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MEMBRANE PROCESSING OF AN AQUEOUS WASTE STREAM FROM A CATALYST MANUFACTURING PLANT

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ABSTRACT

Separation of rhenium from a dilute aqueous waste stream of a catalyst manufacturing plant by a thin film composite polyamide membrane using the principle of reverse osmosis is studied. In the present study, permeate flux increases linearly with applied pressure, with slight increase in percent rejection of rhenium from the wastewater. Over 96% retention of rhenium by the membrane is observed. Increase in concentration of rhenium decreases permeate flux, relatively rapid in the beginning and then gradually, whereas, percent rejection increases marginally with increase in concentration and reaches a value of over 98. An attempt has been made to analyze the separation data by a

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graphical method of combined film theory–Solution–Diffusion model.

Key Words: Reverse osmosis; Rhenium; Aqueous waste stream; Polyamide membrane

INTRODUCTION

Processing of aqueous waste streams from chemical process industries is a rapidly emerging field due to increased public awareness and tightening statutory regulations. The problem of wastewater treatment is more important in a developing country like India due to emerging economic regions and expanding clean water requirements by the industries. Industrial waste is typically disposed off by a number of methods including biological treatment, deep well injection, and land filling and each of them requires environmental clearance, strong technological base, and also some capital investment. Membrane processes offer a number of advantages (1–5) over conventional water and wastewater treatment processes including higher standards, reduced environmental impact of effluents, reduced land requirements, and the potential for mobile treatment units. Except in water desalination, membranes have not found large scale application in water industry, particularly for the treatment of waste water from chemical process industries possibly on account of perceived poor economics, current regulatory standards that can be achieved by conventional treatment processes and limited experience of use of membranes (4). However, in certain application areas, membrane technology offers not only the possibility of water recycle but also concentration of waste and recovery of valuable chemicals (6). It is the recovery of valuable chemicals coupled with water recycle that makes membrane technology very attractive commercially. A typical example is the recovery of metals from plating bath rinse streams where metals are recovered and recycled.

In catalyst manufacturing operations, a number of expensive heavy metals are used to provide active sites for both homogeneous and heterogeneous catalysts for chemical reactions (7,8). Rhenium and platinum compounds are known to catalyze various reactions employed in the preparation of specialty chemicals, petroleum refining (9), petrochemical, and pharmaceutical industries. Incorporation of these active metal species on the catalyst support results in generation of aqueous waste containing dilute concentration of these metals, which is generally discarded and disposed off. Release of this type of aqueous waste not only results in the loss of noble metals but may also give environmental problems, if present at a significant level. Such an aqueous waste stream generated in a catalyst manufacturing plant contained rhenium. Various methods have been tried in the past for the recovery of rhenium from catalysts and ores including conventional precipitation (10,11), solvent extraction (12), ion-exchange (13–16) and each of them have certain limitations. Solvent extraction requires the mixing of solution with organic solvents that absorb the metals selectively, and leaves water with traces of the solvent. Metals are then recovered by stripping of the solvent for its recycle. Ion-exchange resin, on the other hand, selectively picks up the metal from the aqueous solution but requires a third component for its regeneration. It is the recovery of this metal from the regenerant that is complex. Since the cost of noble metals as well as water is constantly increasing, processes that are capable of water recycle in addition to metal recovery are of considerable interest. Membrane forms the basis of one of such processes on account of its inherent characteristics of selective permeation offering possibility of both water recycle and metal recovery, as it does not affect materials being recovered.

Membranes have been tried successfully for the recovery of metals from the aqueous effluents of electroplating industry and concentration of radioactive materials from dilute aqueous effluents for their safe disposal. However, practically nothing has been reported on the application of membranes for the recovery of noble and expensive metals like rhenium and platinum and also on the water recycle from the dilute aqueous streams of catalyst manufacturing operation. We have, therefore, tried to process the dilute aqueous waste stream of a catalyst manufacturing plant by membranes using the principles of reverse osmosis with a view to recovering metal and water for their recycle. Results are summarized in the present communication and analyzed following the combined film theory-solution-diffusion model.

