the recycle flow rate adjustment valves and the retentate flow rate adjustment valve. The system operated entirely in a recycle mode unless samples were removed from the unit. The temperature of the recycling fluid was held constant at 30°C via the heat exchanger located in the feed tank. Samples were taken when a steady-state was achieved. Samples of permeate and retentate were removed via the microprocessor-controlled electromagnetic 3-way sampling valves.

Chromate and PSS concentrations were determined using a Bausch and Lomb Spectronic 1001 ultraviolet (UV) spectrometer. The spectral peaks employed to quantify concentrations were at 254 nm for PSS and 372 nm for chromate.

RESULTS AND DISCUSSION

Figure 4 is a plot of the percentage of chromate removed in the permeate as a function of the percentage of feed removed as permeate for various average applied pressures in the spiral-wound unit. The curve fits shown have no theoretical basis and were determined from the best fit of a linear log-log scale. The chromate feed concentrations varied between 4.9×10^{-5} and 1.23×10^{-4} *M*.

Figure 4 shows that as the applied pressure increases, the separation efficiency of the spiral-wound ultrafiltration process decreases. In order for IEUF to occur, the target species must diffuse across the ultrafiltration membrane at a higher concentration than in the retentate. The rate at which the target species can diffuse to the membrane and enter the permeate stream is nearly independent of pressure because the linear flow rate, turbulence, and boundary layer thickness do not depend significantly on pressure. The rate at which water passes through the membrane increases with increasing pressure for any given retentate conditions. If the pressure were low enough, the target species could diffuse rapidly enough through solution to attain equilibrium across the membrane. However, as the pressure increases, this is no longer true and the permeate concentration

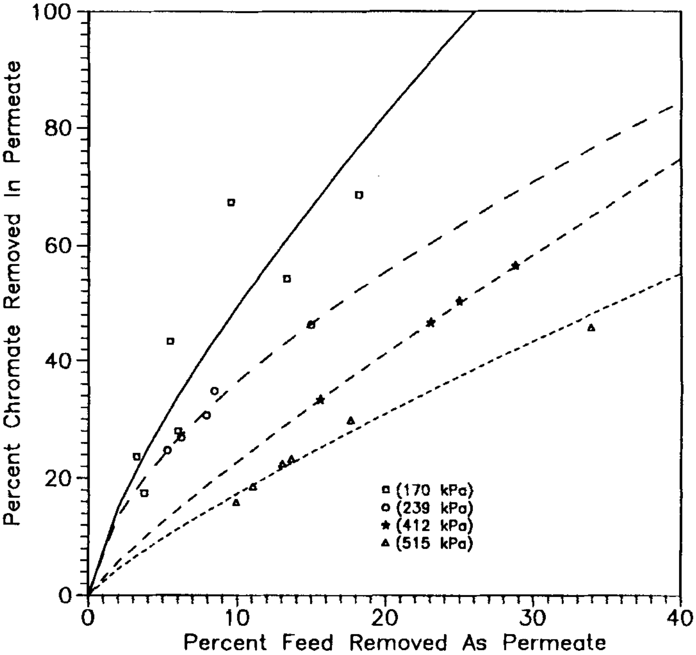

FIG. 4. Percent chromate removed at various applied pressures in a spiral-wound unit.

of target ion decreases. Therefore, the IEUF of chromate using PSS is a diffusionally limited process at high pressures.

Figure 5 is a plot of the percentage of chromate removed in the permeate as a function of the applied pressure for various percentages of feed removed as permeate. Figure 6 shows the percentage of feed which must be removed as a function of the applied pressure in order for a given percentage of chromate to be removed from the original feed solution. The curves given in Figs. 5 and 6 were calculated from the empirical curve fits shown in Fig. 4. These plots demonstrate the efficiency of the IEUF process in removing chromate from contaminated water streams at low applied pressures. For example, when only 1% of the contaminated feed stream has been removed as permeate at an applied pressure of 170 kPa, 10% of the chromate has been removed from the feed.

Since IEUF is diffusionally limited, the best separation would be expected to occur under conditions where the target species had an infinite amount of time to diffuse to and across the ultrafiltration membrane (i.e., equilibrium conditions). SED experiments were utilized to determine the target species permeate concentration under equilibrium conditions.

