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Polyelectrolyte-Enhanced Ultrafiltration of Copper from a Waste Stream

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Abstract

The concentration of copper in a simulated wastewater was successfully reduced from 100 ppm to less than 1 ppm by polyelectrolyte-enhanced ultrafiltration. In polyelectrolyte-enhanced ultrafiltration, copper is ionically bound to the polymeric chain of an anionic polyelectrolyte. Ultrafiltration then filters out this large copper-polyelectrolyte complex. At the same polyelectrolyte-to-copper ratio in the 1:1 to 3:1 (weight basis) range and a feed temperature in the 15 to 40°C range, sodium carboxymethyl cellulose was more efficient for copper removal and exhibited higher flux values than sodium polystyrene sulfonate. The experiments showed that transmembrane pressure has a minimal effect on removal of copper whereas the polyelectrolyte-to-copper ratio has considerable influence. It was also seen that the permeate copper concentration decreased with a decrease in feed temperature. Decreasing the feed temperature also caused a reduction in flux because of an increase in the viscosity of the feed solution.

INTRODUCTION

The potential to reduce the concentration of heavy-metal ions emitted into the environment by improving separation technology can also reduce the cost of waste treatment. The process of removing trace organics from wastewater by micellar-enhanced ultrafiltration (MEUF) (*1–4*) can also be used to remove heavy metal ions (*5*). One distinct disadvantage of MEUF is that it cannot be used for low concentrations of metals (*6*). The total surfactant concentration has to be higher than the critical micellar concentration, otherwise the solutions will contain large amounts of monomers. However, it is possible to use very small quantities of polyelectrolyte since polyelectrolytes do not depolymerize at low concentrations.

In polyelectrolyte-enhanced ultrafiltration (PEUF), an anionic polyelectrolyte, added to the feed, dissociates like a regular electrolyte, with the negative charge remaining on the polymer skeleton and the positive charge (Na^+) passing into solution. This binds the dissolved positive ion (Cu^{2+}). This large molecule, which has a molecular weight larger than the cutoff of the ultrafilter membrane, will be retained during a filtration operation. Thus the permeate, i.e., the filtrate passing through the membrane, has a lower concentration of copper. Separation is basically according to the type of polyelectrolyte, its molecular size, and the number of ionic sites per unit length of the polyelectrolyte molecule.

The aim of the present research was to determine the effects of temperature, transmembrane pressure, and copper-to-polyelectrolyte ratio which affect the removal of copper. It was also decided to compare the effects of two of the best performing polyelectrolytes on copper removal: sodium carboxymethyl cellulose (CMC) and sodium polystyrene sulfonate (PSS) (*7*).

Wastewater streams were simulated by adding a predetermined amount of copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$). Copper (Cu^{2+}) is easily identified by atomic absorption analytical instruments due to its blue color. Tests to determine the effects of Cu^{2+} removal in the presence of another salt were not conducted because NaCl tends to compress the electric double layer and thus reduce the potential of the polyelectrolyte anion. The addition of NaCl reduces the thermodynamic activity of the copper ions present in the feed. Also, Na^+ ions are already present in the sodium CMC and sodium PSS.

THEORY

Ultrafiltration is a membrane separation process in which the solvent and certain dissolved species are separated according to their molecular sizes. The ability of a membrane to retain a particular species of a solution is characterized by its rejection coefficient, R, defined as the fraction of solute retained (*8*):

$$R = 1 - C_p/C_r \tag{1}$$

where C_p is the concentration of the species in the permeate and C_r is the concentration of the species in the retentate.

The lowest molecular weight substance which can be separated from a liquid medium by ultrafiltration is approximately 5000 daltons (*9*). However, smaller molecules can be separated from solution by fixing them to macromolecules. Polyelectrolytes are one such class of macromolecule.

