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Cellulose Triacetate Membrane for Applications in Plating, Fertilizer, and Textile Dye Industry Wastes

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Abstract

Cellulose triacetate (CTA) membranes for use in plating, fertilizer, and textile dye waste treatment were developed from a casting solution made from CTA, dioxane, acetone, maleic anhydride, and methanol. The effects on reverse osmosis performance of the dioxane–acetone ratio, polymer concentration, and the concentrations of methanol and maleic anhydride in the casting solution in addition to evaporation time are reported. The composition of the casting solution, the evaporation time, and the casting and gelling conditions are established for obtaining membranes suitable for the above waste-treatment applications. The results of experiments with the respective industrial wastes are discussed.

INTRODUCTION

Rapid industrialization and the increasing demand for water necessitates proper waste management and reuse of water. The emergence of membrane technology and particularly of reverse osmosis (RO) as a promising waste-treatment procedure indicates possibilities to overcome pollution problems by elimination of toxic contaminants, viruses, and bacteria, and also provides reusable water. Although RO was developed primarily for desalination, its potentials for industrial waste treatment have been realized. Bregman (*1*) and Luttinger (*2*) discussed the possibilities of using RO in industrial waste treatment. Some of the advantages of RO in treating industrial wastes are: 1) it is a continuous process, 2) it requires no rege-

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nerant chemicals, 3) it offers the possibility of recycle of permeate water, and 4) it provides a concentrate for use as a make-up solution when the waste contains a costly chemical.

However, it is necessary to ensure that the membrane possesses sufficient chemical and biological stability to withstand the broad spectrum of chemical characteristics of industrial wastes such as pH, temperature, reducing and oxidizing chemicals present, etc. Conventional cellulose acetate polymer has limitations for applications in industrial waste treatment because of its sensitivity to hydrolysis and its biodegradability. Aromatic polyamide, polyamide hydrazide, etc. are chemically and biologically more stable than cellulose acetate, but they are susceptible to attack by free chlorine (*3*). These polymers are not commercially available in India, whereas cellulose triacetate (CTA), which is better than cellulose acetate (CA) in respect of hydrolytic resistance, is commercially available. Therefore, CTA asymmetric membranes were developed for the express purpose of application in waste treatment.

In the electroplating industry a large volume of water is used for rinsing the plated articles, and consequently the rinse water contains toxic and valuable inorganic salts in low concentrations. The discharge of such wastewaters into natural water streams or municipal sewer results in severe environmental pollution and a reduction in the efficiency of biological treatment processes (*4*, *5*). The application of RO technique in electroplating waste was reviewed by Goetzelmann (*6*) and Shastri (*7*). Extensive research and development in this area using cellulose acetate and other polymers has been reported in the literature (*8–17*).

In the fertilizer industry, the main waste constituents are ammoniacal nitrogen and phosphate along with urea. Patel (*18*) studied different parameters for the application of RO in fertilizer industry waste treatment. However, the alkalinity of the feed and low urea rejection by the cellulose acetate membrane restrained its application.

Textile dye industry wastes are characterized by objectionable color, high biochemical oxygen demand (BOD), chemical oxygen demand (COD), total organic carbon (TOC), and suspended solids. Extremes of pH and substantial concentration of heavy metals like chromium, zinc, and copper are also typical of these discharges. Applications of RO for treatment of waste from textile dye industries are available in the literature (*19–23*).

In this paper the development and the applicability of cellulose triacetate membranes in the treatment of wastes from plating, fertilizer, and textile dye house industries are examined in view of the fact that CTA has a better hydrolytic, chemical, and biological resistance than CA.

EXPERIMENTAL

Cellulose triacetate supplied by Mysore Acetate & Chemicals Co. Ltd., Mandya, was used during the investigation. Membranes were made on glass plates from casting solutions containing CTA, dioxane–acetone mixed solvent, maleic anhydride, and methanol with a thickness of 130–150 μm and gelled in an ice-cold water bath kept at a temperature of 0–2°C after evaporation periods varying from 60 to 150 s. All the membranes, which were tested in an RO kit described elsewhere (*24*), were used without any annealing treatment. The operating pressure and feed flow rates employed were 600 psig (40.8 kg/cm^2, 4133 kPa) and 730 mL/min, respectively. The area of the membranes used was 15.38 cm^2. The RO experiment consisted of determining the rate of permeation of solution through the membrane, the PR (product rate) in liters per square meter per day ($L \cdot m^{-2} \cdot d^{-1}$), and the concentration of the feed and permeate.

