

Modification of Cellulose Acetate: Its Characterization and Application as an Ultrafiltration Membrane

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ABSTRACT: The development of cellulose acetate blend membranes using a commercial grade Mycell cellulose acetate and cellulose diacetate with suitable pore structure is discussed. These membranes were characterized in terms of resistance of the membrane, pure water flux, the molecular weight cutoff, water content, pore size, and porosity. The removal of copper metal ions by this blend membrane using polyethyleneimine as a chelating agent was studied. The effects of copper ion concentration and casting solution composition on separation are also discussed. A possible correlation between feed and permeate concentration of copper ion is evaluated. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 1939–1946, 1998

Key words: cellulose acetate membranes; ultrafiltration; copper metal ion; polyethyleneimine; proteins

INTRODUCTION

In recent years ultrafiltration (UF) and reverse osmosis have become standard procedures for the separation of heavy-metal ions from aqueous solution. Due to relatively large pore size of the membranes,¹ UF cannot be applied directly to recover metal from industrial waste streams. However, UF/microfiltration has been used as pretreatment method or as a means of recovering precipitated materials. Further, UF is used efficiently for product recovery and pollution control in the chemical and electronic as well as food and biotechnological industries.^{2–5}

The estimated separation factors in the case of polymer blend were higher than those of either of the pure components of the polymer.

Hence, it is possible to separate, concentrate, and purify virtually any solution by selection of proper membrane material through blending technique.⁶

The pore sizes of cellulose acetate membranes were modified by incorporating cellulose fortified with cellulose acetate, and the resultant membrane was successful⁷ in separation of high-molecular-weight species.

However, most of the earlier studies for the removal of heavy metals using UF have largely been limited to noncellulosic membranes⁸ such as polysulfone, polyamide, etc. Hence, attention is focused on cellulosic-based blend membranes due to hydrophilic and good fouling resistance of cellulose acetate membranes, and we attempted to develop these membranes by blending commercial grades of cellulose diacetate (CDA) with Mycell cellulose secondary acetate of molding grade, with suitable pore structure. The present article discusses characterization

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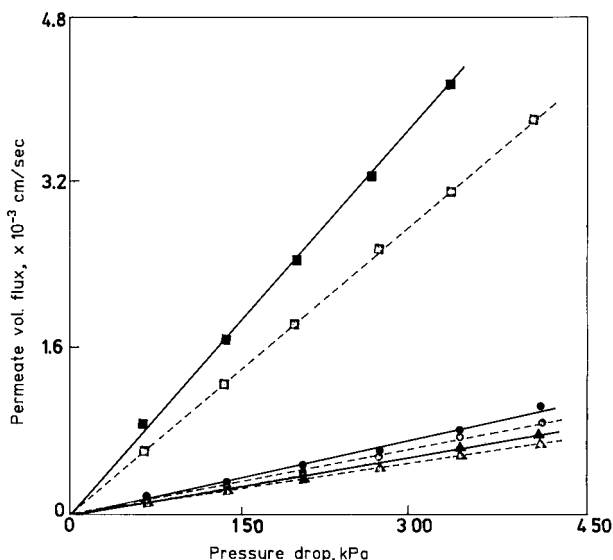


Figure 1 Plot of permeate volume flux versus pressure drop for the membranes having solvent/polymer ratios 4.0 (---) and 4.71 (—): (■) MDB10; (●) MDB30; (▲) MDB50; (□) MDB10C; (○) MDB30C; (△) MDB50C.

and application of these blend membranes for copper ion removal using polyethyleneimine (PEI) as a chelating agent. A possible correlation between feed and permeate concentration of copper is also discussed.