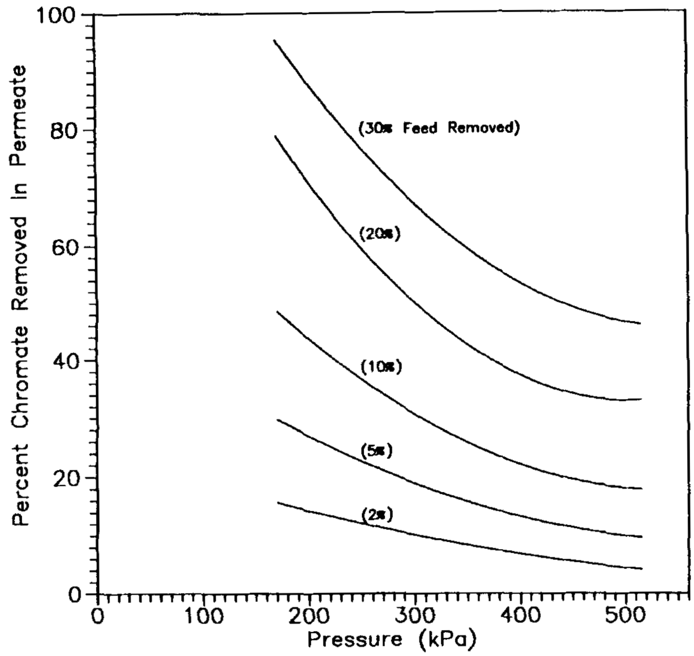

FIG. 5. Percent of chromate removed at various percentages of total feed removed as permeate in a spiral-wound unit.

Figure 7 represents the concentration of the permeate as a function of the concentration of the retentate from the SED experimental data. The two solid lines in the figure depict equilibrium values predicted from a simplified equilibrium model described below. Data obtained at equilibrium PSS concentrations of 0.022 and 0.045 *M* are shown in the figure.

The equilibrium model is based on simple thermodynamic principles presented in detail elsewhere (*22*, *23*). At equilibrium, the ion activity product for the neutral electrolytes on each side of the membrane must be equal (except for the polyelectrolyte ion which cannot pass through the membrane). This equality is expressed as

$$(a_{S,P})^2(a_{C,P}) = (a_{S,R})^2(a_{C,R}) \tag{1}$$

where a is the activity, S is Na^+, C is CrO_4^{2-}, P is permeate, and R is retentate. The activity is given by

$$a_j = \gamma_j[j] \tag{2}$$

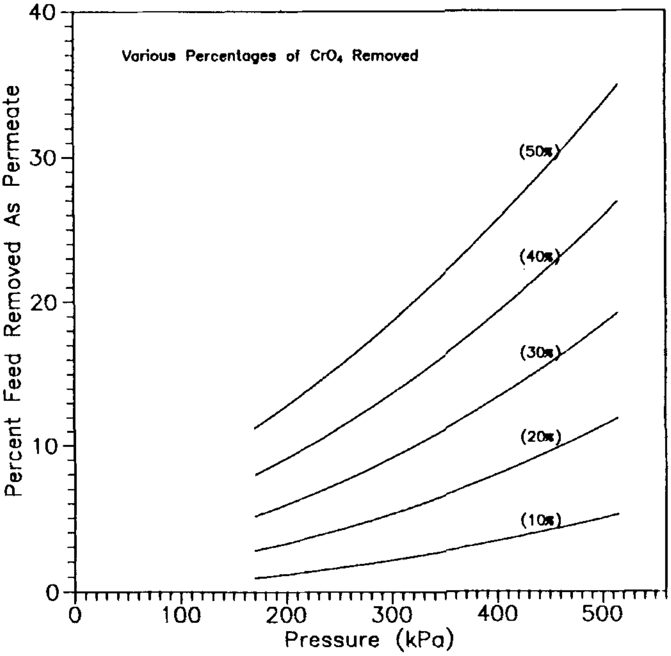

FIG. 6. Percent of feed removed as permeate for various percentages of chromate removed in permeate in a spiral-wound unit.

