Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Development of Liquid Membrane Pertraction for the Removal and Recovery of Chromium from Aqueous Effluents

B. G. Fraser[a]; M. D. Pritzker[a]; R. L. Legge[a]
[a] DEPARTMENT OF CHEMICAL ENGINEERING, UNIVERSITY OF WATERLOO WATERLOO, ONTARIO, CANADA

To cite this Article Fraser, B. G. , Pritzker, M. D. and Legge, R. L.(1994) 'Development of Liquid Membrane Pertraction for the Removal and Recovery of Chromium from Aqueous Effluents', Separation Science and Technology, 29: 16, 2097 — 2116

To link to this Article: DOI: 10.1080/01496399408002192

URL: http://dx.doi.org/10.1080/01496399408002192

SEPARATION SCIENCE AND TECHNOLOGY, 29(16), pp. 2097–2116, 1994

Development of Liquid Membrane Pertraction for the Removal and Recovery of Chromium from Aqueous Effluents

B. G. FRASER, M. D. PRITZKER, and R. L. LEGGE
DEPARTMENT OF CHEMICAL ENGINEERING
UNIVERSITY OF WATERLOO
WATERLOO, ONTARIO N2L 3G1, CANADA

ABSTRACT

Liquid membrane pertraction combines the loading and stripping steps of solvent extraction into a single unit operation, allowing the continuous removal and concentration of a given species. In this paper the feasibility of applying liquid membrane pertraction to the recovery of chromium (Cr(VI)) from aqueous effluents with the objective of reducing levels to below allowable discharge limits has been examined. A continuous laboratory-scale liquid membrane pertractor was constructed to solve a variety of problems associated with the treatment of Cr(VI)-bearing streams. Various operational factors such as feed velocity, strip velocity, membrane velocity, and composition of the inlet feed were then examined. Satisfactory continuous runs lasting up to 22 days were achieved. Chromium levels in synthetic waste could be reduced from 200–300 mg/L down to 1 mg/L, well within most allowable discharge limits. Experiments showed that the strip phase can be concentrated with inlet Cr(VI) concentrations of 2000 ppm Cr(VI), with indications that it should be possible at even higher concentrations.

INTRODUCTION

With increasing demands on the environment and on natural resources, there is a growing need to develop practical technologies that not only can remediate waste streams but also recover valuable components from these effluents. Hexavalent chromium is one metal that has received considerable attention. It is used extensively in such industrial applications as electroplating, electrofinishing, steelmaking, leather tanning, and corrosion inhibition, and it has long been recognized as a toxic substance due to its strong oxidizing potential and ease with which it can cross biological membranes (1).

Current methods for the treatment of chromate in liquid effluents from industrial operations include precipitation, when disposal is the objective, and ion exchange and/or evaporation, when recovery is desired. Both of these processes have certain disadvantages or limitations which have motivated interest in other processes. One such alternative for the treatment of Cr(VI) and other metals in wastewater is the use of liquid membranes (2). Although several variations exist, all liquid membrane processes involve the selective transport of a species from a feed solution across an intermediary liquid or supported liquid membrane phase to a strip solution on the other side. In most cases the outer phases are aqueous and the middle phase is an organic solvent containing an extractant of the desired species.

One of the earliest and most popular liquid membrane processes is the double emulsion or surfactant liquid membrane method (3–7). This technique, which involves the use of an unsupported membrane, has been applied to the treatment of Cr(VI) in a number of studies over the years (5, 8–13). Although capable of achieving rapid mass transfer with very high concentration ratios, the double emulsion method has some drawbacks, such as the need for a separate step to break down the emulsion for recovery of the metal and recycle of the organic and problems associated with swelling of the organic due to occlusion of water and membrane stability (12, 14–16).

The use of supported liquid membranes has received interest since most of these problems can be avoided, although at the cost of lower mass transfer rates and concentration ratios and some difficulty with membrane lifetime (16–21). A variety of such units are available, depending upon the geometrical configuration of the supports, including plate and frame, spiral, tubular, and hollow fibers (16–27). Some of these have been applied to the treatment of Cr(VI) and have met with some success (24, 27–29).

A relatively new supported liquid membrane method which has not received as much attention, but which has many attractive features, is liquid membrane pertraction developed by Boyadzhiev and coworkers (16, 30). The pertractor design includes flat, vertical membrane supports and utilizes gravity whenever possible, making construction and operation simple, inexpensive, flexible, and easy to scale-up. Another advantage is that all three liquid phases are flowing in this system, with velocities that can be independently controlled. Vertical flow and the immiscibility and density differences of the aqueous and organic phases ensure that the interfaces remain stable. By using these differences, the aqueous products can be easily collected at the bottom of the unit.

Boyadzhiev and coworkers (16, 30–33) studied this process for the treatment of several systems, such as dilute aqueous solutions of Cu(II), iodine, phenol, and L-lysine. As yet, however, there has been no reported work on the application of liquid membrane pertraction to Cr(VI)-bearing streams. In view of its potential advantages, it would be useful to explore the feasibility of applying this process to the recovery of Cr(VI) from aqueous industrial effluents and at the same time reduce the Cr(VI) levels in the effluent below acceptable discharge limits. Accordingly, the objectives of this study were to design and construct a laboratory-scale pertractor suitable for the treatment of Cr(VI), assess its robustness and ease of operation, and investigate the effects of various operating parameters (liquid phase flow rates, compositions of inlet streams) on its steady-state behavior. As will be shown, the particular characteristics of the exchange reactions involved necessitated some significant modifications to the design and operation of the pertraction unit.

EXPERIMENTAL PROCEDURE

Chemicals and Chemical Analysis

All chemicals were used as received from the supplier and were of reagent grade or better. Total chromium content in the aqueous phases was measured using a Fissons Model SS-7 Direct Current Plasma (DCP) Spectrometer (ARL Canada, Unionville, Ontario). Standards were prepared using a 1000 mg/L Atomic Absorption Chromium(III) standard (BDH Inc., Toronto, Canada). The detection limit and limit of quantitation were 0.52 and 1.72 mg/L total chromium, respectively.

Due to the high sodium concentration in aqueous strip solutions, chromium values in DCP analysis were artificially elevated due to a positive matrix effect. To adjust for this phenomenon, strip samples were diluted and an appropriate amount of a 30 g/L NaCl solution was added to give all samples a sodium content of 3000 mg/L. DCP was also used to determine the total chromium content in the organic phase. A 100 mg/L Inductively Coupled Plasma Chromium(III) Standard was used (special order from BDH) to prepare calibration standards.

A Dionex 2000i Ion Chromatograph (Sunnydale, California) was used for sulfate analysis. An AS3 anion-exchange column with an AG3 guard column was used with a conductivity detector. The eluent consisted of 3.0 mM $NaHCO_3$ and 2.38 mM Na_2CO_3 at a flow rate of 1.8–2.0 mL/min.