RO experiments were carried out with the following solutions as feed apart from the 0.5% NaCl solution which was employed for characterizing the membranes in terms of NaCl rejection (or separation) and product rate: 1) $NiCl_2$; 2) $NiSO_4$; 3) $NiSO_4 \cdot (NH_4)_2SO_4$; 4) boric acid; 5) Watts nickel plating bath at different dilutions; 6) Nishal AB nickel plating bath at different dilutions; 7) diluted nickel plating bath with brightener; 8) actual nickel plating waste; 9) ammonium sulfate, diammonium phosphate, urea, and ammonium chloride as individual solutes and in a mixture; and 10) organic dye solutions, viz., Atul Scarlet 4 BS, Victoria Blue, and Rhodamine.

The chemical analysis of different substances was carried out as follows for both the feed and permeate samples:

(1) Ni, Ca, and Mg by atomic absorption spectrophotometry
(2) Boric acid by a volummetric identical pH method (*25*)
(3) Sulfate (*26*), diammonium phosphate (*27*) and urea (*28*) by a spectrophotometric method
(4) Sodium chloride and ammonium chloride by conductivity

The solute separation (or rejection), f, was determined by using the relation

$$f, \% = \frac{C_F - C_P}{C_F} \times 100$$

where C represents concentration and the subscripts F and P denote feed and permeate solutions, respectively.

RESULTS AND DISCUSSION

The RO performance of asymmetric membranes depends on the morphology of the membrane developed. The morphology is affected by the composition of the casting solution, the additives present in the casting solution, the evaporation time, the shrinkage temperature, etc. In this paper the effect of solvent composition, polymer concentration, additives such as methanol and maleic anhydride, and evaporation time are discussed.

Because of higher acetyl content and molecular regularity, the solubility of CTA in most common solvents is lower than that of cellulose acetate, ($DS = 2.5$). CTA is soluble in chlorinated hydrocarbons, aniline, phenol, formic acid, benzoic esters (*29*), formamide, and liquid sulfur dioxide (*30*) as well as sulfolane (*31*). However, in view of the necessity for the solvents to miscible with water as well as to have a low boiling point to effect evaporation at room temperature, the above solvents were found unsuitable. Klein and coworkers (*32*) reported that dioxane could be used in place of acetone in a CA membrane system, and Bairinji (*33*) and Mungle (*34*) obtained promising membranes cast from the acetone–dioxane system. Because both acetone and dioxane are water soluble, a solvent system comprised of dioxane and acetone was selected. CA–CTA blend membranes with methanol and maleic acid (*35*, *36*) as additives have been successfully developed. The monomethyl ester of maleic acid has been reported to be a swelling agent (*33*). Maleic anhydride is reported to dissolve in alcohols by the formation of an ester (*37*). Therefore, CTA casting solutions were prepared with acetone–dioxane mixed solvent along with methanol and maleic anhydride as additives.

The dioxane to acetone ratio studied varied from 1.1 to 2.17. In casting solutions having a ratio of 1.17, lumps and gel particles were seen, whereas they were either absent or not significant in casting solutions with solvent ratios of 1.38, 1.71, and 2.17.

The RO performance of membranes cast from casting solutions with varying dioxane–acetone ratios at different evaporation times is given in Table 1. The following trends may be noted from the data presented in Table 1: 1) For any given evaporation time, solute (or NaCl) rejection increases and the corresponding product rate decreases with an increase in the dioxane–acetone ratio; 2) membranes gelled after an evaporation time of 90 s or more and made from casting solutions containing a dioxane–acetone ratio of 1.38 or more exhibited NaCl separation in excess of 90%.

As membranes with NaCl separation in the range of 92–94% could adequately separate divalent ions (*38*), a condition that can give membranes with the above separation range with maximum flux over the range of variables studied could be selected. With this consideration in mind, it can

TABLE 1

RO Performance of CTA Membranes Made from Different Casting Solution Compositions and at Different Evaporation Times[a]

Dioxane–acetone ratio	Evaporation time (s)							
	60		90		120		150	
	Percent separation	Flux $(L \cdot m^{-2} \cdot d^{-1})$	Percent separation	Flux $(L \cdot m^{-2} \cdot d^{-1})$	Percent separation	Flux $(L \cdot m^{-2} \cdot d^{-1})$	Percent separation	Flux $(L \cdot m^{-2} \cdot d^{-1})$
1.11	50.0	978	71.5	768	90.1	591	82.0	689
1.38	74.1	934	94.0	665	92.1	538	90.0	650
1.71	86.2	709	91.8	601	93.7	513	94.1	538
2.17	87.5	670	93.0	562	96.0	489	96.0	469

[a] Casting solution composition, wt%: CTA (9.5); solvent (76.5); methanol (9); maleic anhydride (5). Gelation bath: Ice cold water at 1°C. Operating pressure: 40.8 kg/cm^2. Feed: 5000 ppm NaCl. Feed flow rate: 730 mL/min.

be seen that a favorable combination of flux and solute separation is obtainable for membranes made from a casting solution containing an acetone and dioxane ratio of 1.38 and an evaporation time of 90 s.