A polyelectrolyte is a polymer molecule carrying a large number of charges, i.e., the repeating units contain an ionizing group (*10*). The fundamental parameter which characterizes the polymer is the linear charge density, δ (*11*):

$$\delta = \frac{\beta}{b}\frac{\epsilon^2}{D}kT \tag{2}$$

where D is the dielectric constant ($\approx$ 80), ϵ is the electron charge, kT is the Boltzman term, and β/b is the number of ionic sites per monomeric unit of length b. The factors which influence the degree of ionization are 1) the charge density, 2) the backbone rigidity, 3) the type of ionic site (—COOH, —SO_3H), and 4) the chemical structure of the chain.

MATERIALS AND PROCEDURE

Apparatus

The experimental setup is shown in Fig. 1. The ultrafiltration (UF) unit was a Romicon HFXS-MKII system and contained a process pump (1¼ inch by 1 inch, ¾ hp), a temperature gauge, and pressure gauges at the inlet and outlet of the UF unit (bore side). The retentate stream could be

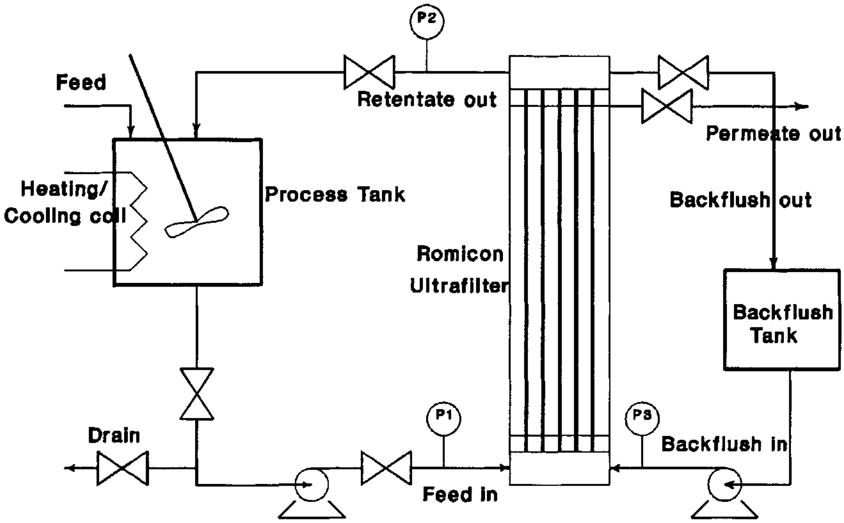

FIG. 1. The experimental setup of the Romicon HFXS-MKII ultrafiltration unit.

fed back to the process tank and the permeate collected for analysis. The Romicon HF 1.1-45-XM50 hollow fiber membrane cartridge used has a nominal molecular weight cutoff of 50,000 daltons and contains 50 parallel hollow fibers (1.1 mm i.d.) potted at both ends of a plastic shell.

The backflush tank system was used to clean the membrane between runs and recover the desired flux. The temperature in the 19-L process tank was controlled by a Forma Scientific Bath and Circulator (model 2325) which passed an ethylene glycol–water solution through a 5-turn stainless steel coil. A stainless steel screen, rated at 200 microns, was used as a prefilter, and the tank was covered with a lid to reduce losses due to evaporation and splashing.

The concentration of the copper in the permeate was determined by using a Perkin-Elmer 2380 Atomic Absorption spectrophotometer. A calibration curve was determined by using concentrations from 1 to 10 ppm since the absorbance usually deviated from a straight line after 15–20 ppm, and all analyses were done with samples diluted by a factor of 10. The polyelectrolyte CMC, obtained from Aldrich Chemical Co., had an average molecular weight of 700,000. The polyelectrolyte PSS, obtained from Scientific Products Inc., had an average molecular weight of 6,000,000. Both polyelectrolytes were used without further purification.