EXPERIMENTAL

Materials

A commercial thin film composite polyamide membrane (Permea-TFC) obtained from M/s Permionics, Baroda was used. It is essentially a three layer membrane wherein the first layer is a 500–2000 Å thick interfacially polymerized active polymer layer on a 50–60 μm thick polysulfone layer casted on a nonwoven polyester for tear resistance and mechanical strength. Rhenium used in the experiments was of 99.9% purity obtained from M/s WC Haraus GmbH, Germany. It was in the form of an aqueous solution (53.3% w/w) of perrhenic acid. Wastewater stream used in the study was obtained from a catalyst and adsorbent manufacturing plant (CATAD, Thane) of Indian Petrochemicals Corporation Limited. It had a pH of 3.9, 100 mg/L rhenium with traces of platinum, and 0.05% (w/w) alumina as suspended particulate matter. It was filtered to remove the suspended particulate matter before use. Ordinary tap water was double distilled with alkaline potassium permanganate before use. It had a specific conductivity of $1-2\times10^{-6}\,\mathrm{ohm}^{-1}\,\mathrm{cm}^{-1}$

Experimental Set Up and Procedure

The experimental set up used for the concentration of rhenium in aqueous waste stream is shown in Fig. 1. It is essentially high-pressure filtration system BHT-2 of M/s Berghof, Germany, consisting of a plastic tank of capacity over 5 L having outlet and inlet connections as shown in the figure. A thermometer reading up to 0.1°C was used to monitor the temperature. A spiral condenser, circulating chilled water, was used in line to avoid increase in temperature during the course of experiment. A flow meter with control valve and a pressure gauge with valve were used to maintain constant flow and desired pressure

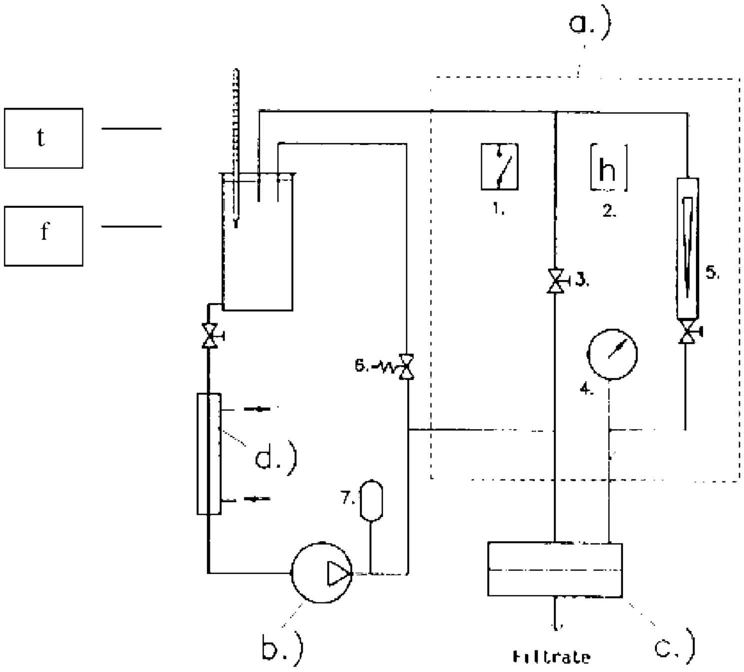

Figure 1. Schematic diagram of experimental set-up. (a) The machine enclosure; (d) condenser; (b) high pressure triplex plunger pump; (c) membrane cell; (f) feed tank; (t) thermometer; (1) on/off switch; (2) timer; (3) flow control valve; (4) pressure gauge; (5) flow meter with valve; (6) safety over pressure valve; (7) pulsation damper.

during the course of experiment. Different pressures ranging from 25 to 90 bar were applied. A high-pressure pump with maximum pressure and output of 100 bar and 5 L/min, respectively was used. Flat sheet membranes of diameter 7.2 cm were used.

Flat sheet membrane of 3.6 cm radius was cut and soaked in water before use. It was then fixed with active layer facing the feed side of the cell with the help of O-rings. Filtered samples were then introduced in the feed chamber and allowed to circulate for 5 min. Different pressure differences of 25, 50, 75 and 90 bars were then applied and allowed to run for 5 min. Then the time taken for the collections of 25 mL of permeate was recorded with a stopwatch reading up to 0.1 sec. Duplicate experiments were done to check reproducibility and results were found to be reproducible. Care was taken to avoid change in concentration of the feed by putting the permeate back into the feed chamber. Different fixed concentrations of the stream were obtained by taking out fixed volume of permeate (500 mL) from the system. The material balance at the end of the experiment was found to be good (±1%).