Hexavalent chromium concentrations in the aqueous phases were measured with a Shimadzu UV-Visible Recording Spectrophotometer (Model UV-160) using a colorimetric diphenyl carbazide method (34). A 1-mL aqueous sample was acidified and diluted until the concentration was less than 1.5 mg/L and the pH was 1.5 ± 0.5. Two milliliters of diphenyl carbazide solution (0.25 g of 1,5-diphenyl carbohydrazide in 50 mL acetone) were added to the aqueous samples, and at least 10 minutes was given to allow full color development before analysis. Calibration standards between 0.1 and 1.5 mg/L Cr(VI) were prepared using a 990-mg/L Chromium(VI) Atomic Absorption Standard Solution (Aldrich, Milwaukee, Wisconsin). Cr(VI) concentrations in the samples were determined from the calibration curve regression line.

Composition of the Liquid Phases

A series of standard loading and stripping experiments, commonly used in solvent extraction studies, were carried out to select appropriate components of the feed, organic, and strip phase inlets and to better understand the reactions involved (35). Only the results as they pertain to operation of the pertractor are given here.

Feed Inlet

As a first study on the use of pertraction for the treatment of Cr(VI) waste, only synthetic solutions in the feed stream to the unit were used. In most cases these consisted of approximately 200 mg/L Cr(VI) made up by dissolving $K_2Cr_2O_7$ in deionized water. This concentration was chosen since it is typical of some industrial effluents such as electroplating rinsewater (36). No other components were added, except for H_2SO_4 to adjust pH. Batch loading experiments with this aqueous feed and the organic showed that the distribution coefficient reached a maximum when the initial pH of the feed was approximately 2. A similar result was reported by Strzelbicki et al. (10). Accordingly, the feed inlet to the pertractor was adjusted to pH 2.

Organic

On the basis of previously reported studies (13, 29, 37) and batch loading and preliminary pertractor runs in our laboratory, the components chosen for the organic phase were 0.5 vol% Aliquat 336 as extractant and 2 vol% *n*-decanol as modifier dissolved in Isopar 2025 (Shell Chemical Co., Toronto, Canada) or Exxsol D-60 (Esso Solvents, Toronto, Canada) solvent. Isopar 2025 is a mixture of isoparaffins with approximately 70% isooctane and the remainder higher molecular weight hydrocarbons. Exxsol D-60 is also a mixture, with an approximate composition of 56% napthenes and 44% paraffins.

Aliquat 336 (trioctyl methylammonium chloride) was found to exhibit faster loading rates and a higher selectivity for Cr(VI) over sulfate than the tertiary amine tri-*n*-octylamine (TOA), in addition to being able to load Cr(VI) over a wider pH range (38). Aliquat 336 also proved more suitable as an extractant as it was chemically stable at the strip–organic interface over extended periods of time. This would be a critical factor in continuous pertraction processes where the organic phase would be continually recirculated. When TOA was used, a white precipitate formed at the strip–organic interface after about 10 hours of operation of the pertractor. Experiments showed that this precipitate contained Cr(III), which was likely due to a reaction of Cr(VI) with TOA. The formation of a precipitate when TOA was used to load Cr(VI) has also been reported by Smith et al. (24).

A complication in using Aliquat 336 is that it contains Cl^- ion, which is not desirable in many electroplating operations. A simple way to prevent chloride from entering the system was to preload the organic phase with the standard aqueous feed in a separate vessel to exchange chloride with Cr(VI) and sulfate and then feed this loaded membrane into the pertractor. This pretreatment was only required once prior to start-up when a fresh batch of the membrane was being prepared since the organic phase was continually recirculated through the unit.

Strip Inlet

The strong affinity of Aliquat 336 for Cr(VI) in the loaded organic phase required a strongly alkaline solution NaOH (3.0 N) to achieve reasonable stripping rates. As will be discussed subsequently, this required a modification in the design of the pertractor as originally reported by Boyadzhiev and coworkers (16, 30). No Cr(VI) was added to the strip inlet except in a few experiments.

RESULTS AND DISCUSSION

Pertractor Design

Based on the unit originally conceived by Boyadzhiev and coworkers (30), a pertractor was constructed consisting of closely spaced, highly porous (~80%), vertical viscose (or regenerated cellulose sponge) supports through which the feed and strip solutions were circulated in an alternating sequence. This entire assembly of supports was fitted inside a rectangular Plexiglas box. The organic membrane phase was circulated upward between the supports by an external pump. The bottom edges of the supports were angled and arranged to direct the feed and strip solutions into the appropriate collectors on opposite sides of the unit. However, problems arose with this design when used with the Aliquat 336 membrane because the highly alkaline solution required for stripping rapidly destroyed the sponge support. A wide variety of materials were tested for a combination of hydrophilicity and compatibility with the stripping solution, e.g., canvas, cotton fabric, cork, phenyl formaldehyde resin, and cotton cheesecloth. Of these, cotton cheesecloth was found to be the most suitable as an alternative support material. Since it is not as rigid as viscose, a new design for the supports was necessary. The alternatives used in this study included an open outer frame made of polyvinyl chloride and solid inner frames made of polyvinyl chloride and Plexiglas (Fig. 1). Tightly stretched layers of cheesecloth over an angled 3 mm thick Plexiglas solid inner frame was ultimately found to be most effective. Trial tests using crystal violet as a flow indicator showed fairly uniform flow across the width and few dead spaces between the Plexiglas and cheesecloth. The unit used in this study consisted of one support for Cr(VI) loading and one support for Cr(VI) stripping. These supports were spaced 4.5 cm apart and fit into slots along the sides of the outer box. The number of cloth layers was varied from 2 to 8 in the test runs.

Although the original motivation for the modification of the support design stemmed from a materials problem, several other important advantages over the original viscose support design were realized. Since the supports are nonporous, the aqueous phases are confined to flow over a thinner layer (Fig. 2) than in the previous design, thereby enhancing mass

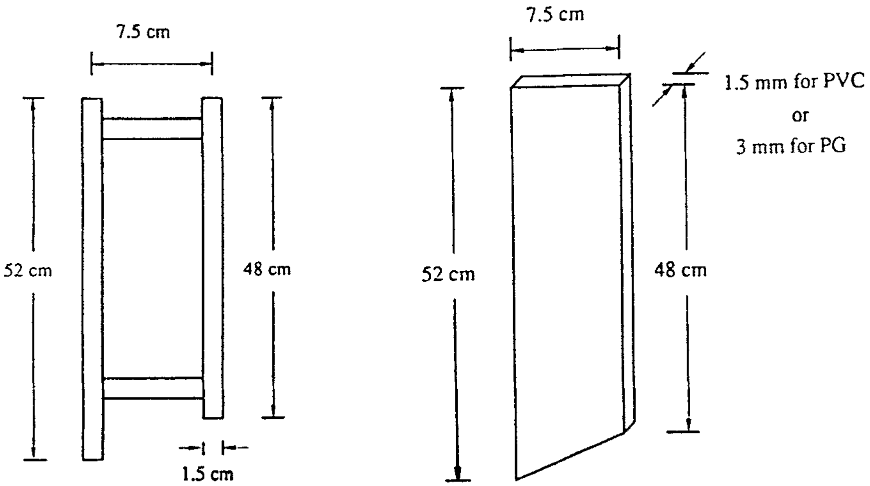

FIG. 1 Schematic diagrams of (left) open outer frame and (right) solid inner frame used as supports for cotton cheesecloth.