Procedure

The desired amount of $CuSO_4 \cdot 5H_2O$ (purified grade) was dissolved in a predetermined amount of deionized water (2.929 g $CuSO_4 \cdot 5H_2O$ in 10 L water) in the feed tank to give a 100-ppm $CuSO_4$ solution. The constant temperature bath fluid was run for approximately 1 hour through the agitated feed mixture to ensure that the feed attained the bath temperature. The general procedure was as follows:

1. Samples of the feed solution were retained for analysis.
2. After the temperature of the feed in the feed tank had attained the set point, the desired polyelectrolyte was added and agitation of the mixture at high speed was continued for a further half hour.
3. The UF unit was turned on, and the inlet and outlet pressures were adjusted to the desired values and the operating conditions were recorded.
4. The run was stopped after the feed tank had almost drained or if the unit clogged.
5. Samples of the permeate were retained for analysis.
6. The flow rates of the permeate were recorded at fixed time intervals.
7. The unit was backflushed and cleaned as outlined by the manufacturer after each run until at least 95% of the pure water flux, as specified by Romicon, was attained.

8. The above procedure was also used at different feed temperatures to determine the effect of temperature on the ionic bonding of the polyelectrolyte to the copper ion.

DISCUSSION OF RESULTS

All experiments were conducted using a feed copper concentration of 100 ppm. Most of the research was done with sodium carboxymethyl cellulose. Experiments with sodium polystyrene sulfonate were basically performed to confirm the results of Reference *7* and the literature surveyed (*12*). Since work had already been conducted using CMC-to-copper ratios of 20:1, 10:1, and 5:1 (*7*), a series of runs was done at lower ratios of 1:1, 2:1, and 3:1. The aim was to determine the influence of temperature and pressure on PEUF and the ionic binding.

The experiments were also aimed at trying to see whether the hollow fiber Romicon Ultrafiltration unit could be used for continuous operation. Most of the time the retentate was piped back into the feed tank. Gel formed on the surface of the membrane quite rapidly, and for extended run periods the permeate flux was found to attain a steady-state value. All samples and flow measurements were done only after steady state had been reached. Hence, it is possible to use the Romicon for continuous operation if the flow of the waste stream into the feed tank is equal to the flow rate of permeate.

Another aim of the experiment was to check the properties of two of the polyelectrolytes by using identical parameters for each of them, and comparing the removal of copper achieved by each of them.

Figure 2a shows the effect of transmembrane pressure and CMC loading at different temperatures. As seen from the figure, the permeate flux is reduced as the CMC-to-copper ratio is increased. The same effect is observed at 15, 30, and 40°C. The flux increases as the temperature of the system is increased. This can be explained by the fact that the viscosity of the feed stream is reduced with an increase in temperature. The figure also shows a sharp reduction in flux as the CMC-to-copper ratio is increased from 1:1 to 2:1, whereas there is not as much of a reduction in flux as the ratio is increased from 2:1 to 3:1.

Figure 2b shows the effect of transmembrane pressure and CMC loading on permeate concentration at different temperatures. The figure shows that the permeate copper concentration is independent of transmembrane pressure at 15, 30, and 40°C. However, increasing the temperature from 15 to 40°C causes an increase in permeate copper concentration. Increasing the CMC-to-copper ratio from 1:1 to 2:1 causes a sharp decrease in permeate copper concentration. However, there is not nearly as much of a difference when the CMC-to-copper ratio is increased from 2:1 to 3:1.

