Affinity Dialysis-A Method of Continuous, Rapid Metal Ion Separation Using Dialysis Membranes and Selective, Water-Soluble Polymers as Extractants

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Affinity Dialysis—A Method of Continuous, Rapid Metal Ion Separation Using Dialysis Membranes and Selective, Water-Soluble Polymers as Extractants

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Abstract

A membrane process utilizing dialysis and selective complexation by water-soluble polymers has been developed. This process, termed affinity dialysis, has been shown to selectively extract and concentrate both cations and anions in a manner similar to ion exchange or solvent extraction. The selective removal of calcium from sodium with selectivity of about 30, removal of chromate ion from dilute streams, and separation of transition metal ions such as Cu/Fe and Cu/Zn have all been successfully demonstrated. Effects of different polymers, polymer concentration, temperature, and flow rates have been studied. The effect of increased polymer concentration is to increase product concentration if appropriate changes in feed, polymer solution, and strip flow rates are made. A continuous polymer solution recycle and regeneration system has been constructed and operated with Cu/Zn and chromate/chloride feed streams. Removal of over 95% of the desired ion in one pass and concentration factors of product over effluent in excess of 100 have been achieved at feed flow rates of 24 gal/d. Product concentrations of greater than 3% from as little as 400 ppm feed have been demonstrated in a continuous process. In addition, the degree of polymer loss to the effluent stream has been shown to be less than 0.01%/d for a typical system. Metal removal from typical feeds is about 0.9 g/m² per 1000 ppm metal in the feed. It is expected that this technique may be useful in the separation of organic and biological materials, as well as for ionic species.

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INTRODUCTION

Dialysis is one of several membrane processes in commercial practice. Other membrane processes such as gas permeation, ultrafiltration, microfiltration, reverse osmosis, and electrodialysis are better known unit operations, but the use of dialyzers for artificial kidney treatments has been one of the most profitable and largest volume uses of membranes (*1*).

Of the membrane processes listed above, dialysis differs from the majority along with electrodialysis in that pressure differential across the membrane is not the driving force behind mass transfer. In electro-dialysis, electrical energy is the motive force behind the separation while in dialysis the concentration gradient from one side of the membrane to the other is the principal driver. Unlike virtually all of the other processes mentioned, permeation of different species in dialysis may occur in both directions across the membrane simultaneously, leading to the recent interest in dialysis membranes for use in bioreactors (*2*). A key difference to note is that dialysis uses only the concentration gradient as the driving force for mass transfer and hence dialysis units need not be designed to withstand high pressure differentials.

This paper will describe a membrane process, affinity dialysis, which uses water-soluble polymeric materials with chelating, adsorption, or specific affinity properties in combination with a semipermeable membrane designed to retain the polymeric material but freely permeable to the species to be chelated or adsorbed. A wide variety of water-soluble polymers may be used but this report will be restricted to the description of the use of two polymers—poly(ethylenimine) (PEI) and poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (Poly-AMPS).

Several types of membranes and membrane devices have been studied using the polymers described above. Cellulose and polysulfone hollow fibers were used. Membrane mass transfer coefficients:

$$Q_F(C_{F1} - C_{F2}) = Q_D(Q_{D2} - Q_{D1}) = KA\Delta C_{lm} \qquad (1)$$

and

$$\Delta C_{lm} = \frac{(C_{F1} - C_{D2}) - (C_{F2} - C_{D1})}{\ln[(C_{F1} - C_{D2})/(C_{F2} - C_{D1})]} \qquad \text{(log mean concentration} \quad (2)\\ \text{gradient}$$

where Q_F = feed flow rate
Q_D = dialysate flow rate

C_{FI} = concentration of solute in feed inlet
C_{F2} = concentration of solute in feed outlet
C_{DI} = concentration of solute in dialysate inlet
C_{D2} = concentration of solute in dialysate outlet
K = mass transfer coefficient
A = membrane area

were determined for aqueous/aqueous systems as a control and on aqueous/polymer solution as a means of determining any effect of the polymer on mass transfer coefficient through the membrane.

Figure 1 is a diagrammatical representation of the affinity dialysis process. For purposes of illustration, Cu(II) ions are shown diffusing from a mixed ion feed stream across a membrane via pore diffusion (3) where they are bound to a chelating polymer. The Cu(II) will continue to concentrate until the bulk of the available binding sites on the polymer are occupied. Other ions not bound as strongly to the polymer (represented by X in the diagram) migrate freely across the membrane in both directions but do not concentrate to the same degree. These nonbound moieties can be removed easily from the Cu(II) enriched polymer stream via a smaller dialysis scrubbing stage. After a suitable pH change to destroy the copper–polymer complex, a separate stripping unit (with another membrane to retain the polymer) allows the Cu(II) to be removed by diffusion.
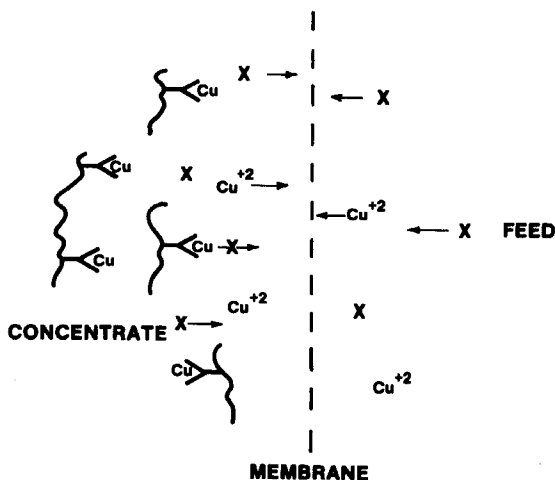

FIG. 1. Schematic of affinity dialysis process.

Although the affinity dialysis process is potentially useful for separating many mixtures of small molecules, only three systems have been studied in these exploratory experiments. Cu(II)/Zn(II), Ca(II)/Na(I), and chromate/chloride separation have been successfully demonstrated using this method. Other applications envisioned but not yet studied include other metal ion separations; purification of streams containing organic acids, glycols, or other adsorbable components; water softening applications using chelating polymers; and separation of biologicals such as hormones, peptides, or pharmaceuticals using selective binding materials such as monoclonal antibodies.

Several other membrane systems have been described which selectively separate ions from solution. In most cases (*4–6*), these processes have been pressure-driven ultrafiltration or reverse osmosis rather than the concentration-gradient-driven process described in this report. In any pressure-driven membrane process with suspended or dissolved materials, concentration polarization occurs (*6*) which can result in substantial loss of flux due to blinding or fouling of the membrane surface on the high pressure side. This limits the concentration of polymer or suspended adsorbent which may be economically useful in any pressure-driven system. Since affinity dialysis does not require significant transmembrane pressures or net fluid flux through the membrane, this polarization or fouling is not expected to occur.

An additional means of selective extraction using membranes involves the use of a selective solvent extractant, immiscible in both the feed solution and the strip reagent used on opposite sides of the membrane (*7*). The extractant is imbibed into the pores of a highly porous membrane, providing a hydraulic barrier to direct aqueous transport across the membrane. Desired ions are then transported across the membrane by the selective carrier via facilitated transport. These systems are prone to loss of selectivity due to excessive transmembrane pressure, forcing the solvent/carrier out of the pores of the membrane—hence developing leaks across the film. An additional problem is the maintenance of the solvent/carrier in such a small volume as the pores of the membrane— the slight solubility of these reagents in the feed stream effluent requires periodic replacement of either the extractant or the entire membrane (*8*).