EXPERIMENTAL

Materials

Commercial grade Mycell cellulose secondary acetate, MYCEL CA 015 (MCA) (acetyl content 38.5 wt %), was recrystallized from acetone and dried in a vacuum oven at 75°C for 24 h with glass transition temperature (T_g) 249°C and molecular weight (MW) = 99 kDa, and used for further work. Mycell CDA 5770 (acetyl content 39.99 wt %) was used after recrystallization from acetone with T_g = 219°C and MW = 115 kDa. The above were obtained from Mysore Acetate and Chemicals Co. Ltd, Mysore, India. Solvent *N,N*-dimethyl formamide (DMF), Analar grade, and copper sulfate from SD's Fine Chemicals, Boisar, India, were used as such. Bovine serum albumin (BSA; MW = 67 kDa; Himedia Laboratories (P)., Bombay, India); egg albumin (MW = 45 kDa; CSIR, Biochemical Centre, Delhi, India); trypsin (MW = 20 kDa) and pepsin

(MW = 35 kDa) from SRL, Bombay, India; and PEI (MW = 30–40 kDa) from Fluka AG, Buchs, Switzerland, were all used as received.

Preparation and Characterization of Membranes

MCA and CDA were blended in different proportions using DMF as a solvent by thoroughly mixing for 4 h at room temperature. The membranes were cast using a casting blade on a glass plate. The cast membranes were evaporated for 30 s at $60 \pm 5\%$ relative humidity, followed by immersion in a gelation bath containing water kept at 10°C. The thickness of spread casting solution was controlled by manually adjusting the height of the casting blade.

Thickness of the cast membranes was measured by micrometer (Mitutoyo, Tokyo, Japan) at various parts of a particular membrane. The thickness of the membrane maintained in this work was 0.22 ± 0.02 mm. The membranes were initially pressurized with distilled water at 414 kPa for 4 h. These prepressurized membranes were used in subsequent UF experiments at 345 kPa using a UF kit supplied by Spectrum (Los Angeles, CA). Further, these membranes were characterized as follows.

Pure Water Flux

The membranes were first washed thoroughly with distilled water, then initially pressurized at

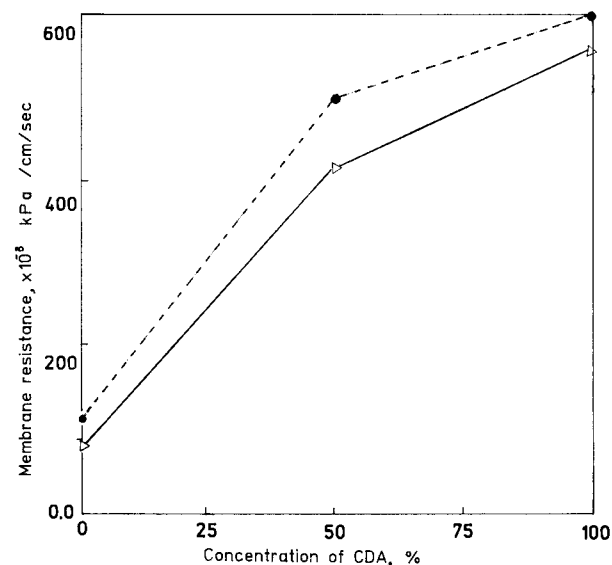


Figure 2 Plot of membrane resistance versus concentration of CDA solvent/polymer ratios (— ● —) 4.0; (— △ —) 4.71.

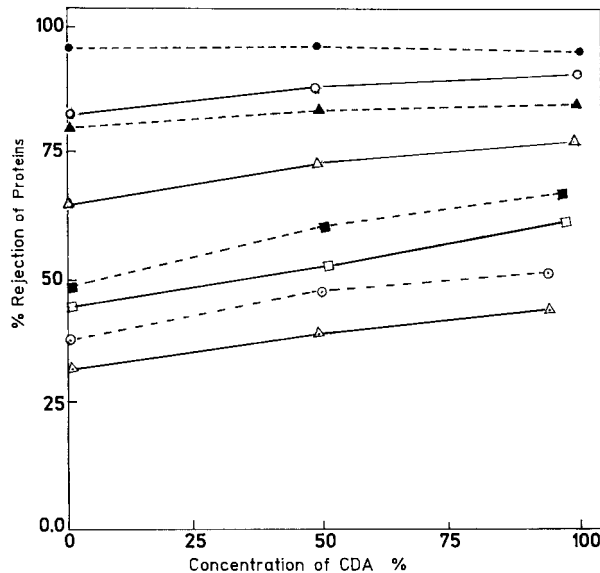


Figure 3 Plot of rejection versus concentration of CDA for the system of pepsin, trypsin, egg albumin, and BSA. Solvent/polymer ratios (---) 4.0; (—) 4.71: (●) BSA; (○) BSA; (▲) EA; (△) EA; (■) Pepsin; (□) Pepsin; (⊙) Trypsin; (△) Trypsin.