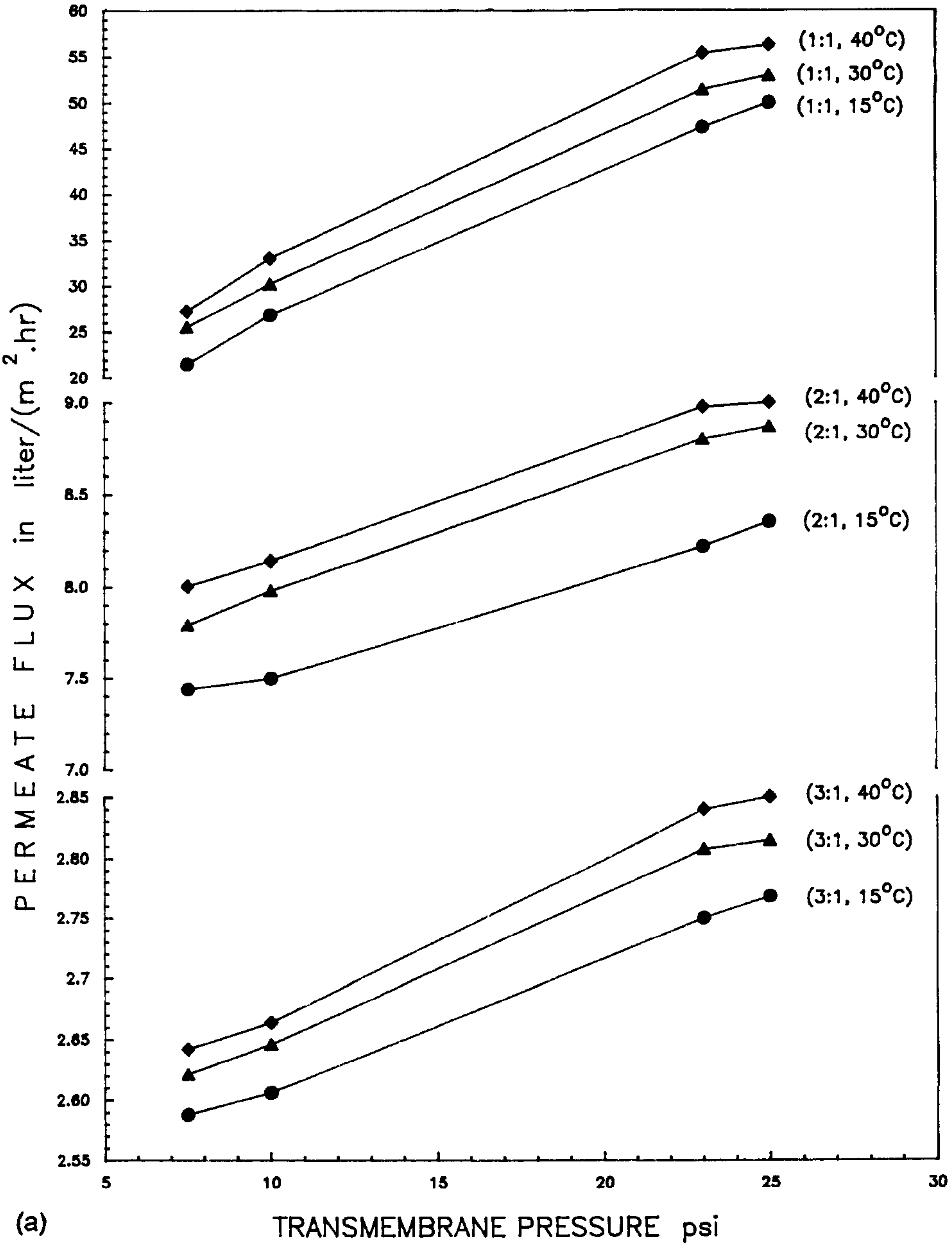

FIG. 2a. Effect of transmembrane pressure and CMC loading on permeate flux at different temperatures.

