HAZARDOUS SOURCE AND WASTE REDUCTION IN METALS FINISHING INDUSTRY BY HYBRID MEMBRANE SEPARATION PROCESS

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Abstract

Short-term and long-term membrane stability tests were conducted with a 50% copper cyanide electroplating bath on commercially available thin film composite reverse osmosis membranes (DESAL3, MS10 and SW30HR). Circular membrane sections of 38.5 cm^2 were tested for flux and salt rejection after exposure to copper cyanide solutions (pH 13.5) on a flat sheet test module. SW30HR exhibited good chemical stability during exposure to the pH extreme of 13.5 for up to 4 months. DESAL3 and MS10 showed deterioration of performance after a one week exposure. Pretreatment studies were carried out on SW30HR membrane for flux enhancement in order to improve the recovery of the reverse osmosis system. SW30HR pretreated with 15 wt% ethanol for 6 hours exhibited an order of magnitude increase in flux accompanied by an increase in ion rejection. The work presented here indicates that SW30HR is a suitable membrane for recycling of high pH copper cyanide rinse waters.

INTRODUCTION

The metal finishing industry has an increasingly difficult problem controlling the effects of its wastewaters. The wastes that could cause problems include rinse waters from metal electroplating solutions, acidic and alkaline cleaning and pickling solutions. These rinse waters, if discharged into the environment without treatment, can pollute natural resources and inhibit or destroy natural biological activities. Specific examples of these detrimental effects include the toxicity of heavy metals and cyanides to various forms of aquatic life[1] and the deleterious effect of copper on biological sewage treatment processes[2].

The Hazardous and Solid Waste Amendments (HWSA) to the Resource Conservation and Recovery Act (RCRA) include specific provisions restricting the land disposal of RCRA wastes. The purpose of these HWSA provisions is to minimize the potential of future risk to human health and the environment by requiring treatment of hazardous wastes prior to their land disposal.

It is estimated that there are approximately 20,000 metals plating job shops throughout the US which generate about 10 million tons per year of plating wastes (including cyanide containing wastes). Spent baths and rinse waters are a major portion of the waste generated by the metal plating/finishing industry because of the volume and heavy metal content.

The metal finishing industry typically uses highly alkaline cyanide plating baths which consist mainly of heavy metal cyanide complexes (Cu, Ag, Cd, Au, Zn etc.) and free cyanide salts. Large volumes of contaminated rinse waters are generated as a result of drag-out from the plating bath to the rinse water

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Table 1: Composition of METEX Bright Cyanide Copper Plating Solution

Chemical	Composition
Copper Cyanide	6.0 oz./gal.
Sodium Cyanide	7.75 oz./gal.
Potassium Hydroxide	2.5 oz./gal.
Metex S-1 Addition Agent (Brightener)	1%
Cupramex PL (mixture of alkaline salts)	5%

tank. From the view point of a relatively small plating operation, these are the most important wastes since they are a constantly flowing, production-connected stream of large volume which cannot be economically impounded for treatment before disposal.

Chemical precipitation of the heavy metals and oxidation of cyanides to less harmful cyanates using wet-air oxidation, electrolytic oxidation, ultraviolet light/ozonation, alkaline chlorination are the primary methods of treating these waste materials[3]. All of these techniques are aimed towards the destruction and removal of the contaminating species from the water. The task is accomplished by the addition of chemicals to the effluent stream to convert undesirable constituents to a less harmful state or whereby they can be effectively removed. Although these techniques are effective in improving the quality of the water effluent, they introduce additional waste disposal problems such as disposal of hydroxide sludge. We are presently involved in the development of a hybrid membrane recovery system involving zero discharge closed loop recovery system to eliminate disposal of waste water and sludge by recycling both the plating bath and the rinse water streams. Point-of-use recycling enables one to reclaim in excess of 90% of the chemicals used, saving energy, reducing pollution and costs dramatically. Recovery and reuse of this waste is estimated to save $150 million a year as raw material and $2 billion a year in disposal costs. Expenditure of $45-55 million could be avoided through recovery and reuse of rinse waters.