Analysis for Rhenium

Permeate and reject samples were analyzed for rhenium content by titration with standard sodium hydroxide solution (0.01 *N*) and also spectrophotometrically (17,18) at 445 nm using thiourea for the development of color. Calibration curve with pure rhenium solutions of different concentrations ranging from 1 to 10 mg/L was used for the estimation. The dependence was linear:

$$\text{Absorbance}\,(445\,\text{nm}) = 0.0316C_{\text{Re}}$$

with a correlation coefficient of 0.9984 where C_{Re} represents the rhenium concentration in mg/L. Appropriate dilution of the reject stream was done to get transmittance or absorbance in the desired range. Estimation of platinum in presence of rhenium was tried spectrophotometrically (18,19) at 403 nm using stannous chloride for the development of color.

RESULTS AND DISCUSSION

Results on the concentration of rhenium in aqueous waste stream with membrane using the principles of reverse osmosis are given in Fig. 2, wherein permeate flux is plotted against applied pressure. Permeate flux increases linearly with applied pressure at all the feed concentrations (correlation coefficient > 0.99). The permeability coefficient was determined from the

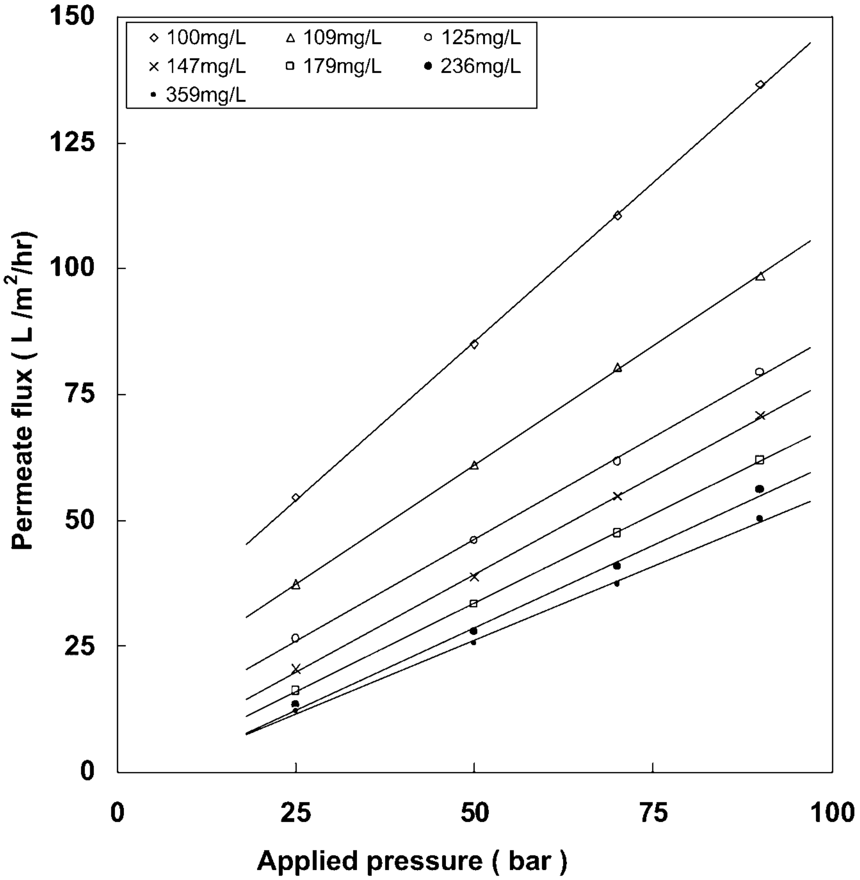

Figure 2. Dependence of permeate flux on applied pressure with TFC membrane.

slope of these straight lines. Further, permeate flux was found to decrease with increasing concentration of rhenium in the feed. Percent rejection of rhenium was calculated from its concentration in the permeate and feed. Percent rejection was found to be above 96, which increased slightly with applied pressure and also with rhenium concentration in the feed (Table 1). Presence of platinum in the permeate could not be detected as there was no development of color. Increase in percent rejection with pressure is expected on account of the fact that water passage increases with pressure while solute flux remains nearly independent of pressure (20). Permeability coefficient determined from the slope of the permeate flux vs. applied pressure straight lines are given in Fig. 3, wherein their