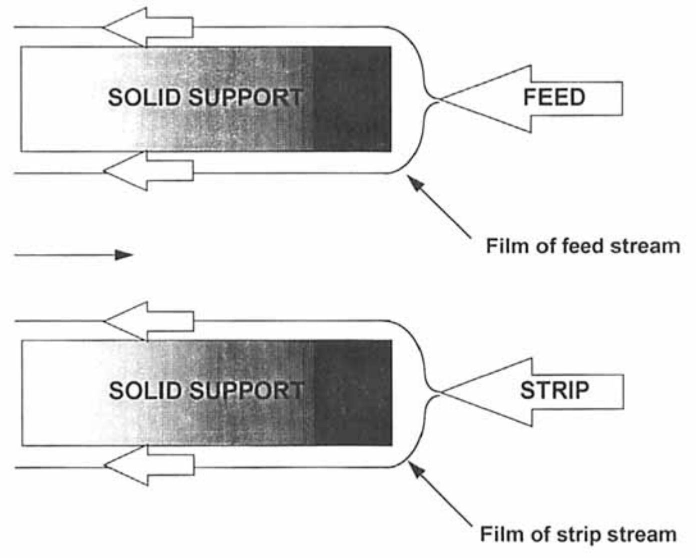

FIG. 2 Flow patterns of liquid phases with the modified pertractor design using nonporous supports.

transfer. With a simpler frame, it was also possible to remove a single support from the unit without interruption in operation.

A schematic of the entire continuous bench-scale pertraction unit is given in Fig. 3. Separate positive displacement pumps were used to control the flow rates of the three streams. Uniform flow of the three phases was ensured through the use of Plexiglas distributors mounted at the inlet of each stream to the unit. Control of solution level in each collector was achieved by adjustment of the height of the corresponding level leg. To obtain representative samples of the discharge streams, solutions were agitated with magnetic stir bars in the feed and strip collectors at the bottom of the unit. The pertractor was operated as a closed unit to minimize losses due to evaporation.

Pertraction Operation

The primary objectives of the test runs were to demonstrate the overall stability and robustness of the pertractor operation and to investigate the effects of various operating variables on its steady-state behavior. Preliminary experiments indicated that 24 hours would ensure that steady-state had been reached for a given set of operating conditions, and consequently samples were collected after this period in all subsequent tests. Table 1

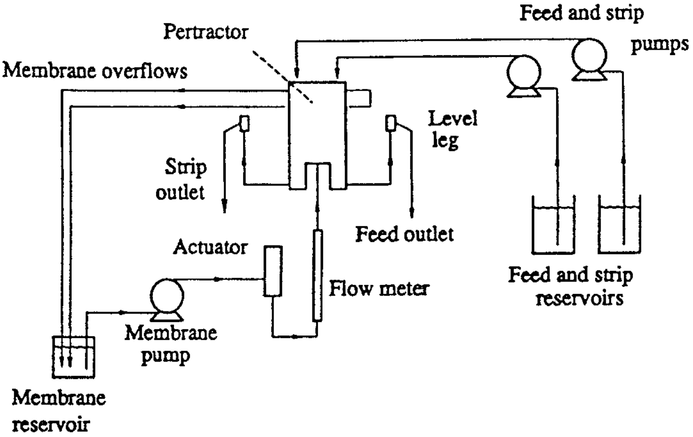

FIG. 3 Schematic of continuous bench-scale liquid membrane pertraction apparatus.

TABLE 1
Summary of Operating Conditions[a]

Run	Variable	Feed velocity (cm/min)	Membrane velocity (cm/min)	Strip velocity (cm/min)	Cr(VI) in strip inlet (mg/L)	Layers of cheesecloth	Solvent[b]	Support type[c]	Support cross-sectional area (cm^2)
1	Feed velocity	0.3–1.8	0	0.4	0	8	I	PVC OOF	2.0
2	Feed velocity	1.9–5.3	16.1	0.5	151	8	I	PVC SIF	1.6
3	Feed velocity	1.7–5.7	31.4	3.1	0	4	E	PG SIF	0.5
4	Feed velocity	2.7–9.4	26.2	2.6	0	2	E	PG SIF	0.3
5	Strip velocity	1.8	0	0.4–1.6	0	8	I	PVC OOF	2.0
6	Strip velocity	1.7	27.9	1.6–3.1	0	4	E	PG SIF	0.5
7	Strip velocity	7.8	27.9	3.1–6.5	0	4	E	PG SIF	0.5
8	Membrane velocity	2.6	0–29.1	0.5	151	8	I	PVC SIF	1.6
9	Membrane velocity	3.8	16.1–29.1	0.5	151	8	I	PVC SIF	1.6
10	Cr(VI) in feed inlet	3.1	4.3	1.1	0	8	I	PVC OOF	2.0
11	Cr(VI) in feed inlet	9.8	27.9	6.6	0	4	E	PG SIF	0.5
12	Cr(VI) in strip inlet	5.6	33.7	3.2	0–2134	4	E	PG SIF	0.5

[a] Densities of feed and strip solutions are 0.997 and 1.110 g/mL, respectively. Membrane cross-section areas: 23.4 cm^2 (Runs 1, 5, and 10), 15.5 cm^2 (Runs 2, 3, 6–9, 11, and 12), 16.5 cm^2 (Run 4).

[b] I = Isopar 2025, E = Exxsol D-60. Densities of Isopar 2025 and Exxsol D-60 membranes are 0.70 and 0.79 g/mL, respectively.

[c] PVC = polyvinyl chloride, PG = Plexiglas, OOF = open outer frame, SIF = solid inner frame.

summarizes operating conditions, the solvent, support type, and number of cheesecloth layers used. It should be noted that, as defined here, each test run corresponds to a series of experiments where one operating variable was systematically changed. Evidence that steady-state had been achieved is supported by comparison of the Cr(VI) mass fluxes across both supports after 24 hours of operation for various runs (Table 2), which shows that there is good agreement in most cases. After some experience with the pertractor, very good reproducibility was achievable. As an example, Table 3 gives a comparison of the response of the pertractor for two similar sets of flow velocities run 4 days apart.