With these preliminary conditions, efforts were made to improve the flux or product rate of the membranes by varying the polymer and additives concentrations. Before discussing the above experiments, a brief explanation of Trend 1) above is in order. The increase in solute rejection and the decrease in product rate with an increase in dioxane concentration can be explained by the mechanism of dense-skin formation. When the evaporation of solvent starts soon after casting by virtue of the solute's lower boiling point, acetone volatilizes faster than dioxane. Because the proportion of acetone in the casting solution decreases more rapidly from a solution containing a smaller acetone fraction than from one containing a larger fraction, the cloud point for CTA precipitation is reached earlier in solutions containing a smaller acetone proportion and a buildup of the skin layer occurs earlier. Therefore, the thickness of the skin layer is greater for a given evaporation time for a solution with a higher dioxane–acetone ratio than for one with a lower ratio. Consequently, the separation increases and the accompanying flux decreases with an increase in the dioxane–acetone ratio.

The effect of CTA concentration on the RO performance of membranes made from casting solutions containing 8–10% CTA can be seen from Table 2. For 8 and 9% CTA concentrations, as evaporation increases, separation increases and product rate decreases. For membranes made from 9.5% CTA solutions, as evaporation time increases, separation in-

TABLE 2

RO Performance of CTA Membranes Made from Casting Solution Containing Different Concentrations of Polymer at Different Evaporation Times[a]

		Evaporation time (s)					
Polymer concentration (%)	Solvent: polymer ratio	60		90		120	
		Percent separation	Flux $(L \cdot m^{-2} \cdot d^{-1})$	Percent separation	Flux $(L \cdot m^{-2} \cdot d^{-1})$	Percent separation	Flux $(L \cdot m^{-2} \cdot d^{-1})$
8.0	9.75	68.4	1149	79.0	914	87.0	797
9.0	8.55	58.4	1594	75.4	1036	77.7	880
9.5	8.05	75.0	936	94.1	660	92.0	524
10.0	7.60	92.2	611	93.5	596	61.4	1075

[a] Casting solution composition, wt%: CTA (8–10); solvent (76–78); methanol (9); maleic anhydride (5). Dioxane:acetone = 1.38. Gelation bath: Water at 0–1°C. Operating pressure: 40.8 kg/cm^2. Feed: 5000 ppm NaCl. Feed flow rate: 730 mL/min.

creases, reaches a maximum at 90 s, and then decreases with an accompanying constant decrease of product rate, whereas separation reaches a maximum for a 90-s evaporation period and then decreases for membranes made from 10% CTA. Product rate remains nearly constant for 60 and 90 s, but increases sharply for 120 s accompanied by low separation. Again, the best performance is for 9.5% CTA with 90 s evaporation time. Lower polymer concentration resulted in a lower viscosity of the casting solution, which is not desirable for casting flat membranes. The reproducibility of membranes made from 10% solution was insufficient, probably due to defects in the membranes caused by gel particles.

The effect of methanol and maleic anhydride is illustrated by the data presented in Table 3. The following observations emerge from these data:

(1) High solute rejection with low product rate are obtainable for membranes made from casting compositions containing neither methanol nor maleic anyhdride.
(2) With only maleic anhydride, slightly higher solute separation accompanied by lower product rate is obtainable compared to membranes made from casting solutions devoid of malic anhydride and methanol.
(3) The highest separation with moderate product rate could be achieved with only methanol, whereas the requisite separation with the highest flux could be obtained in the presence of maleic anhydride and methanol.