414 kPa for about 4 h and subjected to pure water flux (PWF) at 345 kPa using the following equation⁸:

$$Jw = Q/A\Delta t$$

where Q is the permeate amount; Jw is the water flux; Δt is the sampling time; and A is the membrane area.

Resistance of Membrane

The PWF was measured at different transmembrane pressures, viz., at 69, 138, 207, 276, and 345 kPa. The resistance of the membrane (R_m) was evaluated from the slope of plot of water flux versus pressure difference (ΔP) using the following equation⁹:

$$Jw = \Delta P/R_m$$

Water Content

The water content of the membranes was obtained¹⁰ by soaking them in water for 24 h, then mopping with plotting paper and weighing them in closed weighing bottles. The dry weights were determined after the wet samples were placed in a drier at 75°C for 48 h.

% water content

$$= \frac{(\text{Wet sample weight} - \text{Dry sample weight})}{\text{Wet sample weight}} \times 100$$

Molecular Weight Cutoff

Molecular weight cutoff (MWCO) of a membrane is determined¹¹ by identifying an inert solute which has the lowest MW and has solute rejection (SR) of 80–100% in steady-state UF experiments. The percent of SR is calculated as follows:

$$\% \text{ SR} = \left(1 - \frac{C_p}{C_f}\right) \times 100$$

where C_p and C_f are concentrations in ppm of permeate and feed, respectively.

Pore Statistics of Membranes

MW of solutes which have SR above 80% may be used to determine the average pore size of membrane using the equation

$$\% \text{ SR} = 100(\bar{\alpha}/\bar{R})$$

where \bar{R} refers to average pore radius of membrane and $\bar{\alpha}$ is the constant obtained from the

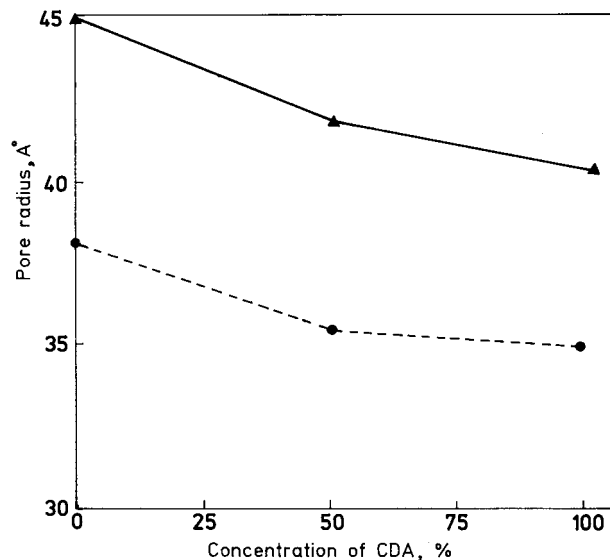


Figure 4 Plot of pore radius versus concentration of CDA. Solvent/polymer ratios (----) 4.0; (—) 4.71.

Table I Characteristics of the Cellulose Acetate Blend Membrane

Membrane	DMF/ Polymer Ratio	Composition (%)		Flux (cm/s at 345 kPa)	Water Content (Qw %)	Pore Radius (Å)	Porosity (%)	No. of Pores/cm ² × 10 ⁻⁹	Membrane Resistance (kPa/cm/s × 10 ⁻³)
		MCA	CDA						
MDB10	4.71	100	0	4677	81.41	44.95	0.268	4.220	86.95
MDB30	4.71	50	50	1299	80.5	41.71	0.059	1.079	427.35
MDB50	4.71	0	100	895	80.0	40.43	0.051	0.993	578.0
MDB10C	4.0	100	0	3939	79.64	38.15	0.224	4.900	113.63
MDB30C	4.0	50	50	916	77.54	35.47	0.058	1.568	500.00
MDB50C	4.0	0	100	823	73.13	35.07	0.050	1.048	694.44