Many of these experiments were carried out during one continuous 22-day stretch. During this time period, flow rates and compositions of the three streams were varied and supports changed without terminating the

TABLE 2
Comparison of Steady-State Cr(VI) Fluxes across the Feed and Strip Supports

	Flux (μg/cm²·min)	
Run[a]	Feed	Strip
1	1.02	0.98
2	1.38	1.39
3	0.87	0.75
4	0.52	0.60
5	1.42	1.24
7	0.81	0.84
9	1.68	1.33
10	2.07	2.07
12	0.87	1.02

[a] Each set of data corresponds to an experiment conducted during the run designated.

TABLE 3
Pertractor Reproducibility Attained for Two Similar Sets of Flow Velocities Run at Different Times

Velocity (cm/min)			Cr(VI) Concentration (mg/L)			
Feed	Strip	Membrane	Feed in	Feed out	Strip	Membrane
8.11	6.82	60	208	92	111	188
7.85	6.60	76	213	91	124	177

operation. The pertractor responded smoothly and reliably to changes, and performance remained stable throughout this period.

Effect of Operating Parameters

Feed Velocity

Runs 1 to 4 were conducted to investigate the effects of the feed stream velocity on the steady-state outlet concentrations of the three streams (Table 1). During each run the flow rates of the other two streams were kept constant. For the purposes of reporting the data, the measured volumetric flow rates have been converted to linear velocities from measurements of the densities and the cross-sectional areas of the liquid streams, also obtained during the test runs. The Cr(VI) level in the feed outlet reported here has been normalized with respect to the concentration in the feed inlet (denoted as $[\mathrm{Cr(VI)}]_{\mathrm{fout}}/[\mathrm{Cr(VI)}]_{\mathrm{fin}}$) to compensate for small differences in the inlet concentration from test to test.

As expected, an increase in the feed velocity in each run caused a rise in the Cr(VI) concentration in the outlet of that stream, presumably due to a lower residence time and less time for loading (Fig. 4a). However, at the same time, it also enabled more Cr(VI) to be transferred into the organic phase, leading to a higher outlet concentration as well (Fig. 4b). The higher Cr(VI) concentration in the membrane, in turn, increased the driving force for transfer at the organic–strip interface and resulted in a higher Cr(VI) level in the strip outlet (Fig. 4c).

An important question concerning pertractor performance is its ability to reduce the Cr(VI) level in the effluent below allowable discharge limits. As shown in Fig. 4(a), this can best be achieved at low feed velocity. The best result shown in the plot corresponds to a feed velocity of 0.3 cm/min during Run 1, when the feed stream was reduced from 296 to 6 mg/L Cr(VI), although pertractor performance was not optimized in this regard. The results of other experiments that are not presented have shown that discharge levels as low as 1 mg/L can be reached, well below most discharge standards.

The results in Figs. 4(a) and 4(c) show that attaining low Cr(VI) levels in the feed outlet by maintaining a low feed velocity comes at the expense of concentrating the metal in the strip phase. Thus, in applications where both of these objectives are desired, a compromise in feed velocity or a multistage operation would probably be required. This situation is not surprising and is the expected behavior for most separation processes. Note also that the outlet membrane and strip concentrations do not increase indefinitely as the feed velocity is raised, but instead level off to limiting values. Since these levels correspond to the maximum fluxes that

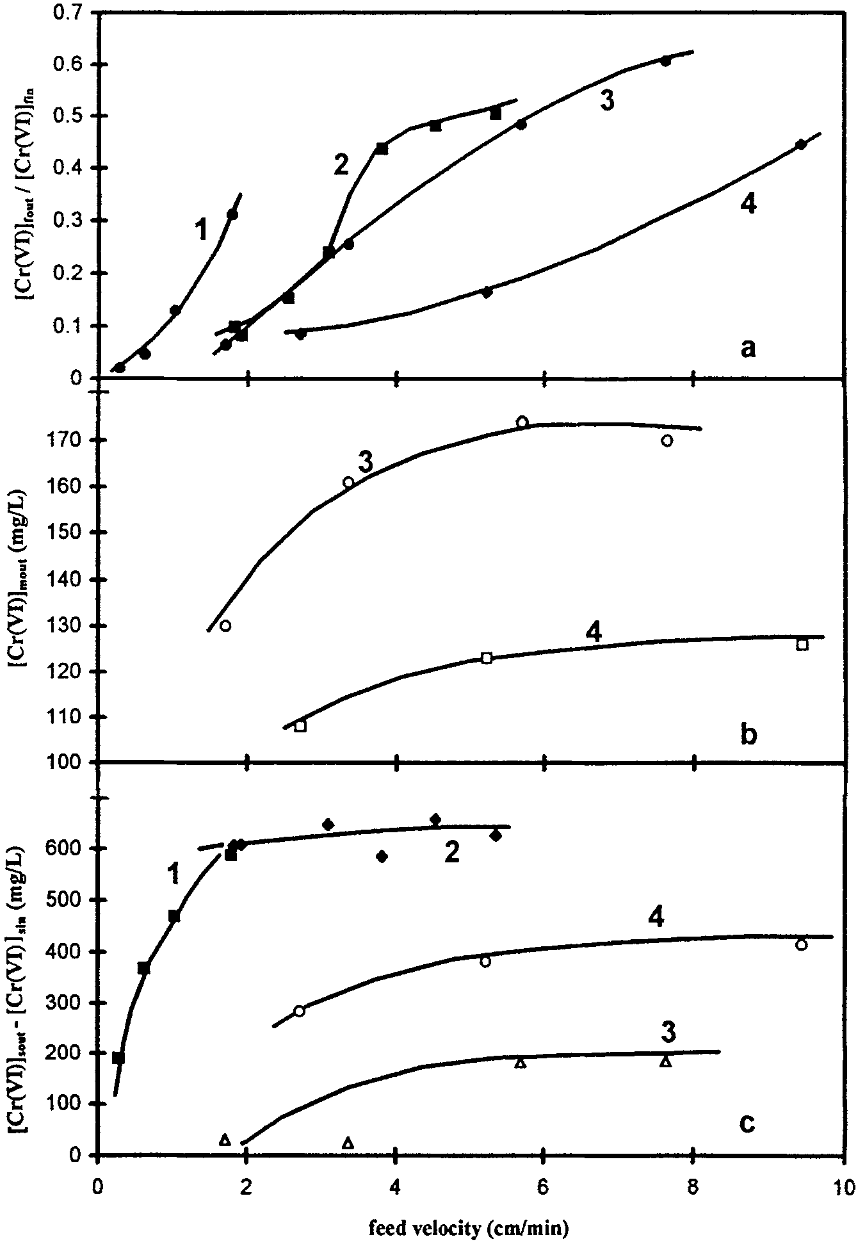

FIG. 4 Effect of feed velocity on the steady-state Cr(VI) concentrations in the pertractor discharges: (a) feed outlet, normalized with respect to the feed inlet concentration; (b) organic outlet; and (c) strip concentration change from inlet to outlet. The number next to each curve denotes the test run.

can be transferred, a further increase in feed velocity will accomplish nothing other than to diminish the efficiency of the process.