An analogue of this technique was recently announced (*9, 10*) by Kim, although such a system has been alluded to by others (*11, 12*). The system can best be described as a membrane solvent extraction contactor. The solvent, although immiscible with water, is retained inside a porous hollow fiber membrane while a stream of feed is passed in a counter-current fashion on the other side of the membrane. Solutes diffuse

through the membrane and are concentrated in the selective solvent. This system is effective in controlling the loss of solvent into the feed due to entrainment of small particles, often called mist or rag by solvent extraction technologists, which are normally present in common solvent extraction systems. However, loss of extractant due to solubility in the aqueous feed and contamination of the solvent with entrained water are significant problems with this system (*10*).

One appealing aspect of the affinity dialysis process is its promise of continuous operation. An additional advantage is the ability to use high concentrations of chelating polymers without the undesirable side effect of concentration polarization or other membrane fouling (*6*). A system with complete polymer loading, stripping, regeneration, and recycle has been designed, assembled, and successfully operated.

Two chemical systems were selected for study using the recycle system. Both are of commercial interest. The first, separation of copper ion from zinc ion, is important in the treatment of acid waste from chemical brightening and etching of brass. The second area of interest is the concentration and recovery of hexavalent chromium from waste streams such as chrome plating plant effluent. It has been reported that as much as 80% of the purchased metal at typical platers is lost in the effluent (*13*). More important, proposed government regulations may force platers to recover this valuable metal, not due to its value, but to its severity as a pollutant.

EXPERIMENTAL SECTION

Extraction Studies

Hollow fiber units normally provided as artificial kidneys by Travenol Laboratories, Inc. as CF Model 12*11 or Hospal as Disscap 080 were disassembled and the hollow fibers removed to provide a membrane source for manufacturing small tube-in-shell units. A few of the earlier experiments were performed utilizing similar fibers from Spectrum Medical Industries, Inc. (Spectrapor 5000 molecular weight cutoff fibers). In all cases the fibers were manufactured from regenerated cellulose. Figure 2 is a schematic of the hollow fiber units which had cases constructed of 316 stainless steel, contained 150 cm^2 of membrane (170 fibers), and had tubesheets made of Dow Corning RTV silicone adhesive. Countercurrent efficiencies of these units were determined by comparing the mass transfer coefficients of these units as a function of dialysate flow
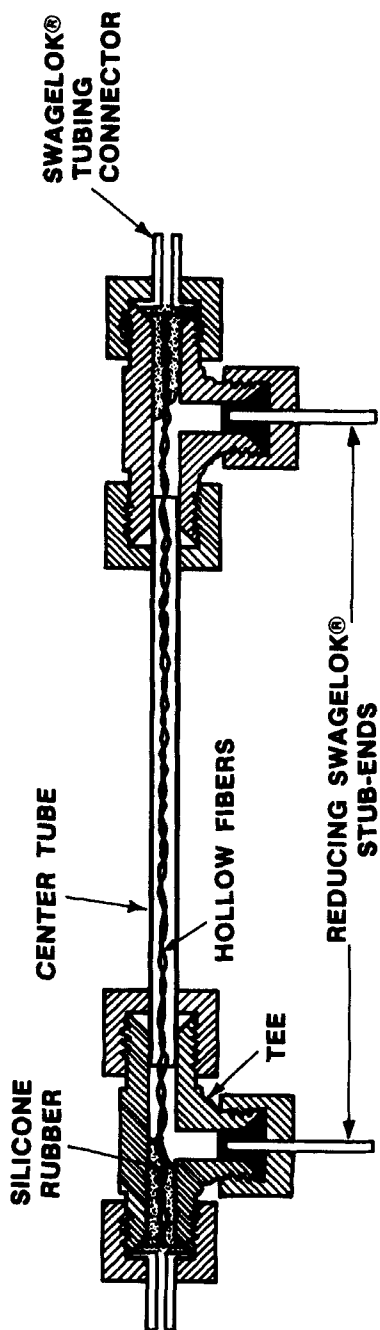
FIG. 2. Schematic of cellulose hollow units. Surface area = 150 cm^2.

rate to the reported values for the Travenol units using Westbrook's calculation method for mass transfer coefficients (*14*).

Initial experiments were conducted using a system with feed flowing single pass through the lumen countercurrent to the polymer solution which was recycled to ensure maximal loading of the polymer with the desired extractable species. Typically a multichannel peristaltic pump (Ismatec IPS) was used to provide flow on both sides of the membrane. In some of the later experiments, a backpressure device was installed on the outlet polymer stream to apply a variable pressure, i.e., 10 psi, to that side of the membrane. That pressure was sufficient to offset the tendency for the polymer solution to draw water through the membrane via osmosis (or more correctly, oncosis in the case of polymers). Analyses for total calcium were performed by EDTA titration using a Hach Co. calcium analysis kit, while colorimetric methods for Cu(II), total chrome, and Cr(VI) were also obtained from Hach to allow monitoring of these ions on a semicontinuous basis. A Shimadzu UV 160 was used for spectral scans and for the colorimetric analyses. Final samples of polymer solution, feed, and reject were submitted for inductively coupled plasma emission spectroscopic analysis as a confirmation of the colorimetric and titration results as well as for sodium and potassium where appropriate. Chloride samples were analyzed using a Corning Chloridimeter. pH was adjusted with the aid of an Orion pH meter calibrated at pH 7.00 with standard buffer.

Hollow fiber membranes were flushed by pumping distilled water through both sides of the fiber units for 10 min prior to use and were kept wet thereafter. All membranes and membrane units were stored in a 2% formaldehyde preservative when not in use.

The continuous countercurrent mode was used for longer term steady-state experiments. The Ismatec peristaltic pump was used for pumping the feed through the shell of the hollow fiber units, and a Sage syringe infusion pump was used to pump polymer solution through the inside of the fibers at a slow, controlled rate countercurrent to the feed flow.

Hollow fiber artificial kidneys obtained from Hospal, 69 Meyzieu, France, designated Disscap 80 and Disscap 140 with 0.8 and 1.4 m^2 surface area were used for the continuous recycle system shown in Fig. 3. In the strip section of the chromate recovery system, a product with 0.1 m^2 surface area obtained from Amicon Corp., Danvers, Massachusetts, was used due to the superior chemical stability of its hollow fibers. That unit had a 3000 molecular weight cutoff while the Disscap units had regenerated cellulose membranes with a 5000 molecular weight cutoff.

Polymer solution, strip, and feed flows were controlled by Ismatec peristaltic pumps while the strip and regeneration reagents were pumped
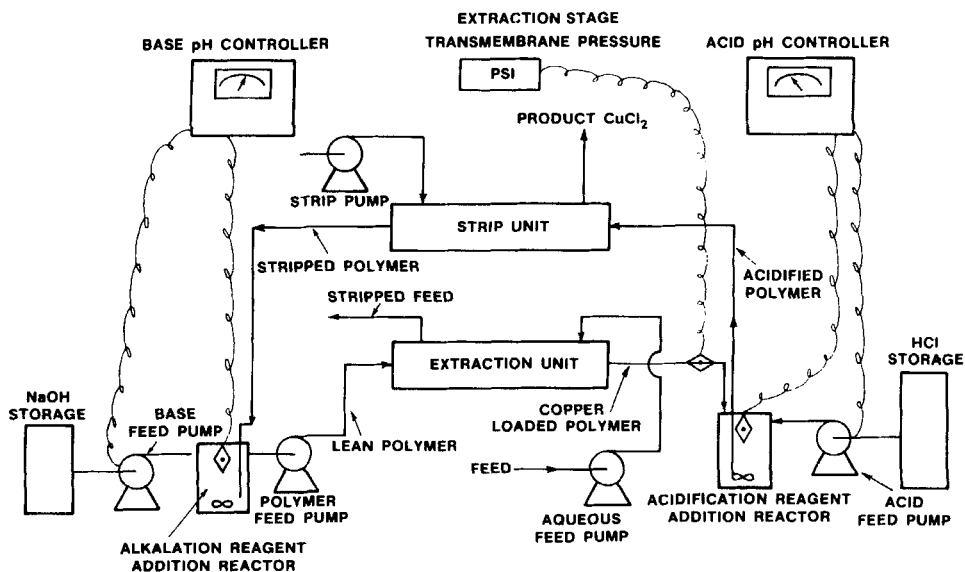
FIG. 3. Schematic of a complete affinity dialysis miniplant with polymer solution stripping, regeneration, and recycle.

with all-Teflon reagent feed pumps obtained from Cole-Parmer. The reagent pumps were slaved to pH controllers to ensure proper rates of reagent addition.