Table 1. Percent Rejection of Rhenium from Aqueous Waste Stream by TFC Membrane

Concentration of Rhenium (mg/L)	Rejection (%)			
	25 (bar)	50 (bar)	70 (bar)	90 (bar)
100	96.6	97.0	97.4	97.7
109	96.9	97.3	97.5	97.7
125	97.3	97.7	98.0	98.2
147	97.7	97.9	98.1	98.2
179	97.8	98.0	98.1	98.2
236	98.1	98.2	98.3	98.4
359	98.1	98.2	98.3	98.4

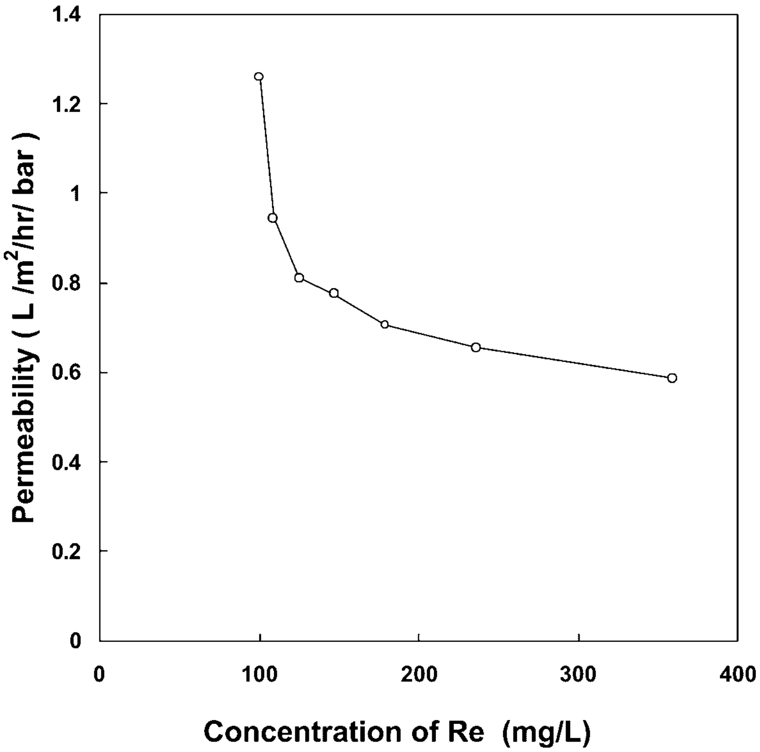

Figure 3. Dependence of membrane permeability on rhenium concentration.

dependence on rhenium concentration is examined. It can be seen from the figure that permeability decreases rapidly in the beginning and then becomes progressively slower attaining practically a constant value.

Concentration of rhenium in the reject stream in reject circulation mode of operation is shown in Fig. 4. Concentration of rhenium increases first slowly and then rapidly as more and more permeate is recovered from the system. Concentration of rhenium in the permeate is very low 2 mg/L in the beginning and gradually increased to 8 mg/L, at a recovery level of over 80% and therefore can be recycled back to the system. The precious metal Re concentrated in the reject stream can thus be easily recovered and recycled back to the system. Membrane processing of dilute aqueous waste stream containing noble metals appears to have considerable potential for reuse of water and also recovery and possible recycle of the metal.