Comparison of the data for Runs 1 and 2 in Fig. 4 yields information on the influence of membrane velocity. As indicated in Table 1, the most important difference in the operating conditions of Runs 1 and 2 with regard to loading is the membrane velocity. An increase in velocity from 0 cm/min in Run 1 to 16.1 cm/min in Run 2 brings about a considerable improvement in Cr(VI) loading, as reflected in a shift in the curve in Fig. 4(a) to the right. This observation suggests that Cr(VI) loading is limited by some sort of resistance at the membrane–feed interface. It is difficult to assess its effect on the stripping reaction on the basis of Fig. 4(c) since the amount of Cr(VI) transferred appears to reach a limit at higher feed velocities.

The influence of the number of cheesecloth layers used can be examined by comparing the data in Fig. 4 for Runs 3 (4 layers) and 4 (2 layers). One observation is the large effect of cheesecloth number on the outlet concentrations of all three phases. As shown in Figs. 4(a) and 4(c), the reduction in the number of layers from 4 to 2 is beneficial, substantially lowering the Cr(VI) concentration in the feed outlet and raising it in the strip outlet.

A change in the number of cheesecloth layers would be expected to alter the residence times of the aqueous phases and mass transfer resistance across the supports. The first of these can only be of secondary importance since otherwise an elevated Cr(VI) concentration in the feed outlet would be expected as the number of layers is reduced rather than the lowering that is observed. It therefore appears that mass transfer resistance is the crucial factor limiting the exchange process at each support, in agreement with the conclusion made on the basis of the effect of membrane velocity on Cr(VI) loading.

Strip Velocity

The effect of the strip velocity on the Cr(VI) concentrations in the three outlet streams can be seen in Fig. 5. Over the experimental conditions evaluated, the results show that the outlet feed concentration is not strongly affected by strip velocity (Fig. 5a). However, at the same time, the Cr(VI) level in the strip outlet decreases as the strip flow rate increases (Fig. 5c), which is not surprising since the residence time of this stream is decreasing. Furthermore, this drop is steep enough at low strip velocities (Run 5) that the Cr(VI) flux from the organic phases diminishes as well. The combined effects of a constant flux entering the organic phase from the feed and a declining flux leaving leads to a rise in the membrane

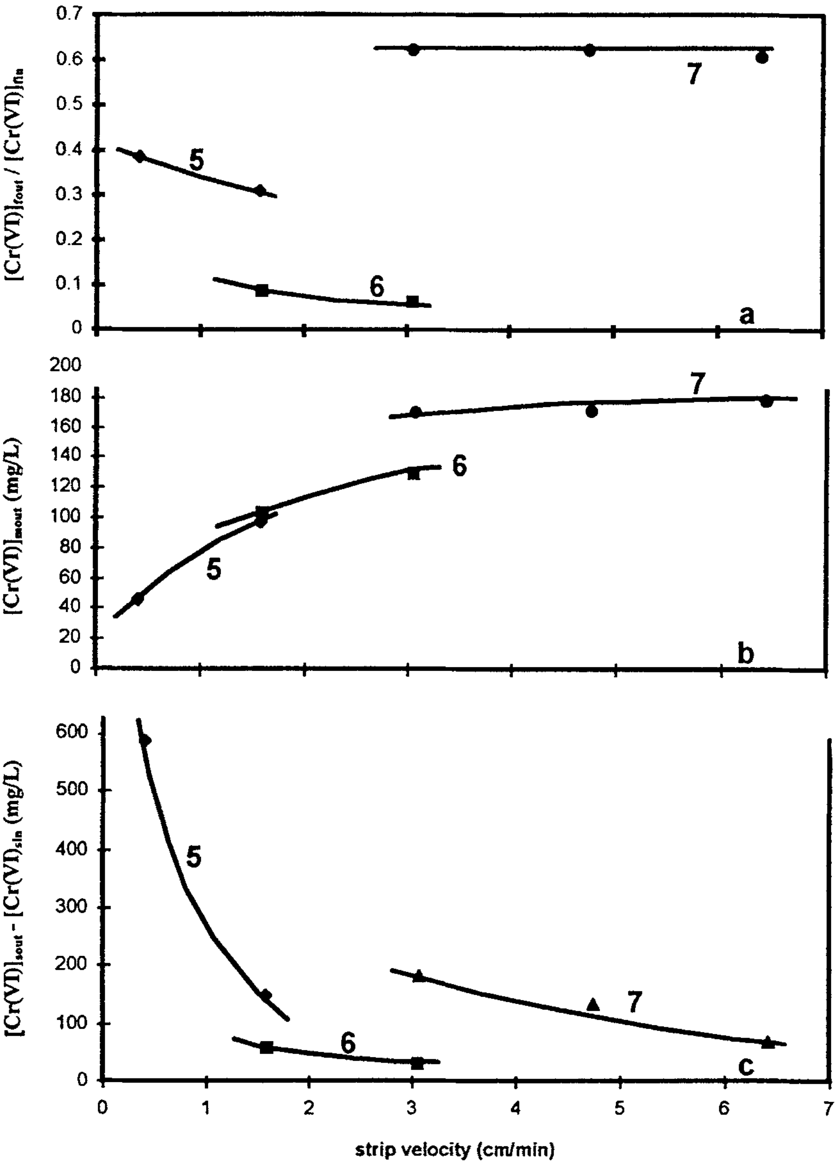

FIG. 5 Effect of strip velocity on the steady-state Cr(VI) concentrations in the pertractor discharges: (a) feed outlet, (b) organic outlet, and (c) strip concentration change from inlet to outlet. The number next to each curve denotes the test run.

concentration with increasing strip velocity, as observed in Fig. 5(b). Under the conditions of these experiments, Aliquat 336 is far enough away from saturation with respect to Cr(VI) that it can accommodate these changes in the flux.

Membrane Velocity

The influence of membrane velocity on Cr(VI) loading was discussed previously with regard to Fig. 4. Its effect on Cr(VI) loading and stripping is shown more completely over a wider velocity range in Fig. 6. The results show that an increase in velocity, particularly above 16 cm/min, improves pertractor performance by simultaneously decreasing the feed outlet concentration and increasing the strip outlet concentration. Similar to the effect observed with the number of cheesecloth layers used on the supports, this confirms the conclusion that resistance at the aqueous–organic interface contributes significantly to mass transfer limitations. This is further substantiated by the data in Fig. 6 which show that the positive effect of membrane velocity on pertractor performance is enhanced by operating at a feed velocity of 3.8 cm/min (Run 9) over that at 2.6 cm/min (Run 8).