Recording pH controllers Model (5997-30) were obtained from Cole-Parmer. Each was equipped with a pH probe mounted in the appropriate reagent addition reactor and controlled the pH within 0.1 unit of the set point.

All chemicals were reagent grade or better and were obtained from a variety of commercial sources. Concentrated HCl and 50% NaOH were used for pH adjustment in the addition reactors to minimize the amount of water added to the system. Poly(ethylenimine) was obtained from BASF (their product designation: Polymin-P). The PEI was diafiltered extensively through a PM10 hollow fiber module from Amicon (minimum 6-fold water exchange) to remove low molecular weight components. After diafiltration, the polymer content was determined gravimetrically. Poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (poly-AMPS) was used as received from Aldrich. A 2.5% w/v solution contains 0.12 meq/mL of sulfonate ion-exchange capacity.

The miniplant was operated for several months in the mode shown, separating either chromate from chloride or copper from zinc. Not shown is a backpressure device located on the polymer recycle loop between the extraction stage and the acid addition reactor. That device ws designed to provide an easily controlled means of applying backpressure to the polymer solution stream in the extraction stage to offset any osmotic pressure due to the high polymer concentrations used. The unit was a ¼-in. stainless steel Swag-lok tee with the straight run drilled out to ¼ in. and small sections of ⅛ in. stainless tubing covered with a section of ¼ in. silicone rubber tubing inserted through the run of the tee. The center section of the silicone tubing was unsupported. The fittings of the ends of the tee were tightened down on the stainless tubing supported silicone tubing to form a seal at the ends. The side-arm of the tee was connected to a regulated nitrogen gas supply. By adjusting the nitrogen pressure on the flexible tubing in the run of the tee, precise backpressure control was possible. By measuring the feed input to the extraction unit and the effluent out of the extraction unit, it was possible to adjust the backpressure to a value such that no net change in flow before and after the extraction stage was observed.

RESULTS AND DISCUSSION

Validation of the Efficiencies of the Hollow Fiber Test Units

Figure 4 represents dialysis results with dialysate flow on the shellside (squares) and tubeside (circles). The average value for the mass transfer coefficient for calcium chloride—1.4×10^{-2} cm/min—is approximately 80% of that reported by Travenol in their literature (corrected for temperature). This discrepancy in mass transfer coefficient is due to the flow dynamics on the shellside of our units. In the original dialyzer, the fiber packing density is both more uniform and higher, thus leading to higher mass transfer coefficients.

Cation Extraction Studies with Recycle of Polymer Solution

Extraction Studies Using Poly(2-Acrylamido-2-methylpropanesulfonic Acid) (Poly-AMPS). Figure 5 shows the increase with time in calcium concentration in 50 mL of a 2.5% solution of poly-AMPS in water. After adjusting the solution pH to 7 with 50% sodium hydroxide, a

FIG. 4. Effect of flow rates and flow channel on the mass transfer coefficient of calcium chloride in 150 cm^2 hollow fiber units. Feed flow at 1.0 mL/min: (O) shellside feed, (X) tubeside feed.

FIG. 5. Extraction of calcium ion using a 2.5% Poly-AMPS solution: 150 cm^2 cellulose hollow fiber unit, feed = 160 ppm calcium ion, 1000 ppm sodium chloride at a flow rate of 0.70 mL/min, polymer solution recirculated at 4.0 mL/min. (O) Polymer calcium concentration, (X) effluent calcium concentration.

unit made from Travenol hollow fibers was used to expose the polymer
solution to a feed stream of 160 ppm calcium ion as the chloride and 1000
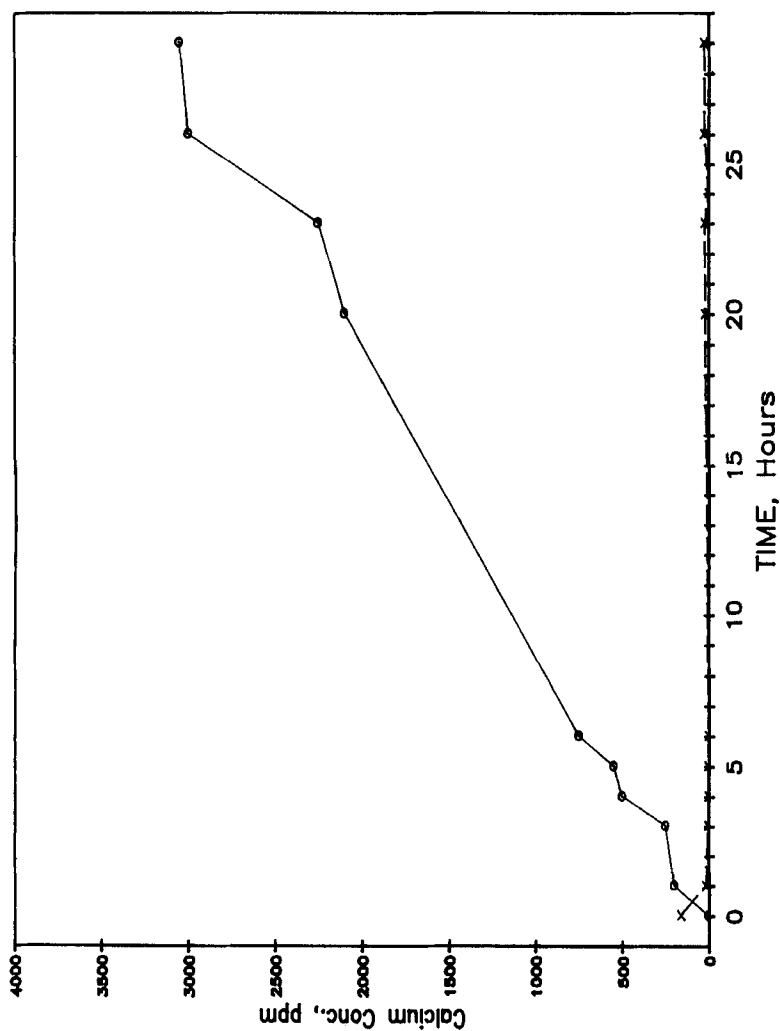ppm sodium chloride. The feed stream was pumped through the fiber
lumen at a rate of 0.70 mL/min and the polymer solution recirculated
countercurrent through the shell at 4.0 mL/min. The volume of the
polymer solution increased from 50 to 70 mL over the course of the 30-h
experiment. The polymer concentration at termination of the experiment
was 3000 ppm calcium chloride while the effluent concentration was 11
ppm, yielding a concentration of polymer/effluent of 273. The concen-
tration factor is defined as the concentration in the polymer divided by
the concentration in the feed and was 55 for this experiment. Calculated
selectivity for Ca/Na was 39 based on the final concentrations of those
species in the effluent and in the polymer solution. Calcium mass
transfer coefficient varied from 0.024 to 0.011 cm/min at the start and
termination of the experiment, respectively. These values are consistent
with the mass transfer coefficient obtained on aqueous solutions of
calcium chloride. Mass transfer coefficients and selectivity were calcu-
lated according to Eqs. (1) and (3), respectively. Selectivity equation:

$$S_{A/B} = \frac{[A_{bound}]}{[A_{free}]} \frac{[B_{free}]}{[B_{bound}]} \tag{3}$$

where $[A_{bound}]$ = total A in polymer solution − A_{free}
$[B_{bound}]$ = total B in polymer solution − B_{free}
X_{free} = X in treated feed

For the selectively calculation, it was assumed that the free ion in the
polymer solution was equal to the ion concentration in the effluent.