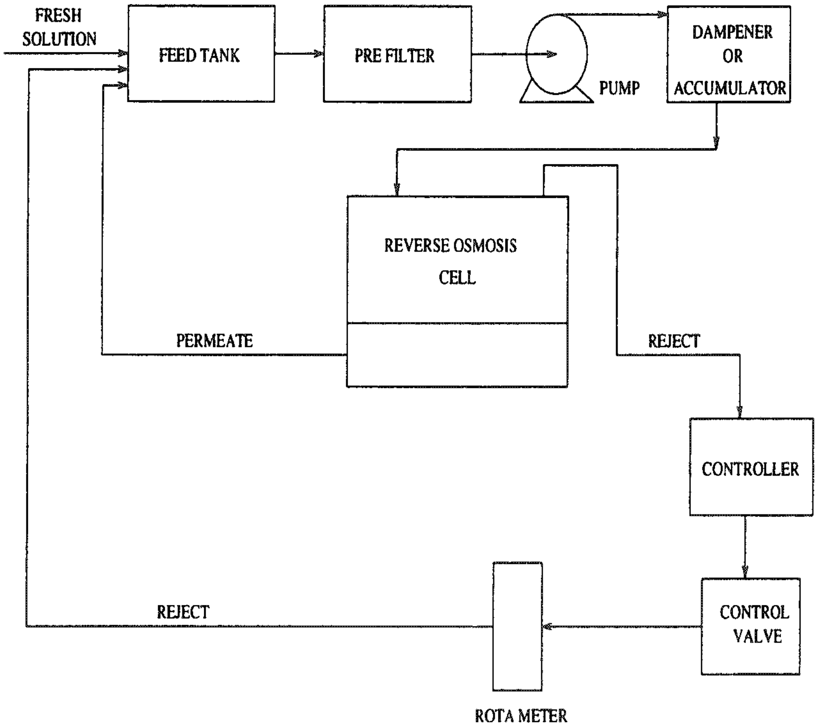
Reverse Osmosis is an attractive alternative to existing techniques in the treatment of metal finishing wastewaters. It is particularly appealing to reclaim valuable chemicals from the process stream as well as purifying water for recycling purposes. Several researchers[4,5,6,7,8,9] have examined the technical feasibility of treating various wastewater streams from nickel and chromium metal finishing operations by reverse osmosis. Zinc cyanide (pH 12.8)[10] and copper cyanide (pH 11.5)[11] rinse waters were also evaluated with reverse osmosis membranes. While these investigators demonstrated that reverse osmosis membranes can be effective in laboratory scale short term experiments, they did not evaluate the efficacy of these materials for long term, process scale conditions. In this manuscript, we present results on the use of reverse osmosis membranes for processing extreme pH (13.5) copper cyanide rinse waters under long term (up to 4 months) conditions. Copper cyanide rinse waters were selected for this investigation due to the urgent need to address the large volumes generated by the metal plating industry.

EXPERIMENTAL

Materials

The membranes selected for this application for an extremely high pH environment were DESAL3-SG from Desalination Systems (Escondido, CA), MS10 from Osmonics (Minnetonka, MN) and SW30HR from FilmTec Corporation (Minneapolis, MN). METEX Bright Cyanide Copper Bath was obtained from McDermid (Waterbury, CT). The composition of this bath is given in Table 1. Potassium Hydroxide, Copper(I) Cyanide, Sodium Chloride and Sodium Cyanide were obtained from Aldrich Chemical Company (Milwaukee, WI). Cupramex PL and Metex S-1 Addition Agent were donated by McDermid (Waterbury, CT). Sodium Chloride was purchased from Aldrich (Milwaukee, WI).

Figure 1: Schematic of experimental set-up used for transport measurements



Experimental set-up

A schematic of the single cell, closed loop recycle reverse osmosis apparatus used for the measurement of flux and rejection is given in Figure 1. The pipings, fittings and the cell were made of SS316. A diaphragm pump (PULSAFEEDER 7660) was used for recycling the salt solution (NaCl, 0.5wt%) through the system. The experiments were conducted at 350 psig pressure and the temperature of feed solution in the tank was maintained constant at 24°C. The conductivities of the feed, reject and permeate were measured with a conductivity dip cell (COLE-PARMER).