Inlet Composition of Aqueous Phases

In most of the experiments of this study, the inlet compositions of the aqueous phases were kept approximately constant; however, a few runs were conducted to investigate the effect of Cr(VI) level and pH of the feed inlet and the effect of Cr(VI) concentration in the strip inlet. Although it is not surprising that the outlet concentration in the feed stream increases with a rising Cr(VI) concentration in its inlet, the strong dependence between the two in the data shown in Fig. 7 is noteworthy. In an operation involving actual industrial effluents, it would be preferable for the discharge to be less sensitive to variations in the inlet. Further experiments need to be done to study the dependence of the pertractor behavior on the Cr(VI) level in the feed inlet for other operating conditions and to determine conditions where the sensitivity is lower.

The pH of the incoming feed is an important consideration in practical situations not only because of its direct influence on Cr(VI) loading but also because of the pH rise that occurs during loading. Due to the likely presence of metal cations in the effluent, too high a pH in the outlet could cause the undesired precipitation of these metals in the pertractor. Batch equilibrium loading experiments of the Cr(VI)/Aliquat 336 system in our laboratory had previously shown that the pH remained virtually constant, provided the initial pH was maintained below 2.2. However, if the initial

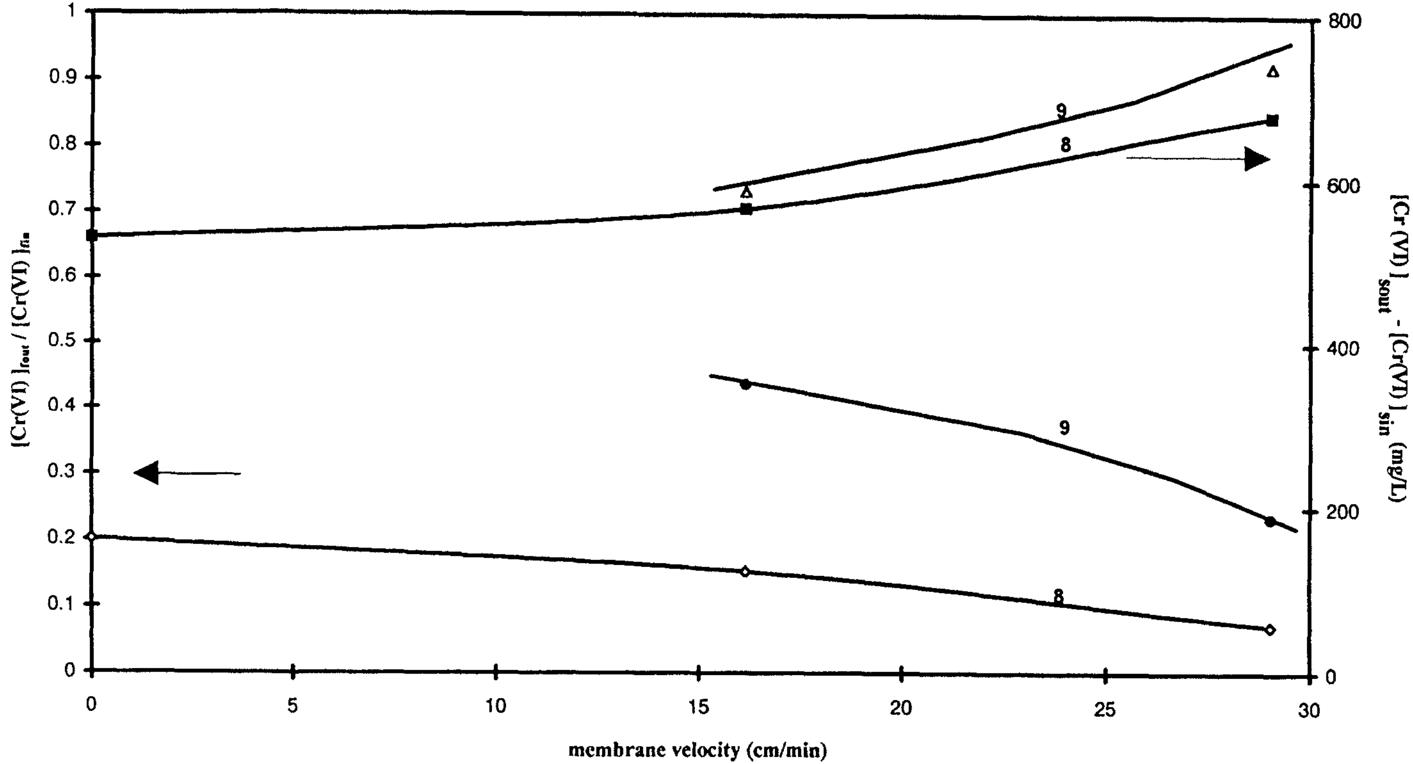

FIG. 6 Effect of membrane velocity on the steady-state Cr(VI) concentrations in the feed and strip outlet streams during test Runs 8 and 9.