The above observations indicate that maleic anhydride alone cannot serve as a swelling agent whereas methanol can. An increase in methanol

TABLE 3
RO Performance of CTA Membranes: Role of Methanol and Maleic Anhydride[a]

Composition of casting solution (g)				Evaporation time (s)			
				90		120	
CTA	Solvent	Maleic anhydride	Methanol	Percent separation	Flux ($L \cdot m^{-2} \cdot d^{-1}$)	Percent separation	Flux ($L \cdot m^{-2} \cdot d^{-1}$)
9.5	76.5	—	—	95.4	191	95.7	240
9.5	76.5	5.0	—	96.5	116	95.8	166
9.5	76.5	—	9.0	97.3	366	97.6	465
9.5	76.5	5.0	9.0	92.8	635	90.0	547

[a] Solvent: Dioxane–acetone in the ratio of 1.38. Gelation bath: Water at 2°C. Operating pressure: 40.8 kg/cm^2. Feed: 5000 ppm NaCl. Feed flow rate: 730 mL/min.

concentration, however, decreases the solubility of the polymer. The necessity of the presence of both methanol and maleic acid indicates that the monoethyl ester of maleic anhydride serves as the swelling agent.

The effects of the proportions of methanol and maleic anhydride in the casting solution on the performance of CTA membranes were investigated, and the data are reported in Table 4. Again, it can be seen that high separation and high flux are obtainable when the concentrations of maleic anhydride and methanol are in the ranges of 3.5 and 9%, respectively.

From the data discussed so far, it is obvious that the membranes perform the best in the following conditions:

(a) *Casting solution composition:* CTA:solvent:methanol:maleic anhydride = 9.5:76.5:9.0:5.0 with dioxane and acetone as the solvents in a dioxane–acetone ratio of 1.38.
(b) *Casting conditions:* Membrane thickness = 130–150 μm, evaporation time = 90 s, annealing temperature = not annealed, and gelation bath = water at 0–2°C.

A few preliminary experiments were carried out to test the suitability of higher alcohols like ethanol and *n*-propanol. The product rate decreased as methanol was replaced by ethanol and ethanol was replaced by *n*-propanol (PR(methanol) > PR(ethanol) > PR(*n*-propanol)] for evaporation times of 90 and 120 s. The product rate decreased with increasing evaporation time. The solute separation, however, did not show a definite trend,

TABLE 4
RO Performance of CTA Membranes: Effect of Methanol and Maleic Anhydride Concentration[a]

Composition of Additives (g)		RO performance	
Maleic anhydride	Methanol	Percent separation	Flux ($L \cdot m^{-2} \cdot d^{-1}$)
5	7	82.0	626
5	9	93.7	636
5	11	67.3	860
3	9	94.2	562
7	9	84.1	709

[a] Composition of solution, g: CTA (9.5); solvent (76.5); maleic anhydride (3–7); methanol (7–11). Dioxane:acetone = 1.38. Gelation bath: Water at 0°C. Evaporation time: 90 s. Operating pressure: 48.8 kg/cm^2. Feed: 5000 ppm NaCl. Feed flow rate: 730 mL/min.

but at the same time it was not significantly diffrent. Similarly, replacing maleic anhydride by phthalic anhydride resulted in a significant drop in the product rate with practically no difference in solute separation. These data also indicate that the CTA:dioxane:methanol:maleic anhydride system seems to be the best.

Before making experiments with a nickel electroplating waste solution, a series of experiments were carried out to test for the separation by CTA membranes of individual components generally found in nickel plating baths, followed by dilute nickel plating baths to simulate rinse wastewaters. The experimental data on rejection of $NiCl_2$, $NiSO_4$, $NiSO_4 \cdot (NH_4)_2SO_4$, and boric acid by CTA membranes are presented in Table 5. The separation of NaCl by the CTA membrane used for the above experiments was about 93%. It can be seen that the separation of all nickel salts was more than 99% and that the rejection of $NiSO_4$ was very close to 99.9%, indicating the possibility of favorable Ni recovery and a considerable reduction in nickel content in the permeate. The accompanying product rate varied between 470 and 510 $L \cdot m^{-2} \cdot d^{-1}$. However, the rejection of boric acid, which was about 67%, is significantly lower than NaCl separation in view of its weakly ionizable character and hydrogen bonding capacity. Yet this rejection of boric acid is considerably higher than with CA membranes in which it is 28% (*39*). The higher rejection of boric acid in CTA is attributable to the increased hydrophobicity of CTA (*40*). The next series of experiments performed were with Watts nickel plating bath and Nishal AB

TABLE 5

RO Performance of CTA Membrane with Solutions of Individual Components of Nickel Plating Bath at Different Concentrations

System	Feed concentration (ppm)	RO performance	
		Percent separation	Product rate ($L \cdot m^{-2} \cdot d^{-1}$)
$NiCl_2 \cdot 6H_2O$	1000	99.6	513
	2000	99.7	508
	3000	99.6	494
$NiSO_4 \cdot 6H_2O$	1000	99.99	503
	2000	99.95	508
	3000	99.99	479
$NiSO_4(NH_4)_2SO_4 \cdot 6H_2O$	1000	99.91	513
	2000	99.95	503
	3000	99.98	494
H_3BO_3	1000	67.2	523