where a_j is the activity of component j, γj is the activity coefficient of component j, and $[j]$ is the concentration of j. The activity coefficients were calculated from the extended Debye–Hückel equations with the Davies modification (*24*). In determining the activity coefficients, only the sodium and the chromate ions (not the polyelectrolyte ions) were assumed to contribute to the ionic strength. In determining the activity coefficient in the permeate, the following equations were used (*24*):

$$-\log (\gamma_{S,P}) = 0.509[\sqrt{I_P}]/[1 + \sqrt{I_P}] - 0.2I_P \tag{3}$$

$$-\log (\gamma_{C,P}) = 4[-\log (\gamma_{S,P})] \tag{4}$$

where I is the ionic strength. The ionic strength in the permeate was calculated as

$$I_P = 0.5([\mathrm{Na}]_P + 4[\mathrm{CrO_4}]_P) \tag{5}$$

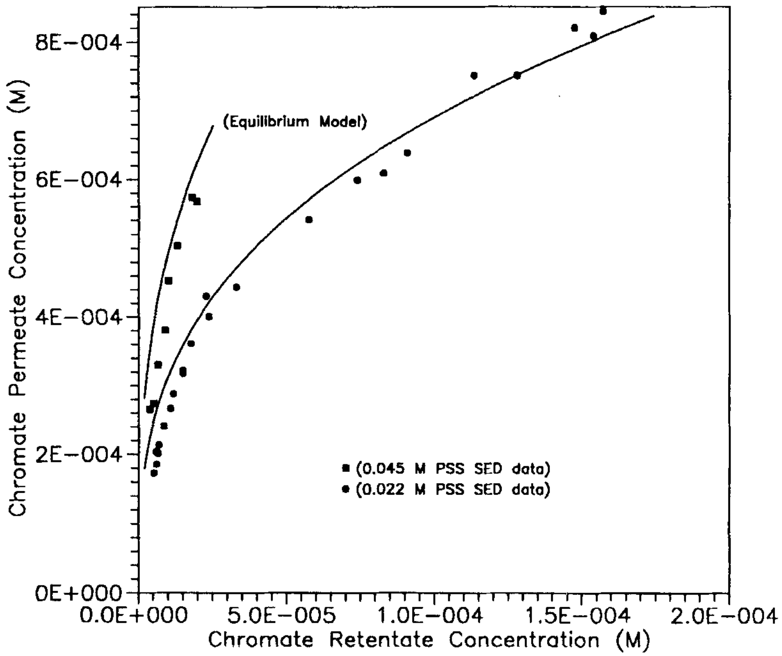

FIG. 7. Comparison of semiequilibrium dialysis data with equilibrium model.

The activity coefficients in the retentate were determined from (*24*)

$$-\log (\gamma_{S,R}) = 0.509[\sqrt{I_R}]/[1 + \sqrt{I_R}] - 0.2I_R \tag{6}$$

$$-\log (\gamma_{C,R}) = 4[-\log (\gamma_{S,R}) \tag{7}$$

The ionic strength in the retentate was calculated as

$$I_R = 0.5([\mathrm{Na}]_R + 4[\mathrm{CrO_4}]_R) \tag{8}$$

The free sodium in the retentate was assumed to be the product of β (equal to the fraction of the charged sites on PSS which do not have counterions bound to them) times the concentration of PSS and is given by

$$[\mathrm{Na}]_R = \beta[\mathrm{PSS}]_R \tag{9}$$

where [PSS] is the concentration of PSS. The value of β was determined by fitting the original SED data with the equilibrium model. The require-

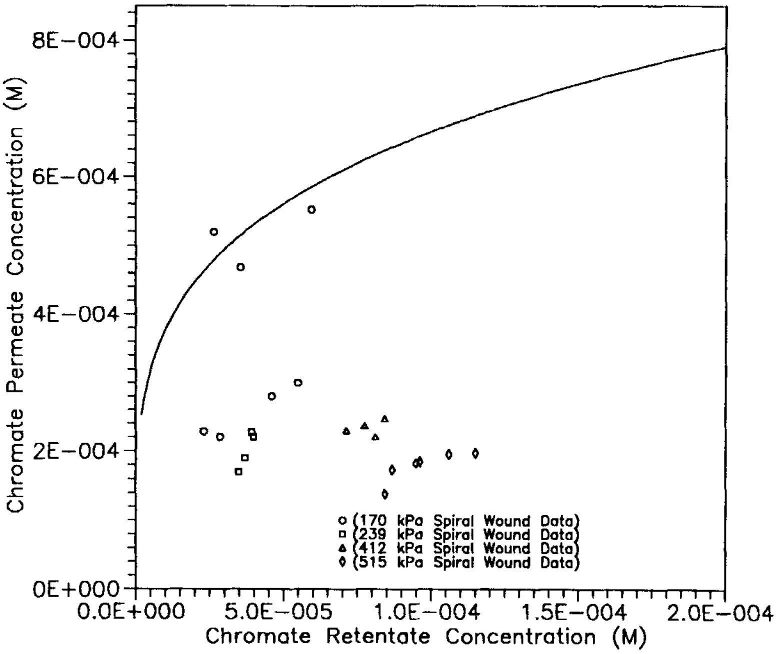

FIG. 8. Comparison of spiral-wound data with equilibrium model.