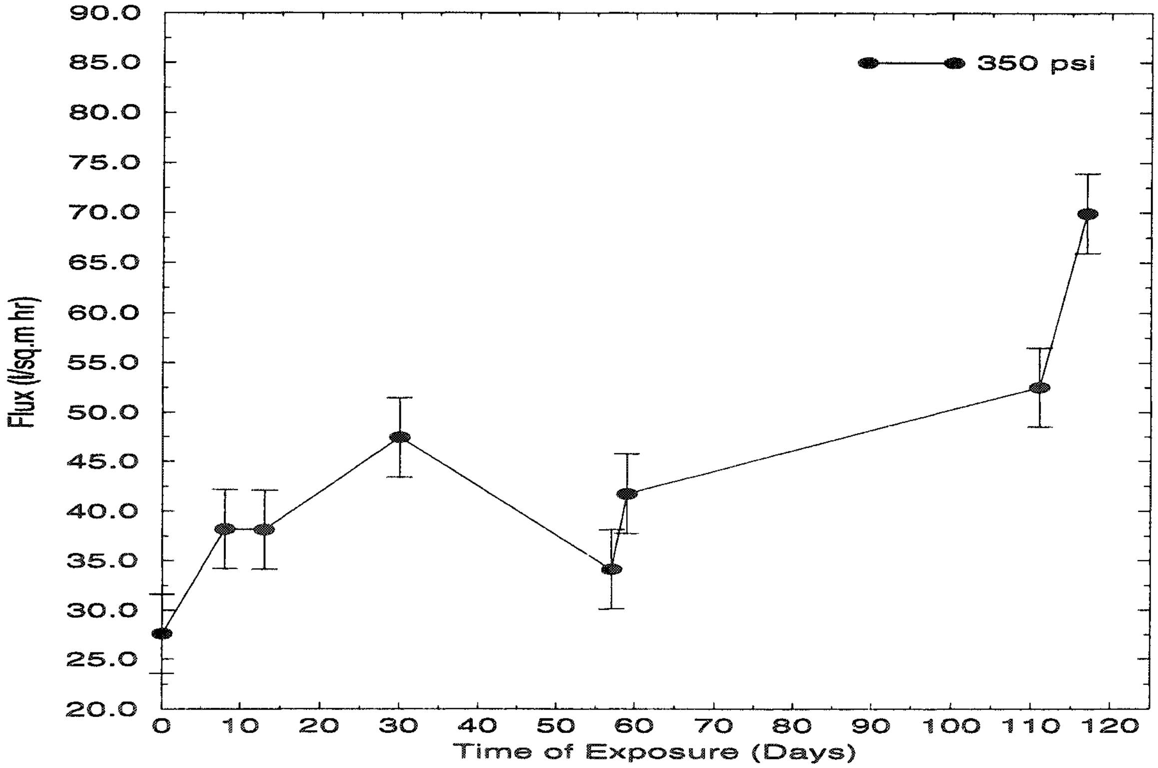
Stability Tests

Fresh sheets of DESAL3, MS10 and SW30HR were cut into circular sections of approximately 38.5 cm^2. These circular sections were then soaked at 24°C in solutions of 50% copper cyanide plating solutions for varying periods of time. The entire circular cut sections were wholly immersed without masking any face, since porous support does not play any role in determining the separation characteristics of the membranes. The membranes were taken out after various intervals of time, rinsed with deionized water and then their performance in terms of pure water flux and salt (NaCl) rejection was measured.

Chemical Pretreatment

Fresh sheets of SW30HR membranes were first exposed to 15wt% ethanol solution for 6 hours and then immersed in 50% copper cyanide plating solutions for various intervals of time. For pretreatment with HF, membranes were exposed to 15wt% HF solutions in water for 8 days and dipped in 50% copper cyanide plating solution as in the case of ethanol pretreatment.

Figure 2: Flux of DESAL3-SG membrane exposed to 50% Copper Bath



Transport Measurements

The permeate flux and the rejection of salt were determined in the flat sheet filtration cell in the laboratory. The rejection was defined as:

$$R = 1 - \frac{C_P}{C_R} \tag{1}$$

where C_P and C_R are bulk permeate and retentate salt concentrations respectively.

RESULTS AND DISCUSSION

In order for a reverse osmosis system to be successfully employed for large scale processing of copper cyanide rinse waters, it is imperative that the membrane materials used be stable under extreme pH (13.5) conditions. Some commercially available thin film composite membranes are purported to survive up to a pH of 12. Thus, the first phase of this research was to investigate the stability of various reverse osmosis membranes after extended periods of exposure to high pH cyanide containing rinse waters.

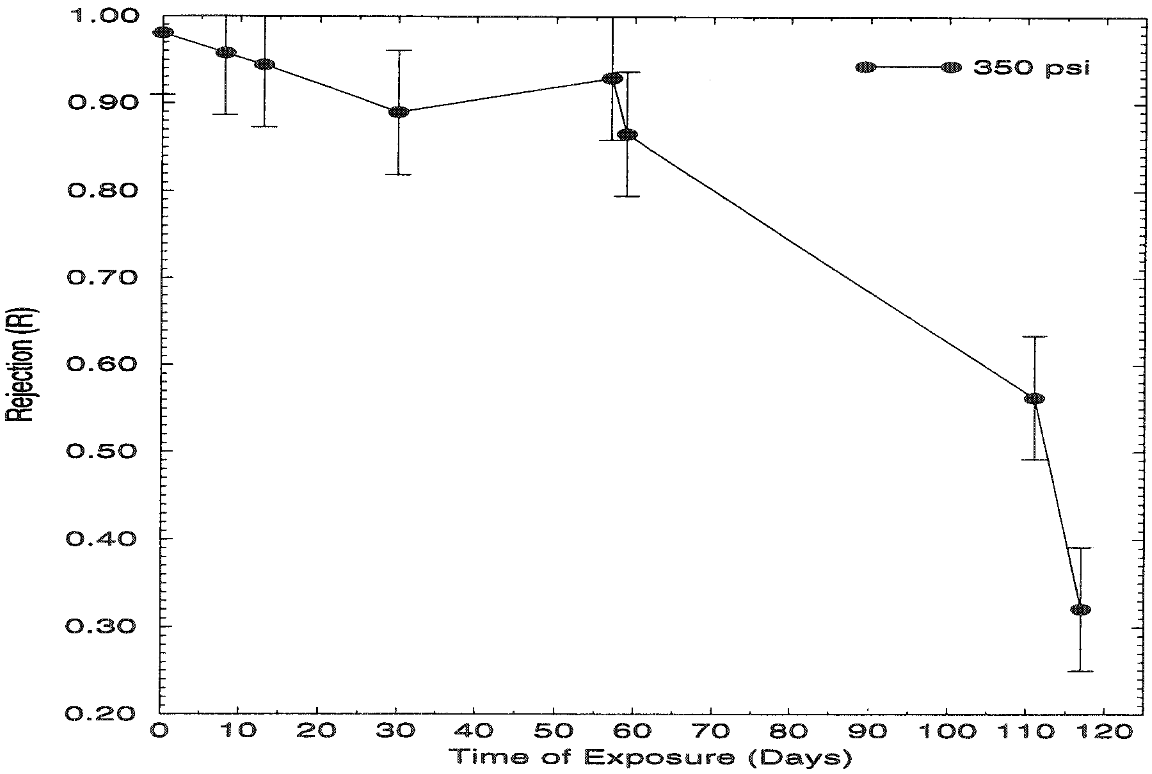
It turns out that due to osmotic limitations, the maximum concentration that can be processed in the reverse osmosis system is estimated to be approximately 50% of the metal plating bath composition. Accordingly, all membranes were exposed to 50% copper cyanide plating solutions (pH 13.5) for various times (up to 4 months) and subsequently evaluated for salt and rejection.