(trade name) nickel plating bath supplied by Canning Mitra Phoenics Ltd., Bombay, at different dilutions to represent rinse water. The experimental results are presented in Table 6. The product rate for different dilutions are given in Fig. 1. It can be seen from Table 6 that Ni^{2+} rejection is $\geq$99.5% at all concentrations; however, the separation of Ni in baths containing sulfate, chloride, and boric acid is less than that observed for single solute systems. It can also be seen that the rejection of boric acid decreases from 69.6 to 38.7% when the concentration of the feed increases from 1 to 50%. In the case of experiments with dilute Nishal AB bath, the Ni^{2+} rejection is again $\geq$99.5% except at a dilution of 50%. It can be seen from Fig. 1 that when Watts nickel bath was treated, the product water flux decreased from 489 to 83 $L \cdot m^{-2} \cdot d^{-1}$ with an increase in bath concentration from 1 to 50%, whereas for Nishal AB bath the decrease of flux is from 513 to 342 $L \cdot m^{-2} \cdot d^{-1}$ for the same concentration change. The difference in behavior of flux with the feeds of two bath solutions is a result of the total dissolved solids being different and contributing to differences in osmotic pressure. Figure 1 can be used to arrive at the practical limit of concentrating the waste economically.

Because plating baths usually contain brighteners (*41*), the effect of brightener on RO performance was also studied. A brightener with the trade name Nishal 168 was added in a 10-mL/L quantity to the plating bath, and the RO performance was evaluated by diluting to 50, 25, 15, 10, and 1% of the original bath concentration. The data are presented in Table 7. Comparison of Tables 6 and 7 shows that the brightener does not affect the performance of the CTA membrane. Actual nickel plating wastewater

TABLE 6
RO Performance of CTA Membrane with Diluted Nickel Plating Baths

Plating bath	Concentration of diluted bath, % of original	% Separation of Ni^{2+}	BO_3^{3-}	SO_4^{2-}
Watts nickel plating bath	1	99.99	69.6	99.3
$NiSO_4 \cdot 6H_2O$ (337.5 g/L) +	10	99.90	56.4	99.3
$NiCl_2 \cdot 6H_2O$ (75 g/L) +	15	99.50	39.5	99.1
H_3BO_3 (37.5 g/L)	25	99.50	38.7	98.8
	50	99.07	—	—
Nishal AB nickel plating bath	1	99.80	—	—
	10	99.99	—	—
	15	99.91	—	—
	25	99.97	—	—
	50	99.15	—	—

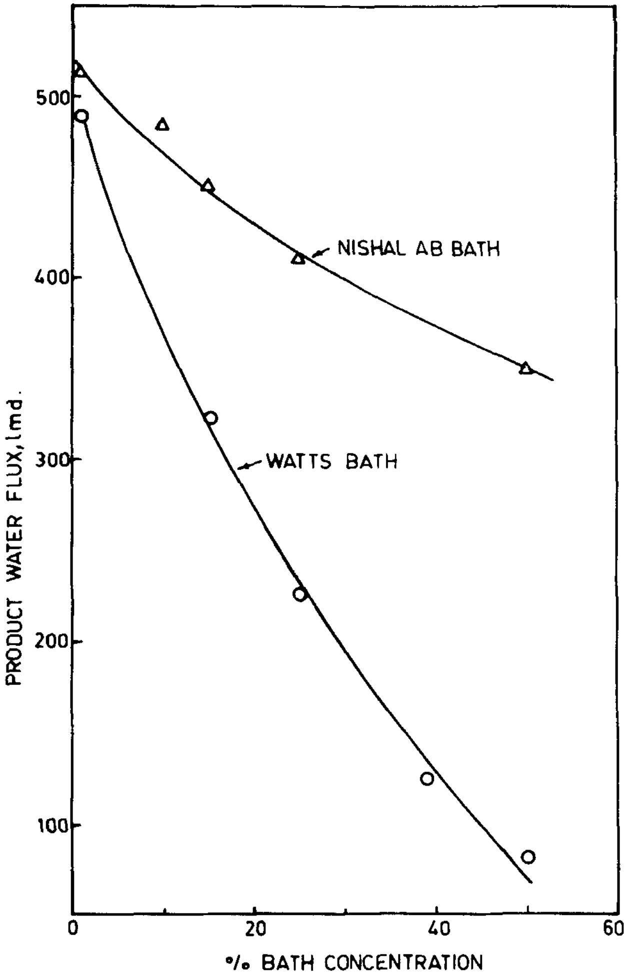

FIG. 1. Effect of concentration of plating on RO product rate through cellulose triacetate membranes.