ment of electroneutrality in the permeate dictates the concentration of chromate in the permeate:

$$[CrO_4]_P = [Na]_P/2 \qquad (10)$$

From the values shown in Fig. 7, $\beta = 0.165$.

Figure 8 is a plot of the concentration of chromate in the permeate versus the concentration of chromate in the retentate for various values of average applied pressure in the sprial-wound unit. The solid line in Fig. 8 represents equilibrium values as predicted by the equilibrium model described above.

As can be seen in Fig. 8, at an applied pressure of 170 kPa the spiral-wound unit operates very close to equilibrium. At pressures greater than 170 kPa, the separating ability of the spiral-wound unit decreases and the process is diffusionally limited.

It is much less expensive and time consuming to obtain ultrafiltration data in a stirred-cell than in a spiral-wound unit. Figure 9 shows the relationship between the percent of chromate removed in the permeate as a function of the percent of feed removed as permeate for various values of average applied pressure for both the stirred-cell and the spiral-wound

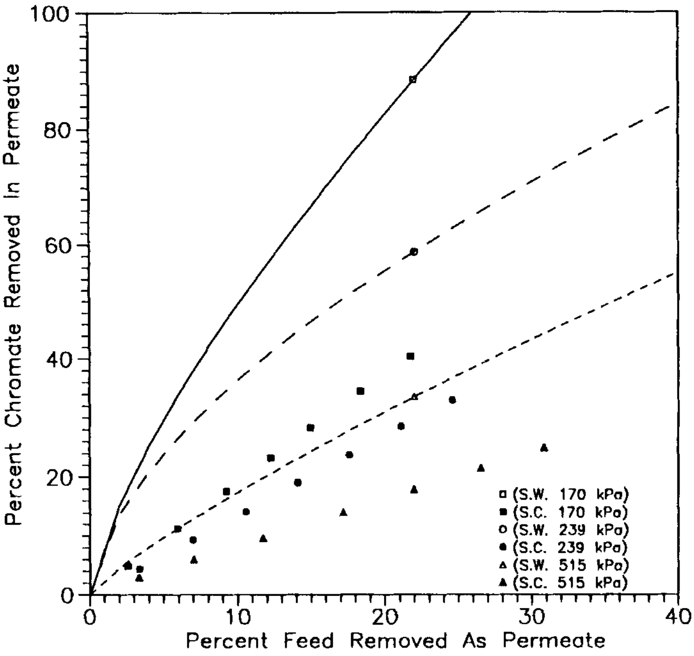

FIG. 9. Percent chromate removed at various applied pressures in a spiral-wound unit and batch-stirred cell.

units. Smooth empirical curves rather than individual data points for the spiral-wound experiments are given in Fig. 9 to enhance clarity. The separation efficiency in the stirred cell is markedly less than that obtained with the spiral wound.

The geometry of the stirred-cell unit is such that a large column of fluid is located above the ultrafiltration membrane. The surface area of the ultrafiltration membrane is small compared to the volume of solution in the stirred cell. Therefore, the diffusional path for a chromate ion is very large if the ion is located near the top of the stirred cell. Hence, diffusional effects can be significant in a stirred cell. On the other hand, the geometry of the spiral-wound ultrafiltration membrane is such that a very thin layer of fluid is present above the surface of the membrane. Therefore, the path a chromate ion must traverse before crossing the membrane is relatively short in the spiral-wound unit compared to the path found in the batch-type stirred cell. Hence, the diffusional effects in the spiral-wound unit are much smaller than the diffusional effects in the stirred-cell unit. Therefore, the separation data from a stirred-cell unit cannot be scaled up directly to a spiral-wound process.