DESAL3

DESAL3-SG from Desalination Systems is a high flux ($\sim$ 30 $l/m^2/hr$), thin film composite polyamide membrane and is known to survive up to a pH of 11.

DESAL3 membranes were statically exposed to 50% copper cyanide plating solutions for various times and were tested for flux and rejection on the experimental system. The membrane showed a substantial decrease in rejection accompanied by an increase in flux (Figs. 2 and 3).

Figure 3: Rejection of DESAL3-SG membrane exposed to 50% Copper Bath



This clearly indicates that breakdown of the chemical structure of the membrane is occuring. It is speculated that hydrolysis of the amide -NHCO- groups is taking place on the membrane in the high pH environment. Amide groups hydrolyze to give amino and carboxylic acid groups. This leads to a breakdown of the polymeric structure which explains the increase in flux and decrease in rejection.

Scanning electron microscopy (SEM) studies were done to characterize the changes in the surface morphology. SEM studies were performed on a Zeiss (Germany) CSM 950 computerized digital scanning system. The samples were coated with 100 A° of gold using a Denton Vacuum Desk II system. They were coated for 30 seconds under 50 millitorr pressure and 40 milliamps current. The micrograph for a membrane exposed to a 50% copper plating bath solution shows clear "patches"(openings) on the surface of the membrane (Figure 5). This is in comparison to fresh DESAL3 which has a smooth homogenous surface (Figure 4). The leakage of salt probably occurs through these openings.

Since DESAL3-SG starts deteriorating on exposure to copper cyanide plating solutions on exposure for just one week, this membrane can be considered unsuitable for the desired application.

MS10

MS-10 membrane from Osmonics is a thin film composite polyamide membrane. The membrane is known to survive in a pH range between 2 and 12. Since the pH of the copper cyanide plating solution is approximately 13.5, static exposure studies were done on this membrane to determine its performance when exposed to these high pH solutions for extended periods of time. Like DESAL3-SG from Desalination Systems, flux increased (Figure 6) with a corresponding decrease in rejection (Figure 7).

Since MS10 is also a polyamide membrane like DESAL3, the increase in flux and the decrease in rejection can be explained by hydrolysis of the amide -NHCO- groups , which leads to break down of the polymeric structure.

SEM studies were also carried out for MS10 in order to study the changes in the surface of this membrane. Fresh MS10 has a granular structure (Figure 8) while a membrane exposed to a 50% plating solution for 45