It is clear from this experiment that a surprisingly high selectivity for
calcium over sodium was observed. The selectivity calculated for the
experiment is much higher than the value observed for typical sulfonate
ion exchange resins (2.6)—analogous in the sense that the IX resin is a
highly water-swollen polymer network with sulfonate ion exchange
groups (15). An additional point of interest is the mass transfer relative to
simple dialysis seen in this experiment in the presence of high polymer
concentration. The similarity of the mass transfer coefficients is strong
evidence of the absence of fouling of the membrane by the polymer. It is
also interesting to note that actual mass transfer (as opposed to mass
transfer coefficients) is higher in the polymer system than with water as
dialysate even though the mass transfer coefficients are similar. This is
due to the assumption made in the calculations (Eq. 1) that the polymer

solution concentration for calcium is zero (assuming the bound calcium no longer interacts).

The Effect of Temperature and Polymer Concentration on Calcium Ion Extraction

To optimize the extraction of a particular species, it is desirable to know the effects of not only the membrane and polymer selected, but also those of the temperature and polymer concentration. A countercurrent, single pass flow scheme was used to examine these variables. The polymer and feed reservoirs were contained in a thermostatted bath capable of both heating and cooling. The membrane unit was insulated by wrapping it in several layers of glass wool and covering it with tape. 160 ppm of calcium ion as the chloride was used as the feed in this experiment. The effect of temperature on the mass transfer coefficient was as anticipated. The coefficient was plotted versus $e^{-1/T}$, and a linear relationship was found (data not shown). Such a relationship is characteristic of processes with a significant energy of activation and is expected for a pore diffusion controlled mechanism (3). For the affinity dialysis systems, the higher the temperature, the better the performance of the system as defined by the rates of transfer and reaction: additional advantages of higher temperature are a decrease in required membrane area and lower polymer side pressure drop. For those systems where the rate-determining step is kinetics limited for one species but not another, variation in temperature may be used to improve the selectivity of the system.

The change in mass transfer coefficient with changes in polymer concentration was also studied. The same 160 ppm calcium ion feed was used. As expected, the higher the polymer concentration, the better the mass transfer. However, the value for 1% polymer was low due to the polymer being loaded to capacity at the flow rates used. Flow rates were 1.0 mL/min feed and 0.08 mL/min polymer solution. Hence 1.92 meq/min of polymer and 4 meq/min of calcium ion were fed to the system in the 1.0% polymer case—leading to saturation of the polymer. This situation did not occur at higher concentrations. Even though the polymer side flow rate was extremely low (0.08 mL/min), the high affinity of the polymer for the calcium ions in effect reduces the stagnation layer at the surface of the membrane on the polymer side. By acting as a sink for the ions passing through the membrane, the polymer reduces the apparent ion concentration in the polymer solution near the membrane

wall, and this results in a high concentration gradient and hence increases the observed mass transfer.

Extraction of Copper(II) with Poly-AMPS

The extraction of Cu(II) from an aqueous solution of copper sulfate was studied. These experiments were performed using a system similar to that used with the Ca/Na—poly-AMPS experiments described above. Polymer solution was recirculated on the shellside at 3.0 mL /min. Results are shown in Fig. 6 for a polymer (poly-AMPS) concentration of 2.5% and a volume of 25 mL. Feed concentration of copper ion was 220 ppm with a feed flow of 0.70 mL/min. The copper concentration continued to increase to a maximum of 14,000 ppm over a period of 7.5 h. This is equivalent to 75% loading of the polymer, assuming two sulfonate groups per copper ion.

Figure 7 illustrates a similar experiment with copper and poly-AMPS but using an Amicon Vitafiber cell culture tube Model PM10 with polysulfone hollow fibers having a nominal 10,000 molecular weight cutoff. A key result of this series of experiments was a dramatic increase in the copper mass transfer coefficient when the polymer was present. With a dialysate of 3.0 mL/min water, the copper mass transfer coefficient was 0.0020 cm/min while with the polymer as the dialysate it increased to 0.015 cm/min. Apparently the capacity of the polymer solution for copper is high enough to overcome the poor flow distribution in the shell of the Amicon unit, thus adding strength to the assumption that, until the polymer is saturated, it acts as a sink for the copper ions and increases the concentration gradient driving force. The polymer loaded to about 15,000 ppm—equivalent to about 80% of capacity.

Cation Extraction Studies with Polymer Solution in Continuous Countercurrent System