collected from Gopal Electroplaters, Bhavnagar, was filtered through filter paper (No. 42) to remove suspended solids. Rejections by CTA membranes were determined with the filtered feed solute. The data are presented in Table 8. The rejection of Ni and TDS were quite appropriate for the removal and concentration of Ni from waste streams. The permeation rate of treated solution was about 580 L·m^{-2}·d^{-1}, sufficient for practical ap-

TABLE 7
RO Performance of CTA Membrane with Diluted Nickel Plating Bath in the Presence of Brightener

Bath and brightener used	Feed in % concentration of original bath	RO performance Separation of Ni^{2+} (%)	 Product rate ($L \cdot m^{-2} \cdot d^{-1}$)
Nishal AB nickel plating bath (125 g/L) with Nishal 168 brightener (10 mL/L)	1	99.95	518
	10	99.98	484
	15	99.93	459
	25	99.98	430
	50	99.40	352

plications. The pH of the waste was 6.8, which is favorable for treatment of such solutions by CTA membranes.

From our studies on nickel separation by RO using CTA, it can be concluded that the method could be applied to a typical waste stream such as from Gopal Electroplaters, where the rinse bath contains about 1120 ppm Ni^{2+}. On treatment, the permeate would contain about 1 ppm Ni^{2+}, which could be recycled for rinsing purposes. The concentrated Ni^{2+} could be reused.

In order to evaluate the feasibility of the application of the RO technique to fertilizer industry waste for the purpose of reusing water and/or recovering chemicals, the separations of urea, ammonium chloride, ammonium sulfate, and diammonium phosphate were measured by separate experiments using single solutes and in an experiment with a feed mixture containing urea, ammonium sulfate, and diammonium phosphate. The experimental results are presented in Tables 9 and 10. From Table 9, it

TABLE 8
RO Performance of CTA Membrane with Actual Nickel Electroplating Waste (source: Gopal Electroplaters, Bhavnagar)

Feed characteristics	RO performance Product rate ($L \cdot m^{-2} \cdot d^{-1}$)	Percent separation of TDS	 Ni^{2+}	 Ca^{2+}	 Mg^{2+}
pH 6.8; Ni^{2+} concentration, 1120 ppm	582	97.2	99.94	96.0	95.0

TABLE 9
RO Performance of CTA Membranes with Components of Fertilizer Waste as Individual Solute Systems at Different Concentrations

Solute	Concentration in feed (ppm)	RO performance: Percent separation	RO performance: Product rate ($L \cdot m^{-2} \cdot d^{-1}$)
$(NH_4)_2SO_4$	1000	98.9	577
	2000	98.2	572
	3000	98.5	562
$(NH_4)_2HPO_4$	1000	99.98	567
	2000	99.95	567
	3000	99.92	557
Urea	1000	55.2	562
	2000	53.3	557
	3000	51.8	557
NH_4Cl	1000	95.05	587
	2000	95.12	577
	3000	95.40	571

can be seen that ammonium chloride is rejected to about 95.3% at all concentrations studied, which is almost the same as for NaCl, whereas the rejection of $(NH_4)_2SO_4$ is higher. The rejection of diammonium phosphate was the highest (99.5%) and that of urea the lowest (50–55%). The high rejection of phosphate and sulfate is due to their high valency (greater than that of chloride) and the low separation of urea is attributable to the fact that it is non-ionizable and has capacity to form H-bonds. The rejection of urea in CTA (55%) is higher than in CA (28%) (*42*) as a result of

TABLE 10
RO Performance of CTA Membrane with Feed Containing a Mixture of Urea, Diammonium Phosphate, and Ammonium Sulfate (200 mg/L each)

Feed composition (% of original feed)	RO performance: Product rate ($L \cdot m^{-2} \cdot d^{-1}$)	Percent separation of PO_4^{3-}	Percent separation of Urea	Percent separation of SO_4^{2-}
Original	533	99.7	53.1	98.8
90	533	99.8	53.5	98.7
70	552	99.8	55.2	98.8
50	582	99.9	55.5	98.5

TABLE 11
RO Performance of Cellulose Triacetate Membrane with Different Organic Dye Solutions (50 ppm of dye)

	RO performance	
Type of dye	Product rate ($L \cdot m^{-2} \cdot d^{-1}$)	Dye separation (%)
Atul's Scarlet 4 BS	523	98.1
Victoria Blue	406	~100.0
Rhodamine	479	85.3

increased hydrophobic interaction with increasing acetyl content (*40*). The product rate is about 560 $L \cdot m^{-2} \cdot d^{-1}$.