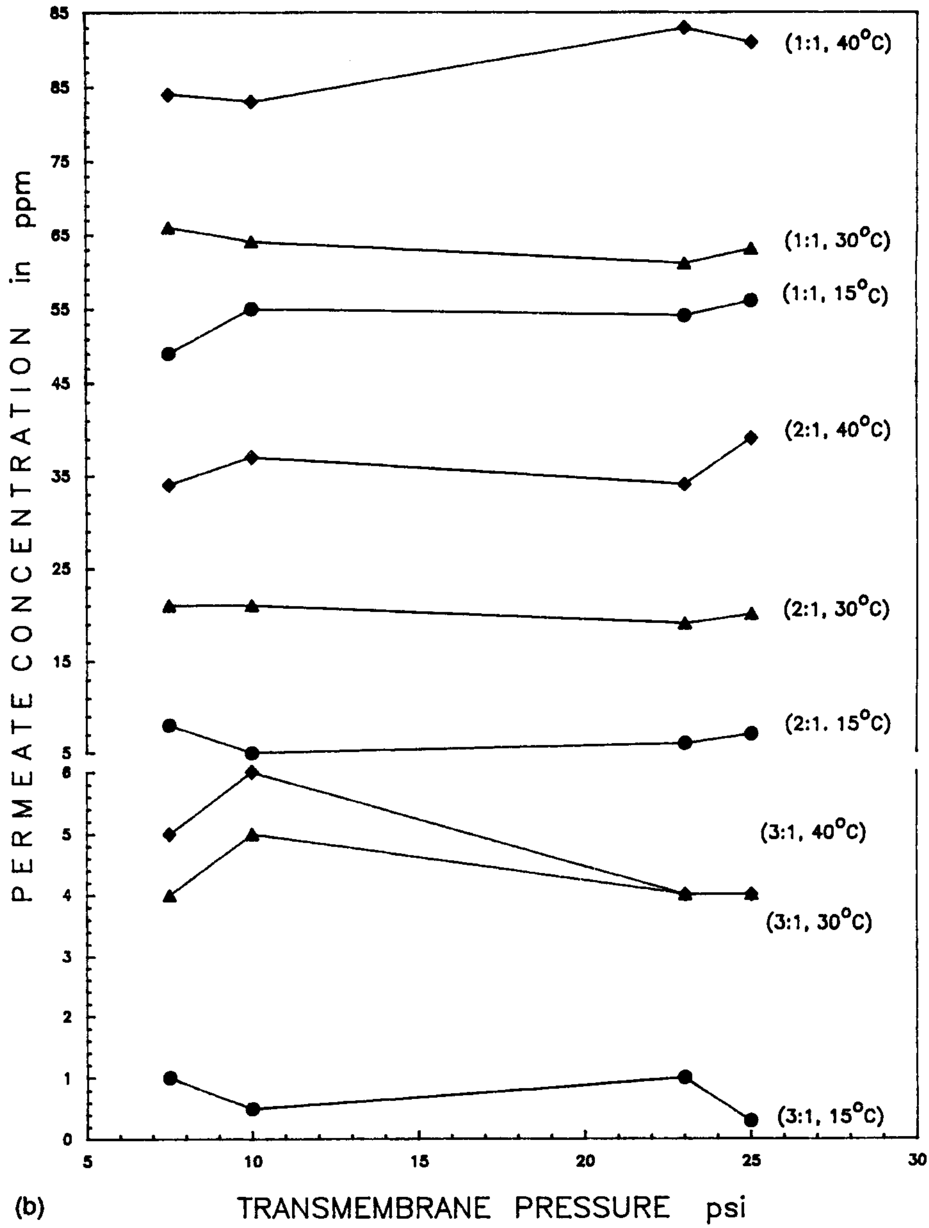

FIG. 2b. Effect of transmembrane pressure and CMC loading on permeate concentration at different temperatures.

Temperature has a minimal influence on the permeate copper concentration at 3:1 CMC loading, with the permeate copper concentration remaining at 5 ppm or less. However, the permeate copper concentrations increased from about 8 to 40 ppm and from 53 to 90 ppm at 2:1 and 1:1 CMC-to-copper ratios, respectively, as the temperature was raised from 15 to 40°C.

Figure 3a shows the effect of temperature on permeate flux at different CMC loadings for constant transmembrane pressure. There is minimal difference between the permeate fluxes at 15, 30, and 40°C for each CMC-to-copper loading. There is a considerable and proportionate reduction in permeate flux at the three temperatures as the loading is increased from 1:1 to 2:1, while there is a less drastic reduction in permeate flux as the CMC loading is increased from 2:1 to 3:1. Figure 3a shows that the permeate flux increases linearly with temperature at a constant transmembrane pressure. The slopes of these lines decrease as the CMC-to-copper ratio is increased.

The influence of feed temperature and CMC loading on permeate concentration at constant transmembrane pressure is seen in Fig. 3b. A more pronounced trend from the one for permeate flux is observed. The slope of the line increases with an increase in temperature at a given CMC-to-copper ratio.