The most probable mode of operation for these systems is continuous countercurrent extraction. To determine the performance of the affinity dialysis system, a series of continuous countercurrent experiments was run at various feed and polymer flow rates. The system of 2.5% poly-AMPS and 160 ppm calcium ion as the chloride was used as a model and the poly-AMPS was adjusted to pH 6.67 as before. The results of six continuous extraction experiments are shown in Table 1. Experiments 1, 2, and 3 show the effect of varying polymer solution flow while feed flow
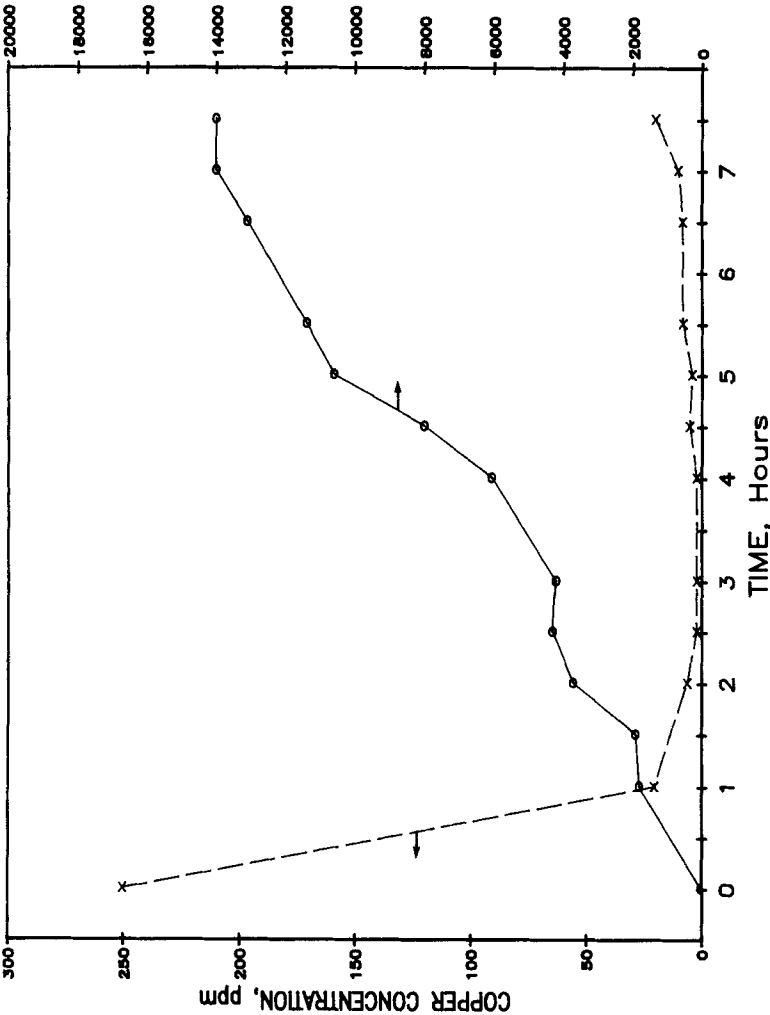
FIG. 6. Recovery of copper with 2.5% Poly-AMPS, pH 6.7, using cellulose hollow fibers: (O) polymer solution copper concentration, (X) effluent copper concentration, feed flow = 0.70 mL/min, polymer flow = 3 mL/min recirculated on the outside of the fiber bundle, feed solution = 220 ppm copper ion as the sulfate.
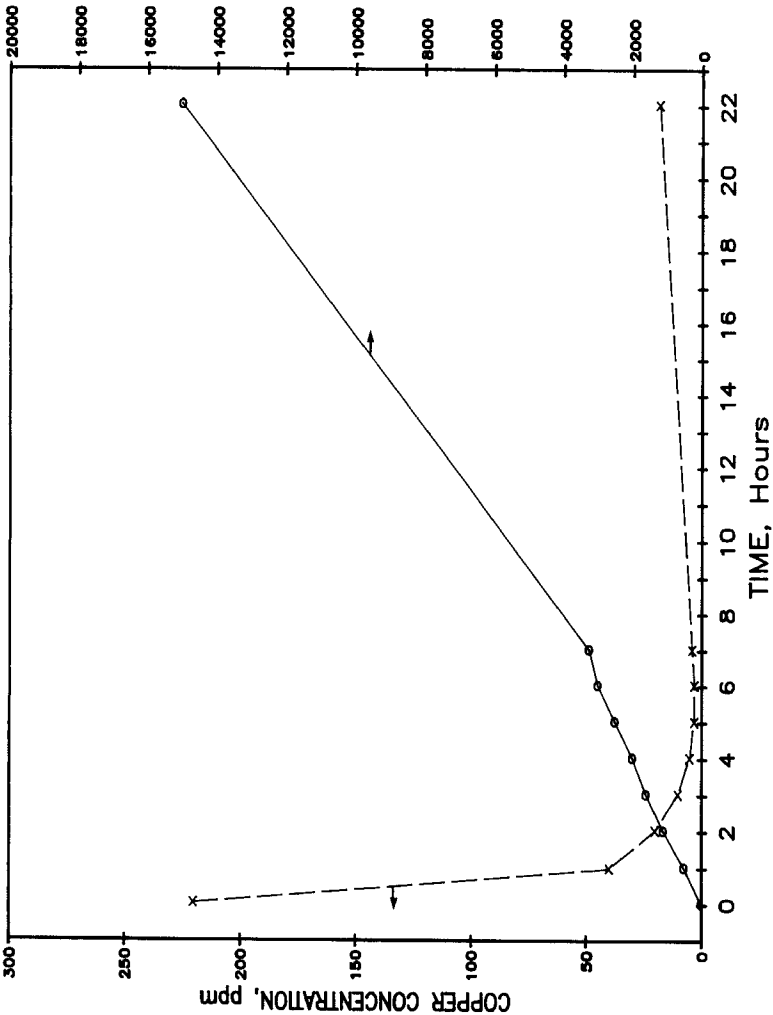
FIG. 7. Recovery of copper with Poly-AMPS, pH 6.7, using Amicon PM-10 hollow fibers: (○) polymer solution copper concentration, (✕) effluent copper concentration, feed flow = 0.50 mL/min, polymer solution recycled outside the fiber at 3.0 mL/min, membrane surface area = 60.0 cm².

TABLE 1

Continuous Countercurrent Flow Experiments with Calcium Chloride and 2.5% Poly-AMPS

Experiment	Feed flow (mL/min)	Polymer flow (mL/min)	% Ca removed	Ca in polymer (ppm)	K (cm/min)
1	2.04	0.36	94	2700	0.038
2	2.04	0.24	94	3190	0.038
3	2.04	0.11	74	4910	0.013
4	1.04	0.21	97	2700	0.027
5	1.04	0.14	92	3750	0.017
6	1.04	0.06	81	4600	0.007
7	1.04	5.20	75	—	0.015
8	2.04	5.20	74	—	0.015

is held constant. Experiments 4, 5, and 6 are similar but have a lower feed flow rate. Typically, an increase in feed flow resulted in an increase in polymer steady-state calcium concentration as did a decrease in polymer flow. Experiments 7 and 8 illustrate the removal of calcium chloride via simple dialysis at similar feed flow rates and excess dialysate flow to simulate the high capacity of the polymer solutions. With the exception of Experiment 6, the mass transfer coefficients are as expected. The low value in that experiment is probably due to the loss of efficiency at the extremely low polymer solution flow rates.

For illustrative purposes, Fig. 8 shows the results from a continuous run (Experiment 5 of Table 1)—principally as an indication of the stability of the system under typical operating conditions.