intersection of plot of SR versus solute MW, as reported by Sarbolouki.¹²

Assuming the membrane is an asymmetric skin type and the flow is through a circular orifice, surface porosity (ε) of the membrane may be evaluated¹³ using

$$\varepsilon = \frac{3\pi\eta J}{\bar{R}\Delta P}$$

where η is the viscosity of permeate; J is the solvent flux in presence of solute; ΔP is applied pressure; and \bar{R} is the average pore radius.

From the values of surface porosity and average pore radius, \bar{R} , the number of pores, n , is computed from

$$n = \varepsilon/\bar{R}^2$$

The effects of metal ion concentration and casting solution composition were also examined and results are discussed.

Metal Ion Separation

When the feed contains only the metal ions, no separation takes place in view of the membranes' large pore size. Hence, a polymeric chelating agent such as PEI was added to the feed so that complexes of PEI with heavy metal were formed which, in turn, increased the size of the permeating species (viz., the metal ion-polymer complex). Different concentrations of copper solution were prepared (viz., 3,000, 2,000, 1,500, and 1,000 ppm) by dissolving in 0.4% PEI aqueous solution. Then all the membranes were tested for separation of copper ion by UF at constant pressure of 345 kPa. The percentage rejection of copper was

calculated from ultraviolet absorbance of feed and permeate at λ max = 625 nm.

RESULTS AND DISCUSSION

In order to study the resistance characteristics of the membrane, the roles of pressure and composition of polymer in casting solution on PWF were carried out. To characterize the membranes in terms of pore statistics and the MWCO, the separation of proteins of different MW was attempted. Finally, the applicability of the membrane for heavy metal ion removal was undertaken and a possible correlation was deduced from experimental findings. The results are discussed as follows.

Effects of Pressure and Polymer Composition of Casting Solution on PWF

The permeate water flux was found to increase as expected in the range 69 to 345 kPa pressure for all the membranes of different compositions of CDA, investigated at solvent/polymer ratios of 4 and 4.71. Results are illustrated in Figure 1.

It can be seen from Figure 1 that PWF increases with the increase in the solvent/polymer ratio. This may be explained on the basis that an increase in the above ratio tends to reduce the polymer fraction and, in turn, to increase the average size of pores on the membrane surface. Further, at the lower solvent/polymer ratio, higher consolidation, alignment, and concentration of polymer chain molecules in the membrane surface tend to decrease the average size of pores on the membrane surface. Similar results were also observed by Kutowy and Sourirajan.¹⁴

Further, for a fixed solvent/polymer ratio, the

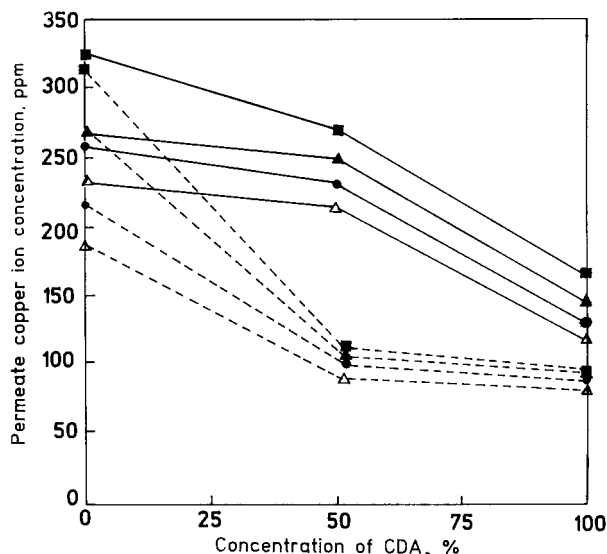


Figure 5 Plot of permeate copper ion concentration versus concentration of CDA for membranes having solvent/polymer ratios 4.0 (---) and 4.71 (—): C_f (■) 3,000 ppm; (▲) 2,000; (●) 1,500; (△) 1,000.