To summarize, permeate flux increases with an increase in transmembrane pressure, as expected. Permeate flux also increases with an increase in feed temperature. When the temperature of the system is increased, the viscosity of the feed solution decreases and hence the flux is expected to increase.

The permeate copper concentration decreases with an increasing polyelectrolyte-to-copper ratio. This agrees with the earlier results obtained by Padgett at higher CMC loadings (*6*). Copper concentration in the permeate decreases with decreasing temperature. The solubility of $CuSO_4 \cdot 5H_2O$ in water increases with an increase in temperature, and hence binding of the copper to the polyelectrolyte may be hindered. The solubility of the polyelectrolyte should also increase with an increase in temperature, but the solubility of copper sulfate in water is much greater than the solubility of the polyelectrolyte (CMC is slightly more soluble than 1% by weight in water at 25°C).

The increase in viscosity exhibited by CMC in water can be explained by the following changes in structure of the polymer molecule. At higher concentrations of sodium carboxymethyl cellulose (greater than 1%), the molecules are in close contact with each other, so there is a smaller tendency for the counterions (sodium) to dissociate from the polymer chain. When the solution is more dilute, the cations move away from the fixed charges

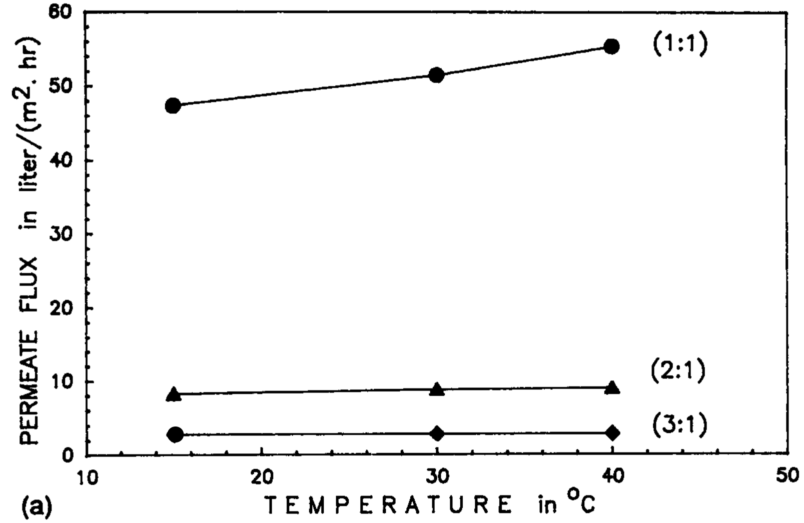

FIG. 3a. Effect of temperature on permeate flux at different CMC loadings for constant transmembrane pressure.

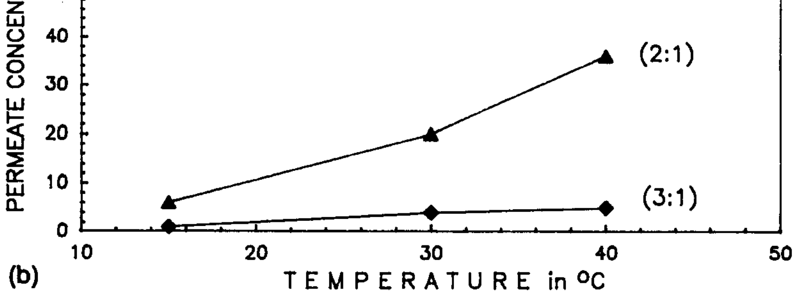

FIG. 3b. Effect of temperature on permeate concentration at different CMC loadings for constant transmembrane pressure.