ANION EXTRACTION STUDIES—THE RECOVERY OF CHROMATE USING PEI

In an attempt to determine the efficacy of affinity dialysis for the extraction of anions, 5% PEI in water was used as the extractant for chromate ion. Twenty-five milliliters of the 5% PEI was recirculated at 4 mL/min on the outside of one of the 150 cm^2 hollow fiber units while 3.0 mL/min of a solution of 400 ppm potassium chromate was pumped single pass through the lumen of the fiber. Removal of the chromate from the feed was typically in the 95% range, and the maximum concentration of chromate in the polymer solution was 2.4% as potassium chromate. Figure 9 shows the increase in polymer solution chromate concentration
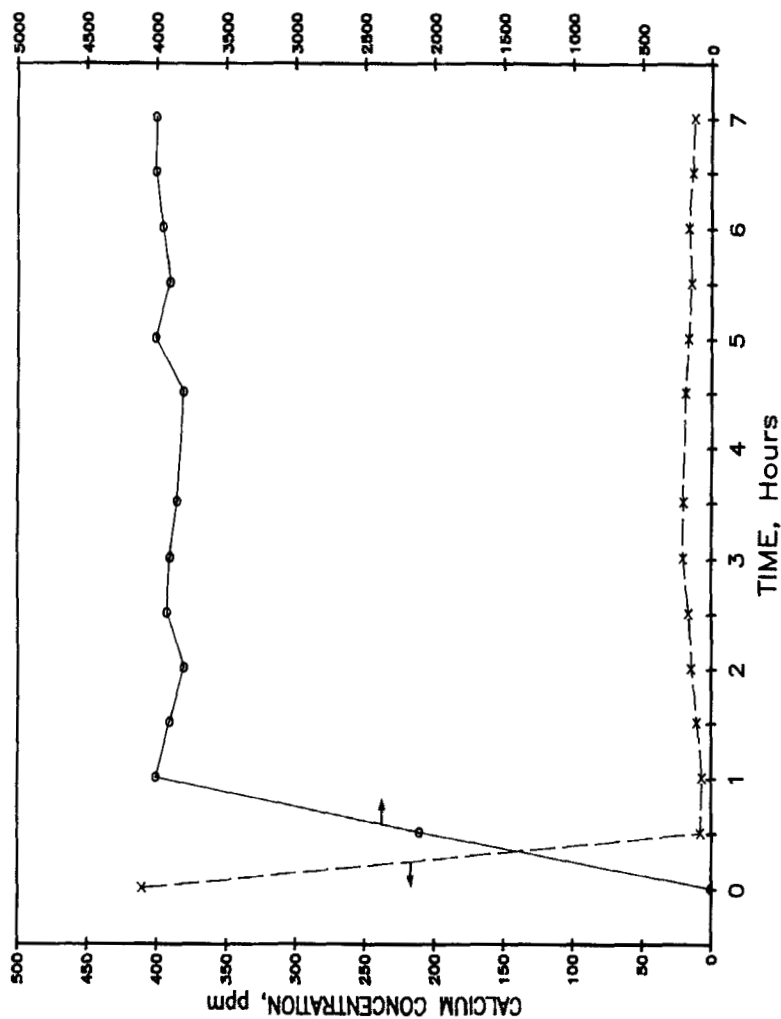
FIG. 8. Calcium recovery with 2.5% Poly-AMPS, pH 6.7, continuous countercurrent flow mode: feed = 1.04 mL/min of 160 ppm calcium ion single pass outside the fiber, polymer = 0.14 mL/min single pass inside the fiber lumen, (○) calcium concentration in the polymer solution, (×) effluent calcium ion concentration.
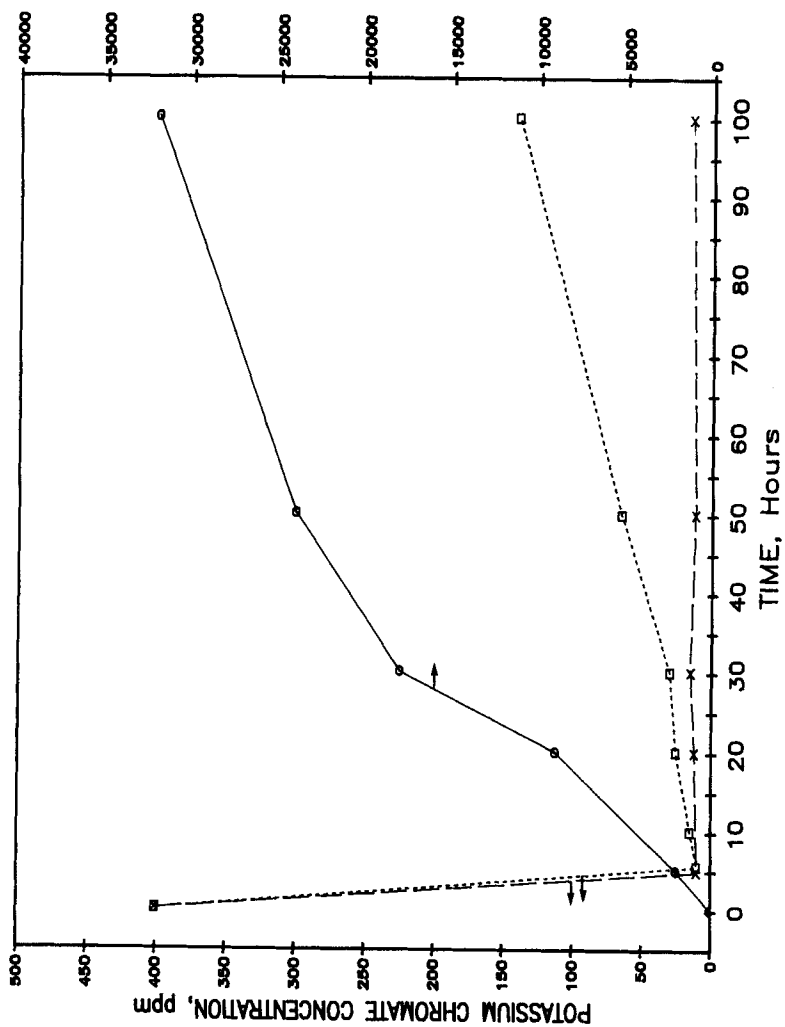
FIG. 9. Recovery of chromate with 5% PEI, pH 7.0, affinity dialysis mode 1: PEI recycled through shell of 150 cm^2 unit at 4.0 mL/min, feed = 400 ppm potassium chromate and 1000 ppm sodium chloride with single pass flow through the fiber lumen at 3.0 mL/min, ($\square$) total chrome in effluent, ($\times$) chrome(VI) in effluent, ($\bigcirc$) total chromate in polymer solution.

and the amount of residual potassium chromate in the effluent as a function of time. The feed stream contained 1000 ppm NaCl to compete with the chromate, and the PEI was adjusted to pH 7.0 with HCl to form the cationic extractant.

For practical considerations, PEI may not be the polymer of choice for this application as the solution tends to turn purple with time, probably due to oxidation of the polymer by chromate to give Cr(III). This may be due to the equilibrium amount of dichromate at pH 7 since the rate of appearance of the purple color was observed to be highly pH dependent and more rapid at the lower pH range. The presence of hydrogen covalently bound to nitrogen may be the culprit in this degradation since Baker and Lonsdale have successfully used tertiary amines for the supported liquid membrane chromate recovery (16).

Stripping Study of the Polymer Poly-AMPS Loaded with Calcium Ion

To determine the feasibility of removing complexed calcium from the polymer via acidification and dialysis, a polymer solution of 2.5% AAMPS loaded with 6000 ppm calcium ion was pumped at 0.25 mL/min countercurrent to a stream of $1.0 N$ HCl (1.0 mL/min). The unit used was a hollow fiber unit with 150 cm^2 surface area. Figure 10 shows the results of that experiment. Over 90% of the calcium ion was removed from the polymer stream in one pass and an average calcium ion concentration in the strip stream of about 1600 ppm as the chloride was obtained. This is by no means the limit of the concentration achievable but is a result of the ratio of the feed to strip flow rates. Experiments to delineate the limits of the feed/strip ratio, minimum acid concentration, and maximum achievable strip concentration will be the subject of future studies. The key result here is the nearly complete removal of the cation from the polymer and the demonstration of the ability to recover the cation in a concentrated form.