flux decreases with the increase in the CDA concentration in the blend. These changes are understandable on the basis that increased CDA in a fixed solvent/polymer ratio tends to decrease the size of supermolecular polymer aggregates in the casting solution, which will result in the formation of smaller pores on the membrane surface.^{14,15}

The hydraulic resistance offered by the membrane was calculated from PWF values; it was found from Figure 2 that R_m for a fixed solvent/polymer ratio increases almost linearly with increased CDA concentration. Further, there is a considerable reduction in R_m when the solvent/polymer ratio is changed from 4.0 to 4.71. These results are in good agreement with the foregoing facts. However, MCA has higher PWF compared with CDA for a given solvent/polymer ratio (Fig. 1). This may be due to the higher hydrophilic nature of MCA, compared with CDA.

Role of Solvent-to-Polymer Ratio on MWCO

In order to determine the MWCO of various membranes, the permeation of proteins of different molecular weights (i.e., trypsin, pepsin, egg albumin, and BSA) through the membrane were studied. The effects of CDA percentage in the blend at different solvent/polymer ratios on percent rejection of proteins are shown in Figure 3.

For a given value of solvent/polymer ratio, an increase in concentration of CDA in the blend results in higher rejection of protein. This is due to the fact that an increase in the CDA concentration reduces the hydrophilicity of the resultant blend and hence the flux. This, in turn, increases the percent separation of protein. Further, an increase in solvent/polymer ratio tends to increase the protein separation at a given CDA concentration. These may be explained on the basis that an increase in ratio increases the void volume of the membrane surface. These changes are again understandable on the basis that increases in solvent/polymer ratio, for a fixed CDA concentration, in the casting solution tend to increase the size of the supermolecular polymer aggregates in the casting solution; this results in the formation of larger-size pores on the membrane surface.^{14,15} Similar experiments were carried out using different membranes.

From the above results, MWCO of the membranes having solvent/polymer ratios of 4.71 and 4.0 were found to be 67 and 45 kDa, respectively,

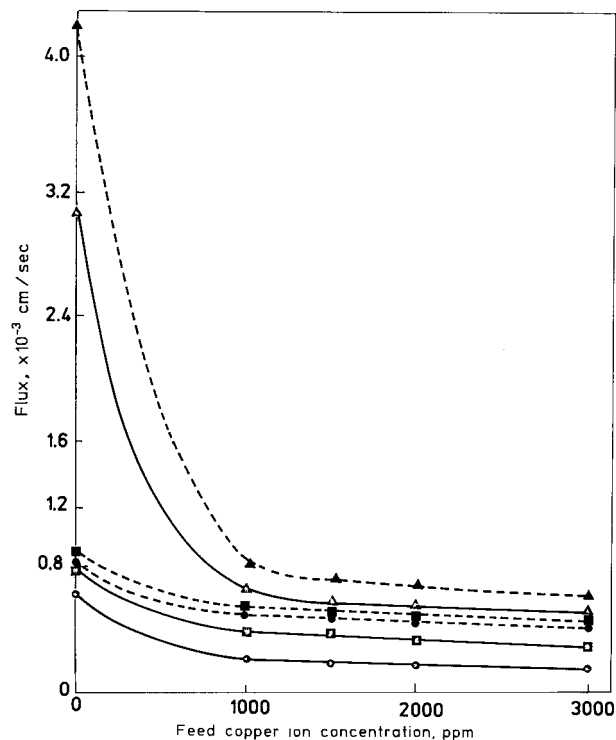


Figure 6 Plot of flux versus feed copper ion concentration for membranes having solvent/polymer ratios 4.0 (—) and 4.71 (---): (▲) MDB10; (■) MDB30; (●) MDB50; (△) MDB10C; (□) MDB30C; (○) MDB50C.