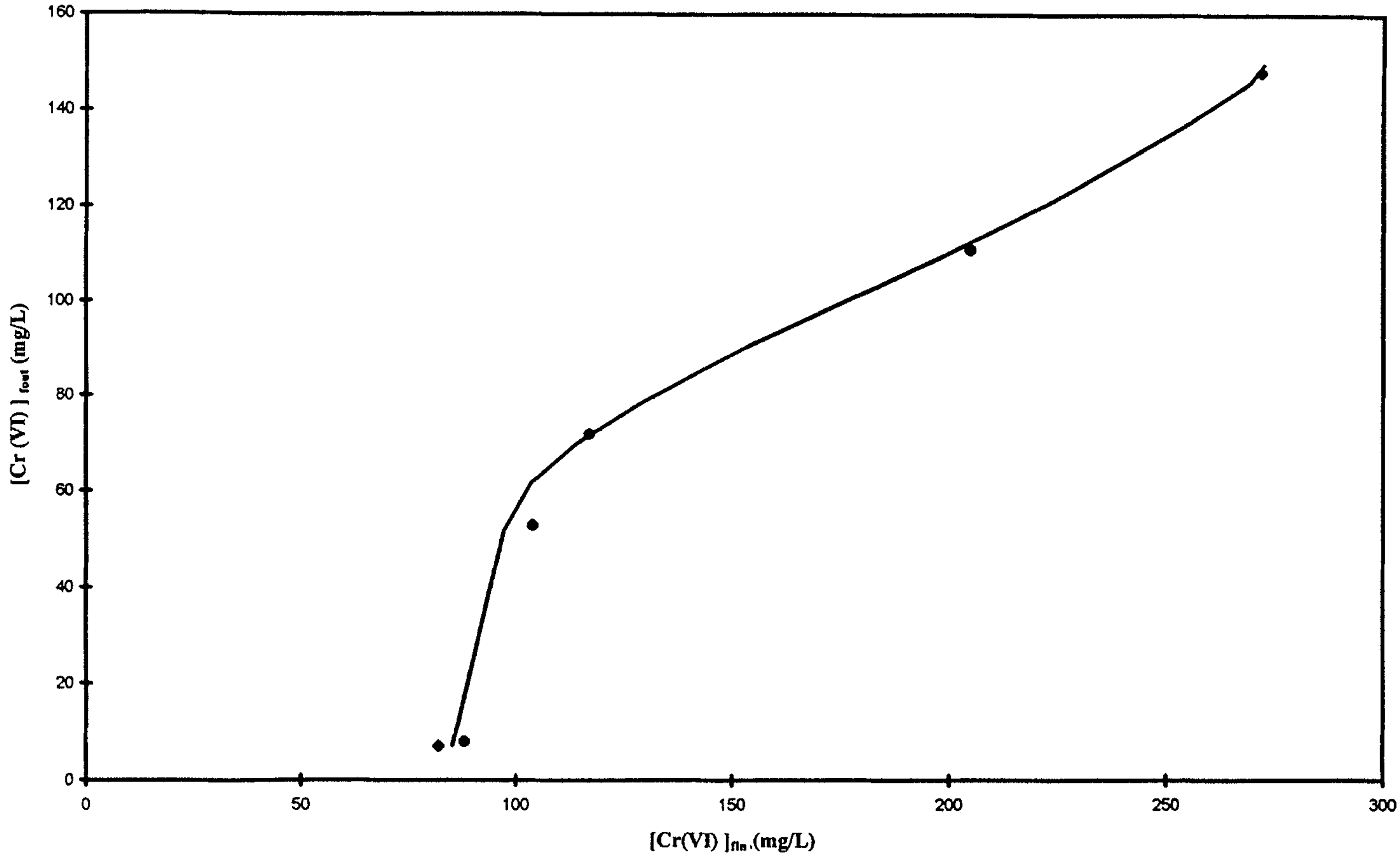

FIG. 7 Effect of Cr(VI) concentration in feed inlet on the steady-state Cr(VI) concentration in the feed outlet during test Runs 10 (◆) and 11 (●).

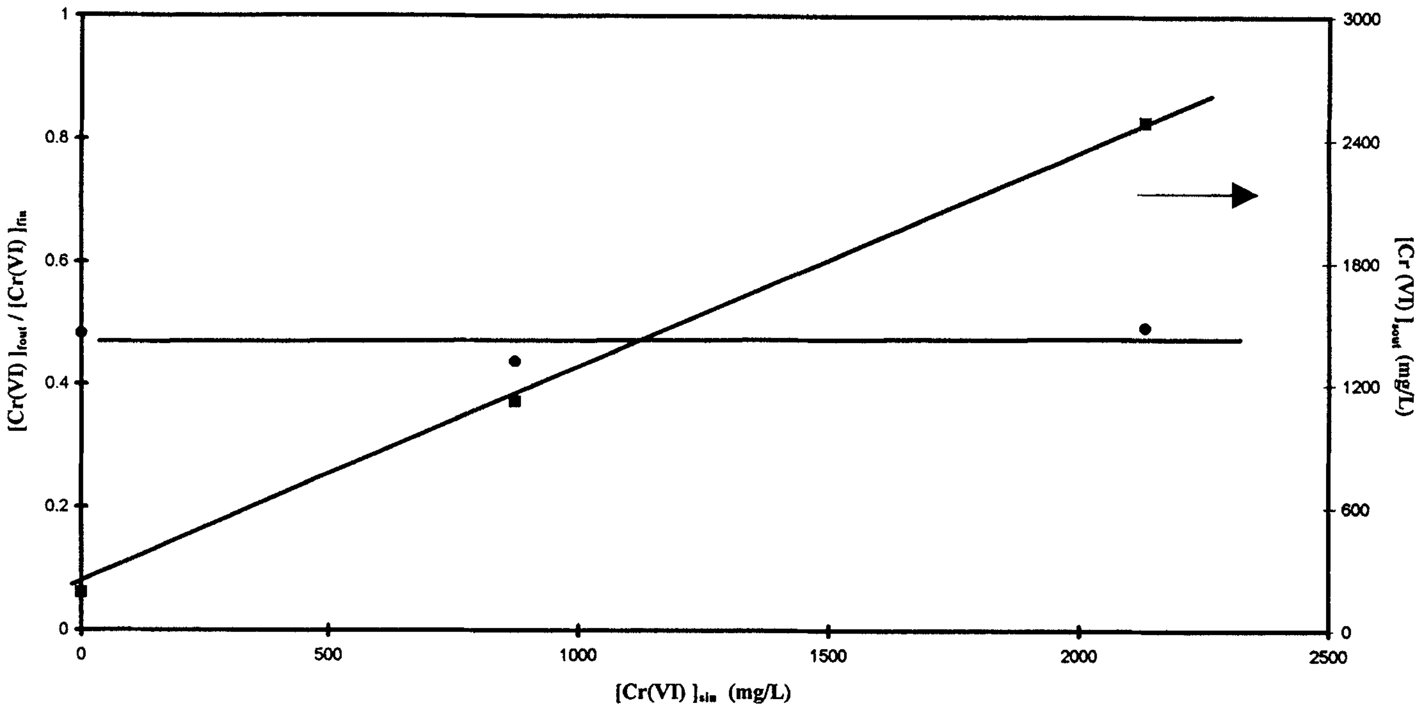

FIG. 8 Effect of Cr(VI) concentration in strip inlet on the steady-state Cr(VI) concentration in the feed outlet (●) and strip outlet (■) during test Run 12.

pH was raised above this level by only 0.5 units, the equilibrium pH rose dramatically to above 10. In order to determine whether this would be a problem in the operation of the pertractor, the effect of inlet pH was studied for values varying between 1.9 and 2.4, the range over which the pH increased very sharply in the equilibrium studies. Fortunately, the pH of the feed stream was found to behave quite differently in these pertraction runs and showed virtually no change as it was discharged. In addition, the Cr(VI) concentrations in the feed and strip outlets were unaffected by the variation of inlet feed pH in these runs. Evidently the exchange reactions at both supports are never close enough to equilibrium for the system to become depleted of H^+ ions, and consequently the question of inlet feed pH should not be an issue during pertractor operation.