Continuous Countercurrent Recycle System

Figure 3 illustrates the continuous recycle system assembled for long-term experiments. A single hollow fiber module was used for each extraction and stripping stage. A detailed description of the system is given in the Experimental Section. Computer modeling of this system is underway to assist in determining the effects of staging the modules,
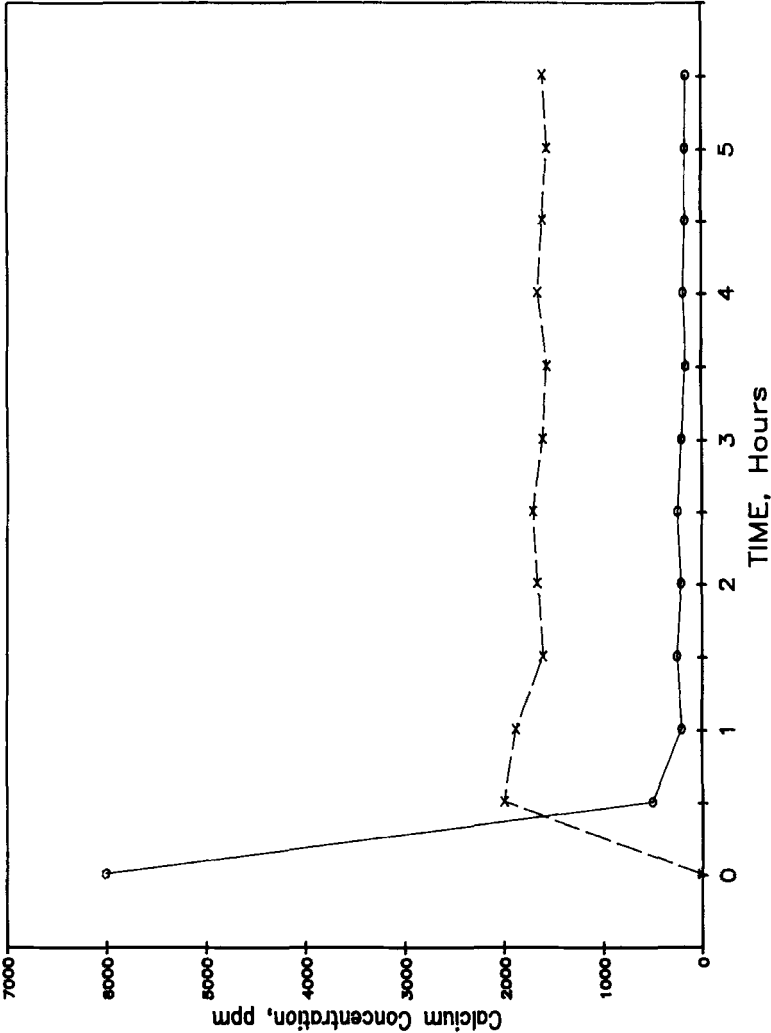
FIG. 10. Removal of calcium from loaded Poly-AMPS via acidification and dialysis: continuous countercurrent flow of 2.5% Poly-AMPS loaded with 6000 ppm calcium ion, feed = 1.0 M HCl shellside flow at 1.0 mL/min, polymer solution flow = 0.25 mL/min in the fiber lumen, 150 cm^2 cellulose hollow fiber unit, (×) calcium ion concentration in effluent HCl, (○) calcium effluent in stripped polymer solution.

maximizing the polymer loading, and minimizing the metal ion concentration in the remaining treated effluent.

Copper/Zinc Separation

The miniplant was run extensively on the separation of copper and zinc. Figure 11 illustrates a typical run with 10% PEI and a feed of low concentration metal ions. Feed concentration was 400 ppm copper ion and 1000 ppm zinc ion as the chlorides. This experiment was run for a longer period—150 h—to provide data on the long-term stability of the system. The figure shows results for a feed flow of 60 mL/min and countercurrent polymer solution flow in the lumen of the fibers at 1.0 mL/min. The strip flow rate was 1.4 mL/min. pH was controlled at 1.0 in the acid addition reactor and 7.0 in the NaOH regeneration unit. In both cases oscillation around the set point of the controllers was 0.5 pH units or less. As can be seen in the figure, the removal of copper ion from the feed was very consistent over the entire experiment as was the minimal amount of zinc removal. However, the concentration of the product stream varied from 15,000 to 28,000 ppm. Very small changes in pressure differential across the membrane in the strip unit can dramatically alter the flow rate of the product by ultrafiltration of water into the feed stream. As little as 5 mmHg pressure differential between the polymer solution and product streams is sufficient to cause a 25% change in product concentration. This problem was exacerbated by the use of a strip unit that was much larger than required. The dashed line in the figure represents the concentration of the copper ion in the product stream normalized to a constant flow volume of strip solution. Clearly this is a more stable result and is consistent with the observed removal rate from the feed stream. Typically the transport of zinc into the polymer stream correlated closely with the ratio of flow rates of the feed and polymer solution streams and was generally at the level expected from simple dialysis (17). The average zinc concentration in the copper concentrate was 700 ppm, giving a 70-fold purification, a 50-fold concentration, and a 97% pure copper product. The residual zinc in the aqueous effluent from the extraction stage was 98% pure. These results are completely consistent with results from studies of the extraction and strip stages separately.

During the course of the experiment depicted in Fig. 11, it was observed that the blue-green copper chloride product solution tended to spread along the bottom of the shell of the strip unit. Since the flow rate calculations based on the observed mass transfer coefficients indicated
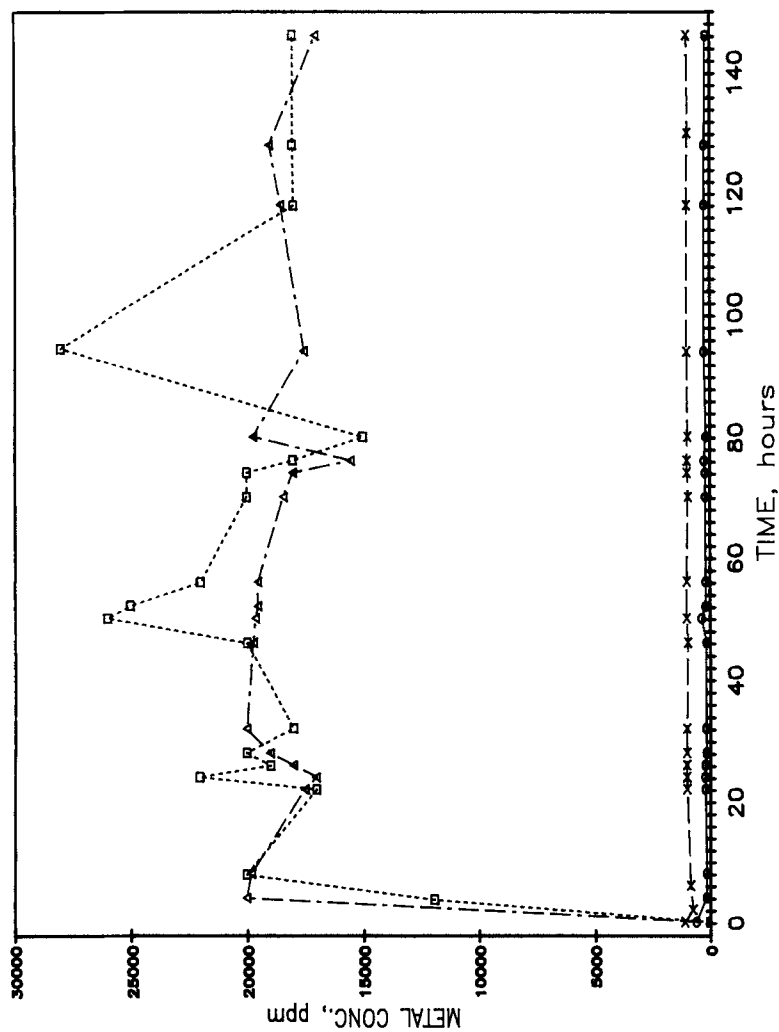
FIG. 11. Continuous strip, regeneration, and recycle affinity dialysis separation of copper and zinc with 10% PEI: feed = 400 ppm copper ion and 1000 ppm zinc ion as the chlorides—fed through the shellside at 60 mL/min, polymer solution fed through the fiber lumens at 1.0 mL/min, strip solution 0.1 M HCl fed through the shellside of the strip unit at 1.4 mL/min, pH of acid addition reactor = 1.0, pH of regeneration reactor = 7.0, strip and extraction units are Disscap 080 and 140, respectively, (×) zinc in aqueous effluent from the extraction unit, (○) copper in that stream, (□) copper in product from strip unit, (△) copper product concentration normalized to strip flow.

than only about 5% of the area in the strip unit should be necessary for the strip section, this observation seemed inconsistent with our expectations. Upon moving the unit from a horizontal to a vertical position with the product outlet port down, the colored product band formed an intensely colored layer approximately ¾ of an inch thick at the base of the unit. This is consistent with the area requirements calculated. The spreading of the band in the horizontal position is apparently due to the high density of the product relative to the strip solution and is a clear indication that, in systems with high product concentrations, the preferred orientation of the modules is in the vertical position with the higher density fluid being removed from the lower port.