Table II Comparison of Experimental and Predicted Values of C_p

Membrane	α	β	C_f (ppm)	C_p Experimental (ppm)	C_p Predicted (ppm)	Deviation (%)
MDB10	380	614	1000	239	235	3.4
			1500	266	270	
			2000	275	290	
			3000	332	315	
MDB30	313	424	1000	222	220	1.1
			1500	239	244	
			2000	258	258	
			3000	278	274	
MDB50	183	416	1000	123	129	4.0
			1500	137	143	
			2000	149	151	
			3000	176	161	
MDB10C	385	924	1000	195	200	5.0
			1500	220	238	
			2000	271	263	
			3000	323	294	
MDB30C	130	341	1000	096	097	2.0
			1500	102	106	
			2000	110	111	
			3000	114	117	
MDB50C	120	320	1000	092	091	1.0
			1500	100	099	
			2000	105	103	
			3000	109	108	

on the basis that MWCO is related to the protein of the lowest molecular weight which has solute rejection beyond 80%. Similar observations were reported by Balakrishna and colleagues¹⁶ and Fane and Fell.¹⁷

Effect of Polymer Concentration on Pore Radius

From the MWCO experiments, the pore radii of these membranes were calculated.¹² It is evident from Figure 4 that at a given solvent/polymer ratio, an increase in CDA concentration in the blend tends to decrease the number of pores and also the pore radius. These changes are understandable on the basis that increase in CDA concentration tends to decrease the size of polymer aggregates in the casting solution, which results in the formation of smaller-size pores on the surface.¹³

However, at a given CDA concentration, an increase in solvent/polymer ratio tends to increase the pore size. These trends are understandable because an increase in solvent/polymer ratio tends to decrease the closely packed paracrystal-

line modules/microlamellae, resulting in pores with larger sizes on the membrane surface.¹²

The porosity of these membranes was also calculated by Velicangil and Howell.¹³ For a given solvent/polymer ratio, porosity and number of pores/cm² decrease with increase in the concentration of CDA, as shown in Table I. On the other hand, at a given CDA concentration, an increase in solvent/polymer ratio tends to increase the porosity of the membrane. These findings are in good accordance with results discussed earlier.

Effect of Polymer Concentration on Water Content of Membrane

The effect of CDA concentration in blend on water content is shown in Table I. It is evident from this table that for a given solvent/polymer ratio, an increase in CDA concentration decreases water content. This is due to the fact that an increase in CDA concentration not only reduces the pore size but also decreases the number of pores, due to a higher rate of polymer aggregation on the

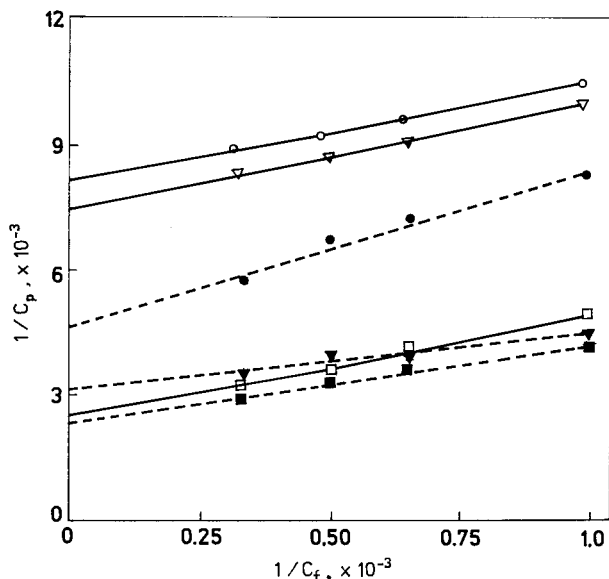


Figure 7 Plot of $1/C_p$ versus $1/C_f$ for membranes having solvent/polymer ratios 4.0 (—) and 4.71 (----): (■) MDB10; (▼) MDB30; (●) MDB50; (□) MDB10C; (▽) MDB30C; (○) MDB50C.

membrane surface.¹⁴ Further, for a given CDA concentration, an increase in solvent/polymer ratio increases water content, as expected.