Table 10 presents data on the rejection of PO_4^{3-}, urea, and SO_4^{2-} as determined in an experiment with feed containing a mixture similar in composition to the combined effluent of the fertilizer industry. It can be seen that the rejections are not significantly affected by the presence of other solutes. Barring urea, it appears that the other components of the effluent could be concentrated.

The possibility of application of CTA membranes for treating textile dye industry wastes is indicated by experiments with some common organic dyes present in such wastes.

The rejection of some of the common dyes by CTA membranes are presented in Table 11. It can be seen that rejection is >98% for all the dyes studied except rhodamine (85.3%). The product rate in these cases range from 400 to 450 $L \cdot m^{-2} \cdot d^{-1}$. The experimental data indicate that CTA membranes could be successfully employed for recovering the dyes and reducing the pollution load caused by the effluent.

CONCLUSIONS

CTA membranes which could be used for industrial waste treatment were made from casting solutions containing dioxane, acetone, methanol, and maleic anhydride. These membranes can be used without heat treatment. Conditions were established to obtain membranes having an NaCl separation of 92–94% with 535–700 $L \cdot m^{-2} \cdot d^{-1}$ flux. These membranes were investigated with a few industrial waste streams. The study indicated that 1) in plating industry waste the chief constituent, such as Ni^{2+}, could be separated up to 99.9% with a reasonable permeate flux for recovery of the chemical economically or for its reuse. However, the separation of boric acid was as low as 67% due to H-bonding. 2) In the case of fertilizer industry waste, the separation of $(NH_4)_2HPO_4$, $(NH_4)_2SO_4$, and NH_4Cl is in the range of 99 to 95% with acceptable flux rates. Here again, the low separation of urea may be attributed to H-bonding, as is the case of boric acid in the plating industry. However, CTA membranes exhibited higher separations for both of these compared to CA membranes. 3) The treatment of dye industry wastes using CTA membranes for the concentration of dyes was quite encouraging, particularly in the cases of Victoria Blue and Atul's Scarlet 4BS, where the separation was found to be in the range of 98 to 100%. The lower separation of rhodamine indicated the need for further modification of membranes if a separation of >95% is to be achieved.

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REFERENCES

1. J. I. Bregman, *Environ. Sci. Technol.*, *4*(4), 296 (1970).
2. L. B. Luttinger and G. Hoche, *Ibid.*, *8*(7), 614 (1974).
3. R. E. Kesting, "Asymmetric Cellulose Acetate Membranes," in *Reverse Osmosis and Synthetic Membranes: Theory–Technology–Engineering* (S. Sourirajan, ed.), National Research Council of Canada, Ottawa, 1977, Chap. 5.
4. E. F. Barth, J. N. English, B. V. Salotto, B. N. Jackson, and M. B. Ettinger, *J. Water Pollut. Control Fed.*, *37*, 163 (1965).
5. *Interaction of Heavy Metals and Biological Sewage Treatment Process*, U.S. Public Health Services Publication 999-WP-22, 1965.
6. W. Goetzelmann, *Galvanotechnik*, *64*(7), 588 (1973).
7. V. S. Shastri, *Reverse Osmosis for the Treatment of Metal Waste Solutions, Energy, Mines and Resources*, Canada Scientific Bulletin C. M. 75-9, 1975.
8. A. Golomb, *Plating*, *57*, 376, 1001 (1970); *59*, 316 (1972); *60*, 482 (1973).
9. A. R. Hauck and S. Sourirajan, *J. Water Pollut. Control Fed.*, *44*(7), 1377 (1972).
10. J. Morse, *Plat. Surf. Finish.*, *64*(11), 47 (1977).
11. R. G. Donnelly, R. L. Goldsmith, K. J. McNulty, D. C. Grant, and M. Tan, *Treatment of Electroplating Waste by Reverse Osmosis*, U.S., NTIS, P.B. Rep. 265393, 1976, p. 106.
12. A. Golomb, "Application of Reverse Osmosis to Electroplating Waste Treatment," in *Reverse Osmosis and Synthetic Membranes: Theory–Technology–Engineering* (S. Sourirajan, ed.), National Research Council of Canada, Ottawa, 1977, p. 481.
13. K. S. Subramanian, M. Malaiyandi, and V. S. Shastri, *Sep. Sci. Technol.*, *15*(5), 1205 (1980).
14. B. A. Farnand, F. D. F. Talbot, T. Matsuura, and S. Sourirajan, in *Synthetic Membranes*, Vol. II (A. F. Turbak, ed.), (ACS Symp. Ser. 154), 1981, p. 339.
15. U. Tadashi, F. Tohru, and S. Mizuho, *Polym. Commun.*, *25*(1), 30 (1984).
16. *Vala Libour Pourchove Upravy*, *1–2*, 39 (1987) (in Czechoslovakian).
17. Nippon Electroplating Engineers K.K., Japanese Kokai Tokyo Koho JP 62,149,892 [87,149,892] (1988).
18. M. D. Patel, R. S. Parmar, R. D. Ahuja, D. J. Mehta, A. S. Kane, M. V. Chandorikar, and H. N. Shah, *Reverse Osmosis: Its Application to Recover Water from Effluent of Fertilizer Industry*, Paper presented at the Second Conference on Water Desalination, CSMCRI, Bhavnagar, 1–3 March, 1972.