The experiment described in Fig. 11 was also used to assess polymer loss to the effluent from the extraction stage. Based on the optical absorption of the copper/PEI complex in the effluent, the loss of polymer was shown to be less than 0.01%/d based on a recirculating polymer solution volume of 1 gal per 250 gal/d of treated feed. It should be noted that, if the loss is due at least in part to lower molecular weight fragments in the polymer, then total losses over significantly longer runs may be lower.

Chromate/Chloride Separation

Due to the importance of hexavalent chromium as a priority pollutant, the separation of chromate ion from chloride ion was studied in the continuous recycle system. Again, 10% PEI was used as the polymer but this time as an anion-exchange polymer rather than as a chelating polymer. In this case the pH of the pregnant polymer solution stream was adjusted to 12.0 prior to the stripping unit using 50% NaOH while the stripped polymer stream was regenerated with concentrated HCl prior to recycle back into the extraction stage. A 1.4-m^2 dialysis unit was used for the extraction module, and feed flow was through the shellside with polymer solution in the lumen. Since cellulose hollow fibers tended to dissolve at the stripping pH, an Amicon 0.1-m^2 polysulfone hollow fiber unit was used as the stripping stage module. Figure 12 illustrates the results of an experiment where a solution of 400 ppm potassium chromate with 1000 ppm sodium chloride was fed at 60 mL/min countercurrent to polymer solution flowing at 0.60 mL/min on the inside of the hollow fibers. Strip flow was set at 1.0 mL/min, and a concentration factor of 75 was found as reflected by the 30,000 ppm chromate product concentration. Over the 50-h run the amount of chromate removed from
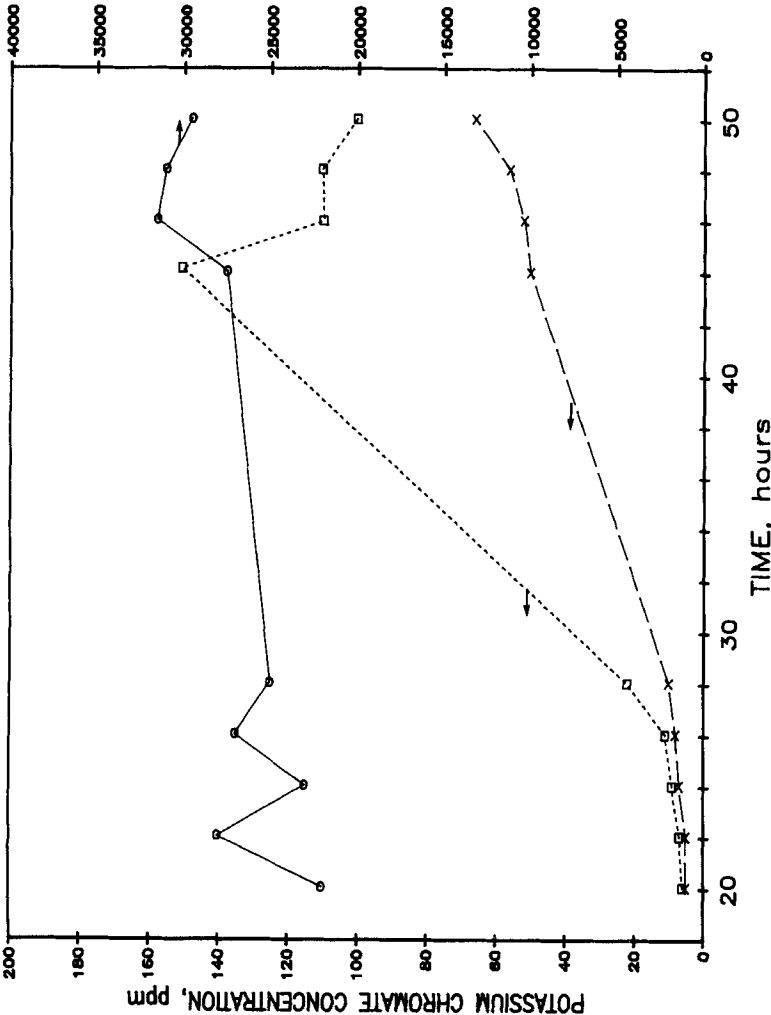
FIG. 12. Continuous strip, regeneration, and recycle affinity dialysis separation of chromate and chloride with 10% PEI: feed = 400 ppm potassium chromate and 1000 ppm sodium chloride—fed through the shellside at 60 mL/min, polymer solution fed through the lumens at 0.60 mL/min, strip solution of water fed through the shellside of the strip unit at 1.0 mL/min, pH of hydroxide strip reactor = 12.0, pH of HCl regeneration reactor = 8.0, extraction unit = Disscap 140, strip unit = Amicon H1P10-20; (×) chrome(VI) in aqueous effluent from extraction stage, (□) total chrome in that stream, (○) chromate in product stream from strip unit.

the feed deteriorated and a dark brown color replaced the bright yellow of the polymer solution. Analysis of hexavalent versus total chromium indicated that some reduction of chromate to chrome(III) was occurring.

It is evident from the results shown in Fig. 12 that many factors are likely to affect the removal of chromate from the feed but that high concentrations of chromate can be readily achieved in the product stream. It is not clear that the formation of chrome(III) is related to the loss in efficiency of the extraction or if some other unrecognized phenomenon may be at least partially responsible. Certainly if substantial quantities of chrome(III) are produced, that product will likely be strongly bound to the PEI by chelation at any of the pH ranges in this experiment. Hence one can assume that a concomitant loss of extraction efficiency would result. However, the incomplete stripping of chromate ion from the loaded polymer solution could also result in a buildup of chromate in the polymer and a loss of capacity for chromate removal from the feed. This is less likely and would not result in a color change in the polymer solution whereas the purple color associated with chrome(III)/PEI complex formation, when mixed with the yellow of the chromate/PEI ion pair, would result in the observed brown color.

CONCLUSIONS

Affinity dialysis is a technologically feasible process for the separation of ions and exhibits stable operation over long periods in a continuous countercurrent operating mode. This process has demonstrated an ability to both concentrate and purify selected ions from streams containing a variety of metal ions at several concentrations. Different membranes and water-soluble polymeric adsorbents have been used to demonstrate the efficacy of affinity dialysis. The presence of the polymeric adsorbent has not resulted in any detectable negative impact on the measured mass transfer coefficients in any of the systems studied and, in fact, has exhibited a positive effect of nearly a full order of magnitude in some systems with poor flow characteristics on the polymer solution side of the membrane.

Affinity dialysis as a complete extraction/strip/recycle system performs much as anticipated based on the study of the extraction and strip stages independently. It was surprising that the system was very stable under rigorous operating conditions and the magnitude of the effect of osmotic/oncotic pressures was not as severe as expected. By restricting the polymer loop to a fixed volume, so that dilution of the polymer cannot

occur, operation of this type of system can be even simpler. The systems performed efficiently and provided a high concentration product with minimal loss of extractant polymer. Mass transfer coefficients for the complete systems studied typically mirrored the values obtained on the separate stages studied independently. Such systems, tailored for specific ions or species, should provide an interesting addition to the current processing technology utilizing membranes.

Acknowledgment

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