Copper Ion Solution Separation

A series of experiments with feed copper ion concentration ranging from 1,000 to 3,000 ppm was performed with six types of membranes; results are discussed below.

Effect of CDA Concentration on Permeate Copper Ion Concentration

An increase in the CDA concentration tends to decrease the permeate copper ion concentration, *viz.*, it increases the SR for a given feed concentration of copper ion; results are shown in Figure 5. This is expected because at a constant solvent/polymer ratio an increase in CDA concentration tends to favor the formation of smaller-size pores and also reduces the number of pores on the membrane surface.

The effects of feed copper ion concentration on the flux at 345 kPa for various membranes are illustrated in Figure 6. The flux has been found to decrease with increase in feed copper ion concentration, as expected. This may be explained as follows: for a fixed transmembrane pressure, at

high feed concentration, the resistance offered by solute (RS) increases in addition to Rm. Further, the RS is due to the combination of resistances offered by (1) cake formation and (2) concentration boundary layer. Hence, at high solute concentration cake formation is enhanced which, in turn, increases the resistance to flow and hence the reduced flux at high feed concentration.¹⁸

Effect of Feed Copper Ion Concentration on Permeate Concentration

For copper sulfate solution, results relating the ultrafiltrate stream concentration to the inlet stream concentration are presented in Table II. It has been found that the permeate concentration increases with the increase in feed concentration.

With the above experimental results, the ultrafiltrate water quality, C_p , was related to feed copper ion concentration at constant transmembrane pressure difference by a simple function of the form

$$C_p = \frac{\alpha C_f}{\beta + C_f} \quad (1)$$

where C_p is the permeate copper ion concentration in ppm and C_f is the feed copper ion concentration in ppm. Also,

$$\text{Rejection coefficient } R = 1 - (C_p/C_f) \quad (2)$$

Substituting eq. (1) into eq. (2),

$$R = 1 - (\alpha/\beta + C_f) \quad (3)$$

The constants α and β depend upon the type of metal and composition of the membrane casting solution.

1. At high feed copper concentration, β is negligible. Equation (3) is then reduced to

$$R = 1 - \alpha/C_f \quad (4)$$

2. At very low feed concentration, C_f is negligible. Equation (3) is then reduced to

$$R = 1 - \alpha/\beta \quad (5)$$

Similar observations were also reported by Osada

and Nakagara⁸ and Bhattacharya¹⁹ at different feed concentrations.

Determination of α and β

The constants α and β are evaluated as follows: The inverse of eq. (1) is of the form

$$1/C_p = \frac{\beta + C_f}{\alpha C_f}$$

$$1/C_p = (\beta/\alpha) \times (1/C_f) + (1/\alpha)$$

Thus the intercept of the plot drawn between $1/C_p$ and $1/C_f$ will be $1/\alpha$ and the slope will give β/α . The plots of $1/C_p$ versus $1/C_f$ for various membranes are presented in Figure 7. The calculated values of α and β for various membranes appear in Table II.

The average deviation, D , is defined as¹⁹

$$\%D = \frac{(C_p \text{ expt} - C_p \text{ pred})/C_p \text{ expt}}{n}$$

where n is the number of data points, and $C_p \text{ expt}$ and $C_p \text{ pred}$ and C_p experimental and predicted, respectively.

The comparison of $C_p \text{ expt}$ and $C_p \text{ pred}$ is given in Table II for all membrane types at various metal ion inlet concentrations.

CONCLUSIONS

The feasibility of removing heavy-metal ions (particularly copper ion with macromolecular chelating agent, i.e., PEI) has been studied using cellulose acetate blend membrane of different grades at various polymer compositions. The membranes were characterized in terms of MWCO, water content, and pore statistics (i.e., pore radius, porosity, and number of pores per unit area). The effect of casting solution composition on the membrane performance was investigated. Experiments were

carried out over a broad range of feed copper ion concentrations (1,000–3,000 ppm) at average transmembrane pressure difference of 345 kPa.

Empirical equations were developed to enable the prediction of the concentration of copper ions in the ultrafiltrate with reasonable accuracy.

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