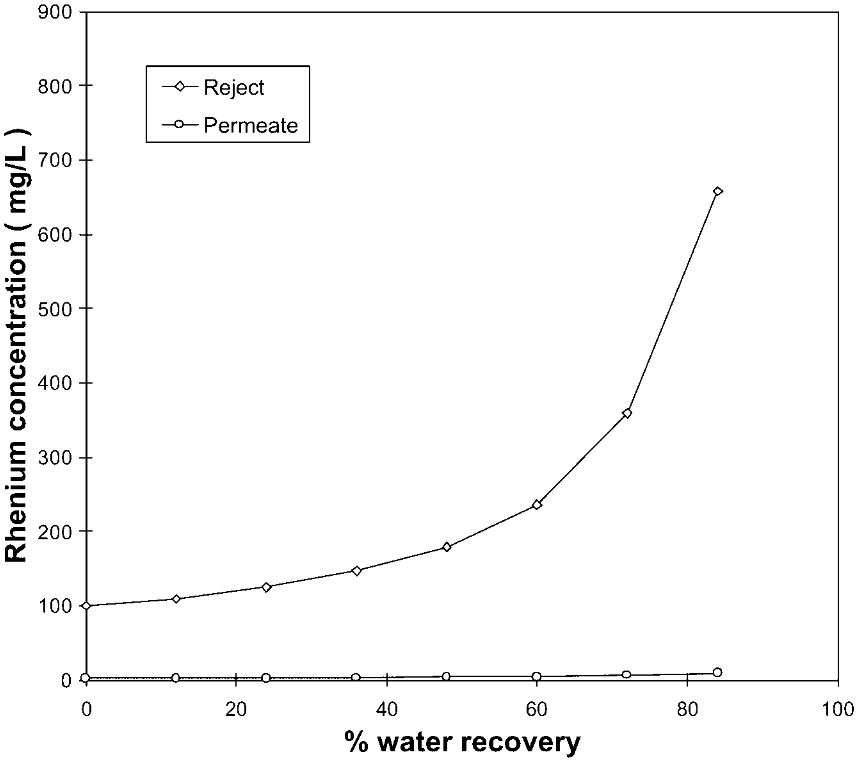

Figure 4. Concentration of rhenium in reject and permeate streams at different water recovery levels.

Analysis of separation data on rhenium from the aqueous waste stream by TFC membrane is attempted by graphical method of the combined film theory and the solution–diffusion model. Results are consistent with classical concentration polarization phenomenon. Assuming that intrinsic rejection is constant under the conditions of operation, the working equations relating permeate flux, J_v, with applied pressure, ΔP and solute rejection, R_0, based on combined film theory and solution–diffusion model, following the work of Murthy and Gupta can be written as (21,22):

$$J_v = A(\Delta P - \Delta\pi) \tag{1}$$

and

$$\ln[\{(1 - R_0)J_v\}/R_0] = \ln[D_{AM}K/\delta] + J_v/k \tag{2}$$

where, A, is the membrane permeability constant, $D_{AM}K/\delta$ is considered as a single parameter related to solute transport given by solution–diffusion model, and k, is the mass transfer coefficient on the high pressure side of the membrane given by the film theory.

Dependence of permeate flux on applied pressure is linear (Fig. 2) for all the feed concentrations as required by Eq. (1). Plots of $\ln[\{(1-R_0)J_V\}/R_0]$ vs. J_V, obtained by using R_0 and J_V values taken at different pressures but at different constant feed concentrations, are linear with a correlation coefficient (>0.98) indicating applicability of the combined solution–diffusion–film theory for the separation of rhenium from the aqueous waste stream with TFC membrane. Values of $D_{AM}K/\delta$ and k at different feed concentrations, obtained from the intercept and slope respectively of the straight lines are given in Table 2. It can be

Table 2. Values of Parameters ($D_{AM}K/\delta$) and k for the Separation of Rhenium from Waste Water with TFC Polyamide Membrane

Concentration of Rhenium (mg/L)	$(D_{AM}K/\delta)\times 10^5$ (cm/sec)	$k\times 10^4$ (cm/sec)
100	4.02	44.65
109	2.30	25.67
125	1.55	21.93
147	0.98	14.38
179	0.74	11.16
236	0.55	9.55
359	0.49	8.51

inferred from the linear dependence of $\ln[\{(1-R_0)J_V\}/R_0]$ on J_V and values of transport parameters summarized in Table 2 that:

(i) both solute transport parameter, $D_{AM}K/\delta$ and mass transfer coefficient, k, are independent of the applied pressure,
(ii) values of $D_{AM}K/\delta$ and k decrease with increase in concentration of rhenium in the solution, and
(iii) decrease in $D_{AM}K/\delta$ with increase in feed concentration is more pronounced in comparison that of k.

$D_{AM}K/\delta$ characterizes membrane–solution interface as well as membrane morphology, whereas k determines mass transfer at the membrane solution interface. It appears from the above observations that perrhenate interacts with the membrane surface and modifies the structure of the membrane solution interface, the extent of which increases with increase in rhenium concentration in the solution. The interaction of bulky perrhenate oxo-anion with the membrane inhibits its diffusion in the interfacial boundary layer and also through the membrane.

CONCLUSION

Separation of rhenium from dilute aqueous waste stream of a catalyst manufacturing plant is carried out with TFC polyamide membrane. Rejection of rhenium was found to be over 96% which increased marginally further with increase in pressure and feed concentration and reached over 98% under the conditions of operation. Membrane processing, therefore, has considerable potential for the treatment of dilute aqueous waste streams containing precious metals for water purification and recovery of metals.

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