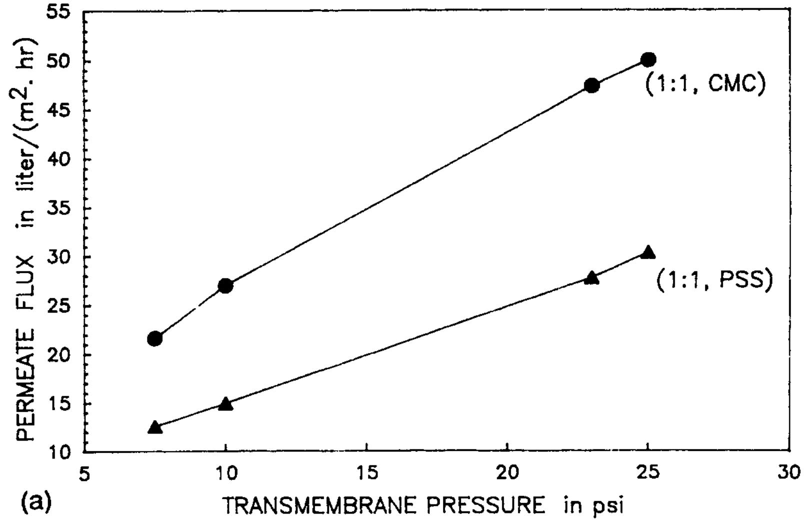

FIG. 4a. Effect of transmembrane pressure and polyelectrolyte type on permeate flux.

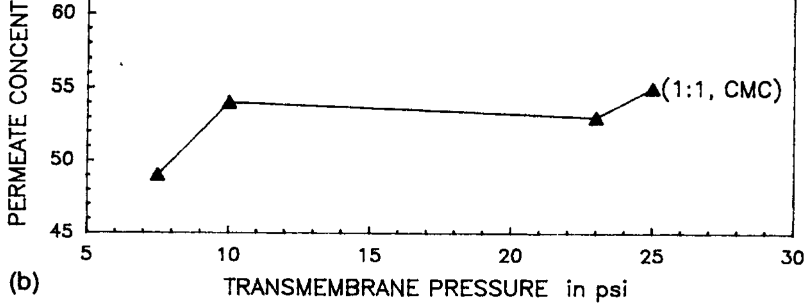

FIG. 4b. Effect of transmembrane pressure and polyelectrolyte type on permeate concentration.

into the aqueous region. This leaves a net charge on the polymer chain. These like charges tend to repel each other, and that causes the polymer chains to uncoil to their maximum lengths, thus increasing their effective charge densities.

As the effective chain length is increased, there will be a corresponding rise in viscosity. Viscosity can also be increased by reducing the temperature. Hence, for the same concentration of polyelectrolyte, the effective charge density will increase when the temperature is reduced.

Figures 4a and 4b show the difference between CMC and PSS. Permeate flux was higher for CMC than PSS. The molecular weight of PSS was higher than the molecular weight of CMC, and this caused an increase in the viscosity. The permeate concentration of copper was higher using PSS, and this could be attributed to the difference in rigidity, the charge density, or the chemical structure of the chain. The maximum extensions of polysulfonics is about 75% (*12*), hence polysaccharides will probably exhibit a higher effective charge with a decrease in feed temperature.

CONCLUSIONS

The removal of copper from aqueous solutions of $CuSO_4$ by sodium carboxymethyl cellulose was better than that by sodium polystyrene sulfonate. This is most probably due to the differences in rigidity and effective linear charge density of the polymers. The permeate concentration of copper was found to be essentially independent of the transmembrane pressure within the range studied.

For CMC, the permeate concentration was reduced with an increase in the polyelectrolyte-to-copper ratio from 1:1 to 3:1. Based on this decreasing Cu^{2+} concentration in the permeate with an increase in polyelectrolyte loading, there may be a loading in excess of 3:1 which would remove all of the Cu^{2+}. Permeate flux increased with an increase in transmembrane pressure, as expected. At the higher loading of the polyelectrolyte (3:1), the flux stayed relatively constant after the gel layer formed.

The permeate flux increased with an increase in temperature at a given polyelectrolyte-to-copper ratio due to a reduction in the viscosity of the feed, as expected. Conversely, the permeate flux decreased with an increase in the polyelectrolyte-to-copper ratio at a given temperature. The concentration of copper in the permeate decreased with a decrease in the feed temperature.

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