Several conclusions can be drawn from the preceding discussion. IEUF is a diffusionally limited process which works best at low pressures and is most efficient at low permeate volumes. The spiral-wound unit operates near equilibrium IEUF conditions at low applied pressures. Finally, stirred-cell experimental data cannot be directly scaled up to the spiral-wound process in IEUF.

SYMBOLS

a_j	activity of component j
γ_j	activity coefficient of component j
$[j]$	concentration of component j
I	ionic strength
β	1 minus fractional counterion binding on PSS or the fraction of unbound charges on the PSS

Subscripts

S	Na^+
C	CrO_4^{2-}
P	permeate
R	retentate

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REFERENCES

1. R. O. Dunn, J. F. Scamehorn, and S. D. Christian, *Sep. Sci. Technol., 20,* 257 (1985).
2. J. F. Scamehorn, R. T. Ellington, S. D. Christian, W. Penny, R. O. Dunn, and S. N. Bhat, *AIChE Symp. Ser., 82,* 48 (1986).
3. R. O. Dunn, J. F. Scamehorn, and S. D. Christian, *Sep. Sci. Technol., 22,* 763 (1987).
4. L. L. Gibbs, J. F. Scamehorn, and S. D. Christian, *J. Membr. Sci., 30,* 67 (1987).
5. G. A. Smith, S. D. Christian, E. E. Tucker, and J. F. Scamehorn, *ACS Symp. Ser., 342,* 184 (1987).

6. S. N. Bhat, G. A. Smith, E. E. Tucker, S. D. Christian, and J. F. Scamehorn, *Ind. Eng. Chem. Res.*, *26*, 1217 (1987).
7. S. D. Christian, S. N. Bhat, E. E. Tucker, J. F. Scamehorn, and D. A. El-Sayed, *AIChE J.*, *34*, 189 (1988).
8. J. F. Scamehorn, S. D. Christian, and R. T. Ellington, in *Surfactant Based Separation Processes* (J. F. Scamehorn and J. H. Harwell, eds.), Dekker, New York, 1989, Chap. 2.
9. S. D. Christian and J. F. Scamehorn, in *Surfactant Based Separation Processes* (J. F. Scamehorn and J. H. Harwell, eds.), Dekker, New York, 1989, Chap. 1.
10. R. O. Dunn, J. F. Scamehorn, and S. D. Christian, *Colloids Surf.*, *35*, 45 (1989).
11. K. J. Sasaki, S. L. Burnett, S. D. Christian, E. E. Tucker, and J. F. Scamehorn, *Langmuir*, *5*, 363 (1989).
12. J. F. Scamehorn, S. D. Christian, E. E. Tucker, and B. I. Tan, *Colloids Surf.*, *49*, 259 (1990).
13. S. D. Christian, E. E. Tucker, J. F. Scamehorn, B. H. Lee, and K. J. Sasaki, *Langmuir*, *5*, 876 (1989).
14. J. F. Rathman and J. F. Scamehorn, *J. Phys. Chem.*, *88*, 5807 (1984).
15. J. F. Rathman and J. F. Scamehorn, *Langmuir*, *3*, 372 (1987).
16. T. Sasaki, M. Hattori, J. Sasaki, and K. Nukina, *Bull. Chem. Soc. Jpn.*, *48*, 1397 (1975).
17. J. A. Beunen and E. Ruckenstein, *J. Colloid Interface Sci.*, *96*, 469 (1983).
18. D. J. Stigter, *J. Phys. Chem.*, *68*, 3603 (1964).
19. A. Schwarz and G. E. Boyd, *Ibid.*, *69*, 4268 (1965).
20. W. J. Moore, *Physical Chemistry*, 4th ed., Prentice-Hall, Englewood Cliffs, New Jersey, 1972, pp. 544–546.
21. P. W. Atkins, *Physical Chemistry*, 3rd ed., Freeman, New York, 1986, pp. 609–610.
22. I. M. Klotz and R. M. Rosenberg, *Chemical Thermodynamics*, 4th ed., Benjamin/Cummings, Menlo Park, New Jersey, 1986, Chaps. 8 and 12.
23. R. E. Balzhiser, M. R. Samuels, and J. D. Eliassen, *Chemical Engineering Thermodynamics*, Prentice-Hall, Englewood Cliffs, New Jersey, 1972, Chaps 9 and 10.
24. S. Glasstone, *Thermodynamics for Chemists*, Van Nostrand, Princeton, New Jersey, 1947, p. 419.

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