Figure 4: SEM of Fresh DESAL3-SG membrane

Figure 5: SEM of DESAL3-SG exposed to 50% Copper Bath for 45 days

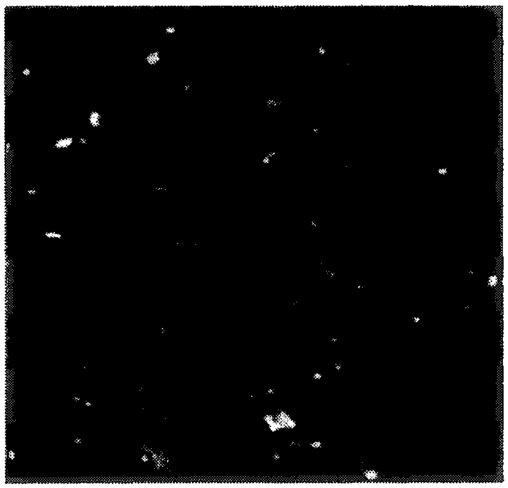


Figure 6: Flux of MS10 membrane exposed to 50% Copper Bath

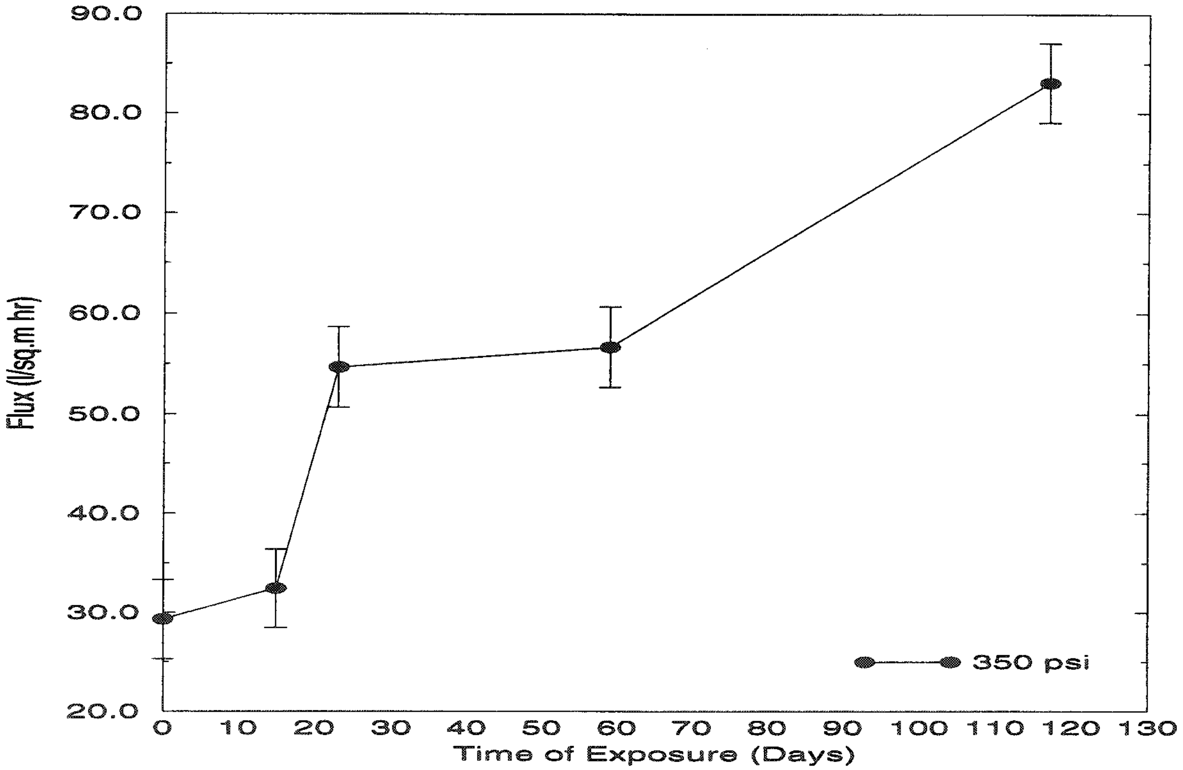


Figure 7: Rejection of MS10 membrane exposed to 50% Copper Bath

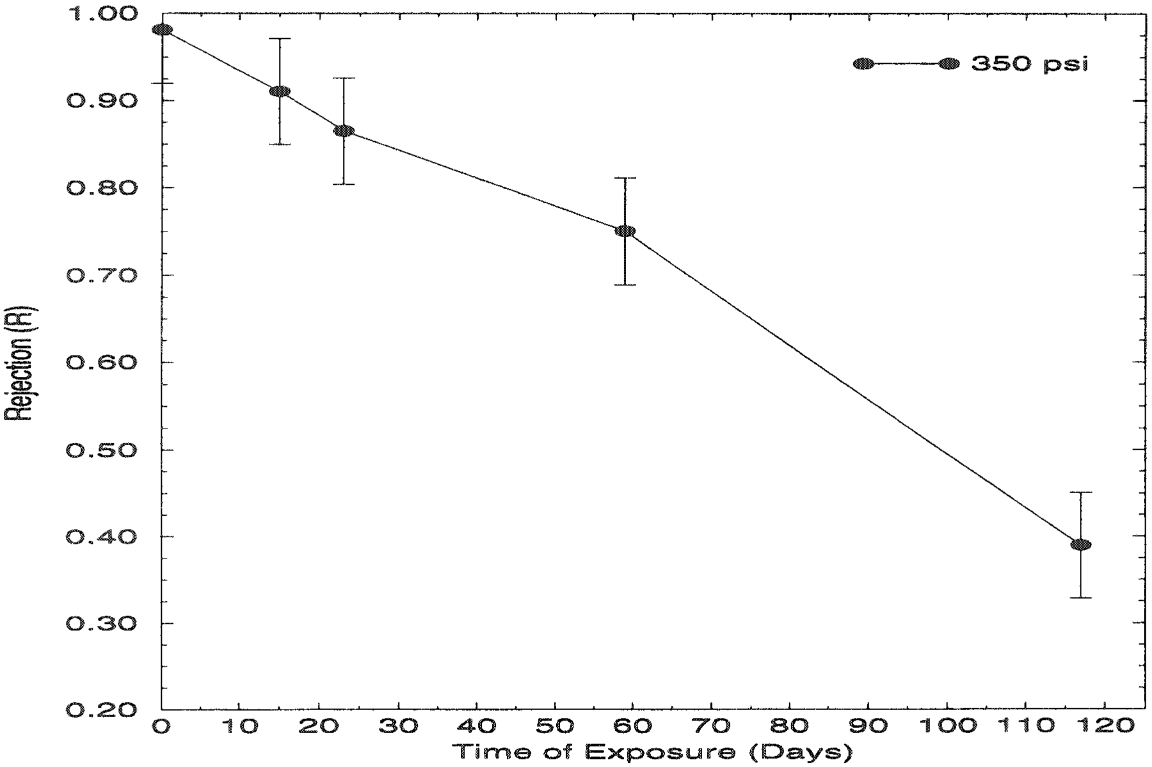
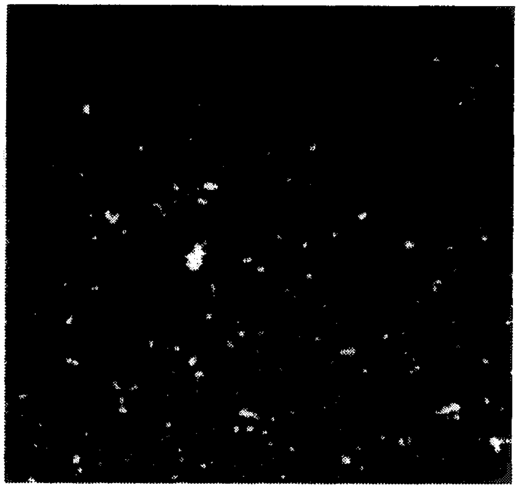


Figure 8: SEM of Fresh MS10 membrane



days was found to have patches (Figure 9) as observed for DESAL3 (Figure 5). Again it seems reasonable to assume that salt leaks though these patches (breakdown regions).

Since MS10 also starts deteriorating on exposure to high pH cyanide solutions for period of one week, this membrane can also be considered unsuitable for the desired application.

SW30HR

The SW30HR membrane from FilmTec is a relatively low flux ($\sim 6.0\ l/m^2/hr$) membrane and is known to withstand a pH up to 11.

This membrane was also exposed to the copper cyanide plating solution and was tested for flux and rejection. No decrease in flux or rejection has been observed even on exposure up to a period of 4 months (Figures 10 and 11).

These results indicate that the membrane remains intact and no significant breakdown of the polymeric structure occurs.

From SEM studies, virgin SW30HR was found to have a ridge and valley structure (Figure 12) and after exposure to a 50% copper plating bath solution for 45 days, the ridge and valley structure of the membrane remained unaffected (Figure 13). Hence SW30HR membrane was selected to be the membrane of choice for the desired application.

Pretreatment Studies

Among the membranes selected, only SW30HR survives the high pH environment of copper cyanide rinse waters. However, it is an extremely low flux membrane (approximately 6.0 $l/m^2/hr$). Therefore pretreatment studies were done on this membrane to improve its flux and hence the recovery of the reverse osmosis system. Previous studies[12,13] have shown that hydrofluoric acid[12] and ethanol[13] can be used as reagents for the enhancement of the flux and rejection of some reverse osmosis membranes.

Ethanol

Fresh SW30HR membranes were exposed to 15wt% ethanol solution for 6 hours and then dipped in 50 % copper cyanide plating solutions for various intervals of time. The resulting membrane showed approximately a 5 times increase in flux accompanied by an increase in rejection (Figures 10 and 11).

The increase in flux observed on treatment with ethanol could be attributed to its mild solvent characteristics with respect to polyamides. Hildebrand solubility parameters are very good indicators of the