In many envisaged applications where the recovery of highly concentrated Cr(VI) solutions is desired, it will be most practical if part of the strip outlet stream could be returned for reuse and the remainder replenished with a NaOH solution before being recirculated back through the pertractor. Thus, it is important to assess the performance of the pertractor when the strip inlet already contains significant amounts of Cr(VI). Results are shown (Fig. 8) for experiments in which the strip inlet concentration was varied from 0 to 2134 mg/L with all other parameters held constant. Over this range, the strip outlet concentration varied linearly with the inlet concentration. Most importantly, concentration of the strip phase by approximately 350 mg/L was possible at the highest inlet concentration using the same 3.0 N NaOH level as in the previous runs. At the same time, the data show that performance on the feed side of the unit was unaffected.

CONCLUSIONS

It is apparent from this study that liquid membrane pertraction can be used for the removal and concentration of Cr(VI) from aqueous effluents. The particular characteristics of the Cr(VI)/Aliquat 336/NaOH system utilized in the pertractor necessitated several important modifications to its design and operation. The unit performed smoothly and stably during continuous test runs. Moreover, the modifications were found to have some important advantages over the original design. The effect of a number of operating parameters, such as design and composition of the membrane supports, velocities of the three liquid streams, and inlet compositions of the aqueous phases, was also studied. Further work is needed to optimize operating conditions with respect to lowering the Cr(VI) in the effluent discharge and raising the Cr(VI) flux into the strip phase.

It will be advantageous to develop a pertractor mathematical model for the Cr(VI)/Aliquat 336/NaOH system for the purposes of design optimization and technoeconomic evaluation. This will allow the possible advantages of using this technology for Cr(VI) treatment to be assessed and the applications for which it is most appropriate to be ascertained. The data obtained in this study will be useful in developing such a model.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the Ontario Ministry of the Environment which sponsored this research project under their Research Grant Program (Project 545G). They also express their thanks to M. Knechtel who typed the manuscript and to P. Kristof who prepared the figures.

REFERENCES

1. American Petroleum Institute, *The Sources, Chemistry, Fate and Effects of Chromium in Aquatic Environments*, Washington, D.C., 1981.
2. R. D. Noble and J. D. Way (Eds.), *Liquid Membranes. Theory and Applications* (ACS Symposium Series 347), American Chemical Society, 1987.
3. N. N. Li, *AIChE J.*, *17*, 459 (1971).
4. R. P. Cahn and N. N. Li, *Sep. Sci.*, *9*, 505 (1974).
5. A. M. Hochhauser and E. L. Cussler, *AIChE Symp. Ser.*, *152*, 136 (1975).
6. T. P. Martin and G. A. Davies, *Hydrometallurgy*, *2*, 315 (1977).
7. G. Casamatta, C. Chavarie and H. Angelino, *AIChE J.*, *24*, 945 (1978).
8. T. Kitagawa, Y. Nishikawa, J. W. Frankenfeld, and N. N. Li, *Environ. Sci. Technol.*, *11*, 602 (1977).
9. E. J. Fuller and N. N. Li, *J. Membr. Sci.*, *18*, 251 (1984).
10. J. Strzelbicki, W. A. Charewicz, and A. Mackiewicz, *Sep. Sci. Technol.*, *19*, 321 (1984).
11. E. Salazar, M. I. Ortiz, and J. Irabien, *Inst. Chem. Eng. Symp. Ser.*, *119*, 279 (1990).
12. Y. Mori, H. Uemae, S. Hibino, and W. Eguchi, *Int. Chem. Eng.*, *30*, 124 (1990).
13. E. Salazar, M. I. Ortiz, A. M. Urtiago, and J. Irabien, *Ind. Eng. Chem. Res.*, *31*, 1523 (1992).
14. S. Matsumoto, T. Inoue, M. Kohda, and K. Ikura, *J. Colloid Interface Sci.*, *7*, 555 (1980).
15. P. Colinart, S. Delephine, G. Trouve, and H. Renon, *J. Membr. Sci.*, *20*, 167 (1984).
16. L. Boyadzhiev, *Sep. Sci. Technol.*, *25*, 187 (1990).
17. R. W. Baker, M. E. Tuttle, D. J. Kelly and H. K. Lonsdale, *J. Membr. Sci.*, *2*, 213 (1977).
18. H. K. Lonsdale, *Ibid.*, *10*, 81 (1982).
19. P. R. Danesi, *Sep. Sci. Technol.*, *19*, 857 (1984).
20. P. R. Danesi, L. Reichley, and P. G. Rickert, *J. Membr. Sci.*, *31*, 117 (1987).
21. R. M. Izatt, J. D. Lamb, and R. L. Bruening, *Sep. Sci. Technol.*, *23*, 1645 (1988).
22. K. H. Lee, D. F. Evans, and E. L. Cussler, *AIChE J.*, *24*, 860 (1978).
23. T. Largman and S. Sifniades, *Hydrometallurgy*, *3*, 153 (1978).

24. K. L. Smith, W. C. Babcock, R. W. Baker, and M. G. Conrod, in *Chemistry in Water Reuse,* Vol. 1 (J. Cooper, Ed.), Ann Arbor Science, Ann Arbor, Michigan, 1981, p. 311.
25. M. Teramoto and H. Tanimoto, *Sep. Sci. Technol., 18,* 871 (1983).
26. A Sengupta, R. Basu, R. Prasad, and K. K. Sirkar, *Ibid., 23,* 1735 (1988).
27. M. Teramoto, N. Tohno, N. Ohnishi, and H. Matsuyama, *Ibid., 24,* 981 (1989).
28. O. Loiacono, E. Drioli, and R. Molinari, *J. Membr. Sci., 28,* 123 (1986).
29. R. Molinari, E. Drioli, and P. Pantano, *Sep. Sci. Technol., 24,* 1015 (1989).
30. L. Boyadzhiev, E. Bezenshek, and Z. Lazarova, *J. Membr. Sci., 21,* 137 (1984).
31. L. Boyadzhiev and Z. Lazarova, *Chem. Eng. Sci., 42,* 1131 (1987).
32. L. Boyadzhiev and E. Bezenshek, *J. Membr. Sci., 37,* 277 (1988).
33. L. Boyadzhiev and I. Atanassova, *Biotechnol. Bioeng., 38,* 1059 (1991).
34. American Public Health Association, American Waterworks Association and Water Pollution Control Federation, *Standard Methods for the Examination of Water and Wastewater,* 15th ed., Washington, D.C., 1980.
35. B. G. Fraser, M.A.Sc. Thesis, University of Waterloo, Waterloo, Canada, 1993.
36. Environment Canada, *Recovery of Chromium from Plating Shop Wastewaters* (Environmental Protection Series Report EPS 3/SF/1), 1990.
37. E. Salazar, M. I. Ortiz, and A. M. Urtiaga, *Ind. Eng. Chem. Res., 31,* 1516 (1992).
38. M. W. Horn, B. G. Fraser, M. D. Pritzker, and R. L. Legge, *Sep. Sci. Technol., 29,* 535 (1994).

Received by editor February 7, 1994