19. C. A. Brandon, J. S. Johnson, R. F. Minturn, and J. J. Porter, *Text. Chem. Color.*, *5*(7), 134 (1973).
20. C. A. Brandon and T. N. Sargen, "Renovation of Textile Dyeing and Finishing Waste Waters by Hyperfiltration for Population Abatement by Resource and Energy Recovery through Complete Recycle," *DECHEMA-Monogr.*, *80*(Teil 1, No. 1616–1638), 191 (1976).
21. C. A. Brandon, *Ind. Water Eng.*, *12*(6), 14 (1976).
22. A. M. Al Nashar, *Desalination*, *20*(1–3), 267 (1977).
23. H. Cohen and S. Loeb, "Industrial Waste Treatment by Means of Reverse Osmosis Membranes," in *Reverse Osmosis and Synthetic Membranes: Theory–Technology–Engineering* (S. Sourirajan, ed.), National Research Council of Canada, Ottawa, 1977, p. 519.
24. V. P. Pandya, B. J. Bhallala, R. M. Kava, and D. J. Mehta, *Curr. Sci.*, *42*(8), 270 (1973).
25. I. M. Kolthoff and P. J. Elving (eds.), *Treatise on Analytical Chemistry*, Part II, Section A, Vol. 10, Wiley, New York, 1978, p. 56.
26. D. F. Boltz and J. A. Howell, *Colorimetric Determination of Nonmetals*, Wiley, New York, 1978, p. 473.
27. Ref. *25*, p. 243.
28. *Analytical Methods for Fertilizer Waste Waters*, Gujarat State Fertilizer Co. Ltd., 1972.
29. E. Hauser, *The Chemistry of Cellulose*, 3rd ed., Wiley, New York, 1947, p. 269.
30. H. J. H. Fenton and A. J. Berry, *Proc. Cambridge Phys. Soc.*, *20*(I), 16 (1920).
31. R. E. Ketsing and W. J. Subonsky, *Second Quarterly Report to O.S.W.*, Phillico-Ford Publication U-4290, USDI, December, 1967.
32. B. Keilin, *Res. Dev. Prog. Rep. 117*, O.S.W., USDI, 1964.
33. R. Bairinji, J. Matsui, and A. Negishi, *Chem. Abstr.*, *79*, 68025y (1973).
34. C. R. Mungle et al., *Ibid.*, *84*, 152502n (1976).
35. S. V. Joshi and D. J. Mehta, *Indian Chem. J.*, *11*(10), 21 (1977).
36. S. V. Joshi and D. J. Mehta, *Ibid.*, *12*(4), 22 (1977).
37. R. E. Kirk and D. F. Othmer (eds.), *Encyclopedia of Chemical Technology*, Vol. 8, Interscience, New York, 1952, p. 682.
38. R. Rangarajan, T. Matsuura, E. C. Goodhue, and S. Sourirajan, *Ind. Eng. Chem. Process Des. Dev.*, *15*, 529 (1976).
39. A. Golomb, *Plating*, *59*, 316 (1972).
40. C. E. Reid and E. J. Breton, *J. Appl. Polym. Sci.*, *1*, 133 (1959).
41. C. L. Faust and W. H. Safranek, in *Encyclopedia of Chemical Technology*, Vol. 5 (R. E. Kirk and D. F. Othmer, eds.), Interscience, New York, 1954, p. 635.
42. H. K. Lonsdale, in *Progress in Separation and Purification*, Vol. 3 (E. S. Perry and C. J. Van Oss, eds.), Wiley-Interscience, New York, 1970, p. 191.

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