Figure 9: SEM of MS10 exposed to 50 % Copper Bath for 45 days

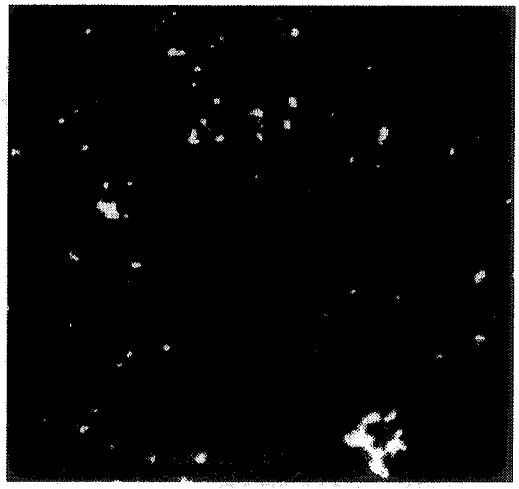


Figure 10: Flux of SW30HR membrane exposed to 50% Copper Bath

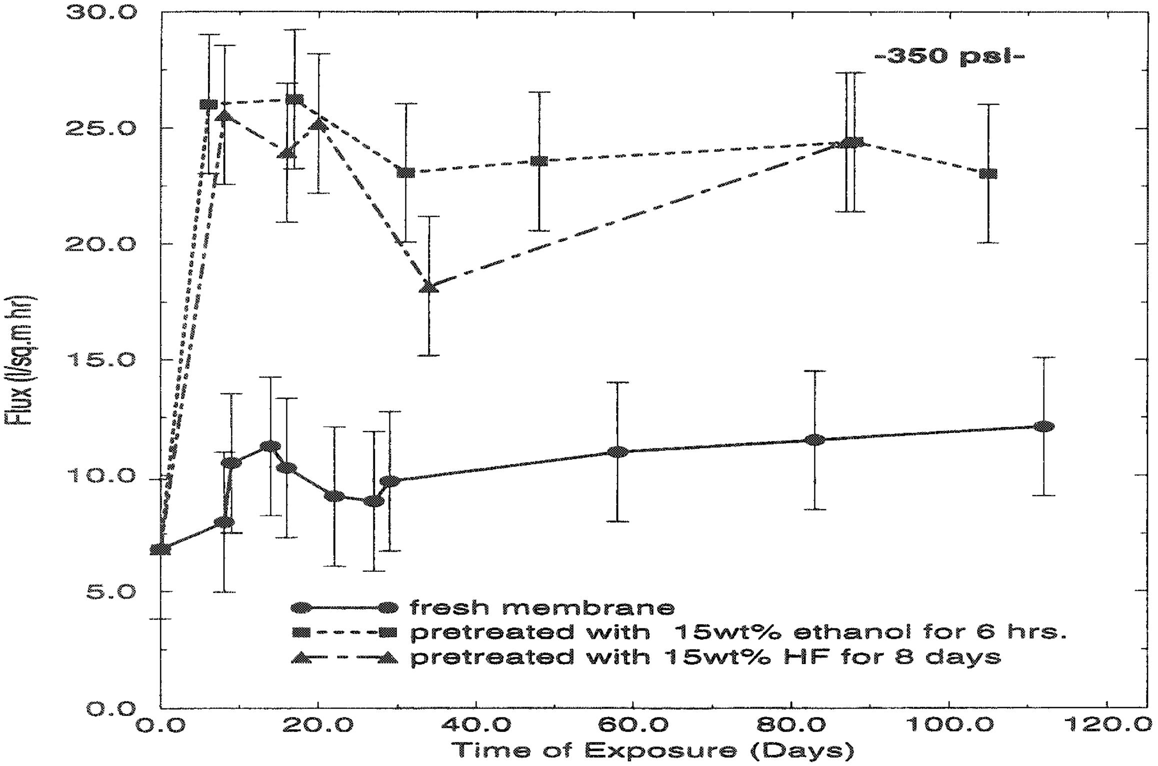


Figure 11: Rejection of SW30HR membrane exposed to 50% Copper Bath

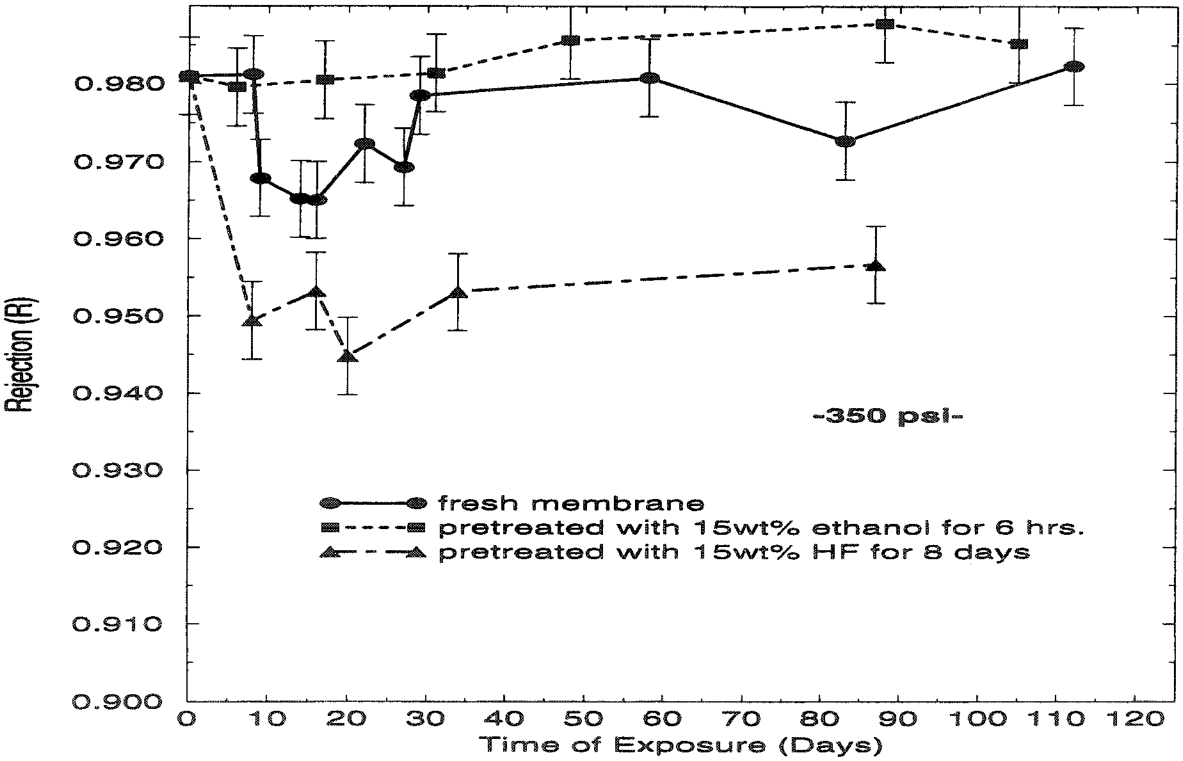


Figure 12: SEM of Fresh SW30HR membrane

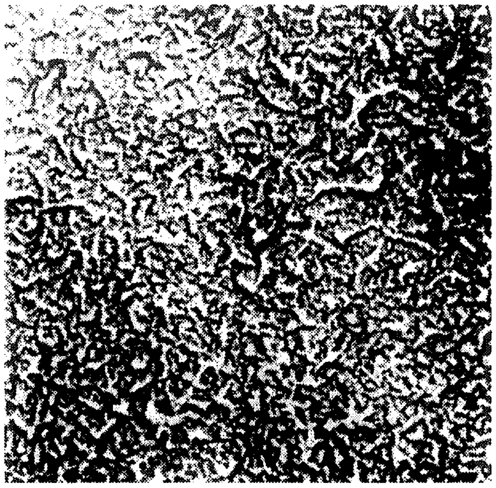
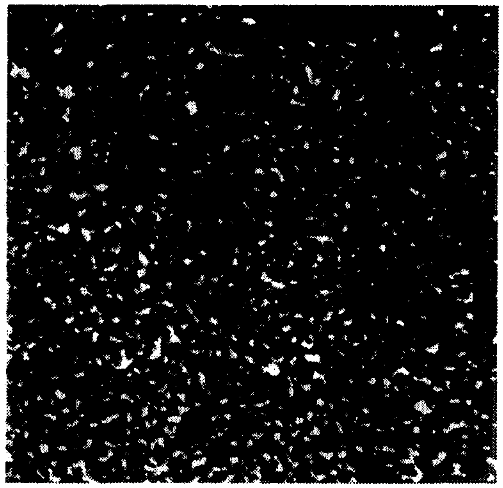


Figure 13: SEM of SW30HR exposed to 50% Copper Bath for 45 days



ability of certain organic solvents to act as solvents or swelling agents for the membrane[14]. The value of the solubility parameter of ethanol is 26.6 $MPa^{\frac{1}{2}}$ and 23 $MPa^{\frac{1}{2}}$ for the membrane[15] which makes ethanol a swelling agent for the membrane. The increase in rejection can explained by Brown's theory of latex formation[16,17] which suggests that the imperfections or defects in membranes are removed . The removal of small molecular fragments because of partial dissolution in alcohols along with the elimination of defects due to compression effects makes the membrane smoother and thinner. This combination of defect elimination and partial dissolution causes an increase in both flux and rejection[13].

Hydrofluoric Acid

Virgin SW30HR membranes were pre-exposed to 15wt% HF solution in water. For this pretreatment, the resulting membrane exhibited approximately a 5 times increase in flux accompanied by a decrease in rejection. (Figures 10 and 11).

The increase in flux of SW30HR can be explained by partial hydrolysis and increase in hydrophilicity[12] of the membrane. The decrease in rejection is probably occuring due to a reaction taking place between the fluorinated membrane and the cyanides. It is speculated that since acids cause partial hydrolysis, cyanides break the membrane structure much faster when compared to a membrane that has not been pretreated with acids.

Therefore, ethanol clearly is a much better pretreating agent because it causes an increase in rejection, it acts a lot faster (hours compared to days with HF) and is not a hazardous chemical.

CONCLUSIONS

- Due to osmotic back pressure limitations, the maximum level of recovery achievable is 50% of the bath concentration.
- DESAL3 and MS10 undergo breakdown of the chemical structure and are hence considered unsuitable for recycling copper cyanide rinse waters.
- SW30HR membranes are stable for up to 4 months to a pH extreme of ~ 13.5 and show the most promise for the desired application.
- Pretreatment of SW30HR membranes with ethanol is desirable since it can improve the recovery of reverse osmosis systems approximately 5 fold.

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