Indian Journal of Chemical Technology
Vol. 15, March 2008, pp. 107-112

Separation of cadmium ions and estimation of membrane transport parameters of a nanofiltration membrane

Z V P Murthy* & Latesh B Chaudhari
Department of Chemical Engineering, S V National Institute of Technology, Surat 395 007, India
Email: zvpm2000@yahoo.com; zvpm@ched.svnit.ac.in
Received 7 May 2007; revised 20 November 2007

Nanofiltration (NF) has been widely used to separate solutes from dilute solutions where, in general, high rejection of the solute is not required. In the present work, performance of a commercial TFC-NF-300 membrane has been studied to separate cadmium salt from dilute synthetic wastewaters at different operating conditions. The operating variables studied are applied pressure (3-20 atm), feed salt concentration (10-250 ppm) and feed flowrates. The feed and permeates are analyzed for solute concentration by conductivity method, which represents well for the concentration of a single metal solute in a solution. It is observed that the rejection of cadmium ions increases with increase in feed pressure and decreases with increase in feed concentration at constant feed flowrate. The maximum observed rejection efficiency of the metal is found to be 75.76 and 61.47% for an initial feed concentration of 10 and 250 ppm, respectively. Membrane transport parameters are estimated using Spiegler-Kedem model based on irreversible thermodynamics.

Keywords: Nanofiltration, Rejection, Permeate flux, Cadmium, Membrane transport model

Heavy metals are considered as one of the serious environmental contaminants because of their high toxicity. Cadmium is one of the main toxic pollutants generated by industrial activities. As per Bureau of Indian Standards (IS: 10500-1983), the limit for cadmium in drinking water is 0.01 mg/L. Membrane techniques have been used to remove cadmium from wastewaters14. Nanofiltration (NF), which is considered to be intermediate between reverse osmosis (RO) and ultrafiltration (UF), has gained importance due to its selective rejection. When high rejections are not needed, for example as in the case of brine, NF suits the situation instead of RO, which requires higher pressures. The rejection of solutes by NF membranes is mainly influenced by two basic membrane characteristics: membrane charge and membrane pore size. These characteristics control two main solute retention mechanisms, charge exclusion and size exclusion. In the charge exclusion, between the charge anions in the NF membrane and the co-ions (i.e., anions) in the influent, the Donnan potential is created and because of this potential, co-ions in the influent are rejected; because of the electro-neutrality requirements in the influent, the counter-ions (i.e., cations) are rejected as well. Size exclusion or sieving is based on the relation between the pore size and the size of permeating species5,6. Several research works have been carried out to describe the influence of various operating variables like pH, temperature, concentration, surface charge, surface morphology, concentration polarization on the ion rejection/separation of NF membranes7,11. The membrane transport models used to interpret the RO data can also be used for NF data12. Numerous models were used/proposed to describe and predict solute rejections/flux by RO/NF membranes12-19. Qdais and Moussa1 demonstrated both RO and NF technologies for the treatment of wastewater containing copper and cadmium ions. They used total dissolved solids (TDS) as an indicator for monitoring the performance of RO and NF membranes.

The main aim of the present work is to investigate the capability of a commercial thin-film composite polyamide nanofiltration membrane (Perma-TFC-NF-300) in removing cadmium salt from synthetic wastewaters. NF experiments are performed by changing operating variables such as the feed concentration, feed flowrate, pH and feed pressure, and corresponding permeate fluxes and rejections are measured. Also, the membrane parameters are found by using Spiegler-Kedem model based on irreversible thermodynamics.

Experimental Procedure

Materials and Methods

Synthetic samples of wastewater were prepared by adding required amounts of cadmium chloride...
(CdCl₂·2H₂O) to distilled water. Several solutions were prepared with different concentrations (10 to 250 ppm) of cadmium chloride. To monitor the performance of the NF process in the rejection of cadmium, the conductivity was used as an indicator of performance as was reported in the literature for single metal salt solutions. The conductivity of feed and permeate were measured by using a microprocessor based conductivity meter. The conductivity was measured each time at 30±1°C. The experimental set-up is shown in Fig. 1. A rectangular flat membrane was used for the experiments. The membrane housing cell, shown in Fig. 1, is made of stainless steel with two halves fastened together with high tensile bolts. The top half of cell contained the flow distribution chamber and the bottom half is used as the membrane support system. The membrane required support to prevent rupture at high hydrostatic pressures. The following arrangements of special supports were used: a perforated 1 mm thick stainless steel plate was laid over with a stainless steel gauge of 300 mesh size, which is topped by a Whatman filter paper and followed by the actual membrane with its active thin layer exposed to the high pressure fluid. This arrangement provides sufficient mechanical support to the test membrane at high pressures. The upper half of the test cell contains a groove for the arrangement of HDPE ‘O’ ring to avoid leakage at high pressure operation. Experiments were performed with a commercial thinfilm composite polyamide membrane Perma-TFC-NF-300 (Permonics, Vadodara, India), hereafter referred as NF-300 membrane. This membrane has three layers. The first layer is a 5-20 µm polymer layer that does the actual rejection. The second layer is made of polysulfone of 50 µm thickness, which provides support to the first layer (skin layer) as a substrate for cross-linking of composite layer. The third layer, used for resistance and strength, is made of polyester with a thickness of about 150 µm. The Perma-TFC membranes are capable of withstanding pH in the range 2-12, pressure up to 30 atm and temperatures up to 50°C. The NF-300 membrane is characterized by 300 Dalton cut-off. The 1 mm thin channel passage in the membrane test cell and the high cross-flow feed rates used in the experimentation enables the system in controlling the concentration polarization. Before conducting the actual experiments for the rejection of cadmium salt, the NF-300 membrane was subjected to stabilization at 20 atm, which is the maximum pressure used in the experiments, for 2 h to avoid possible membrane compaction during the experimentation. Experiments were performed for 2 h, for each set of rejection data, in batch circulation mode and the permeate samples were collected from high pressure to low pressure for a particular feed concentration and feed flowrate. Both permeate and concentrate were returned to the feed vessel in order to keep a constant concentration. Samples of permeate were collected at a given time interval, to measure the salt rejection (R) and permeate volume flux (Jᵥ). After each set of experiments for a given feed concentration, the set-up was rinsed with distilled water for 30 min at 4 atm to clean the system. This procedure was followed by measurement of pure water permeability (PWP) with distilled water to ensure that the initial membrane PWP is restored. The experiments were carried out for different feed concentrations (10, 50, 100, 150, 200 and 250 ppm), feed flowrates (8, 10, 12, 14 and 16 L/min), feed pressures (3, 5, 7, 10, 12, 15, 18 and 20 atm) and the corresponding R and Jᵥ were measured.

Membrane transport model

The transport of solute through NF membranes can be described by irreversible thermodynamics, where the membrane is considered as a black-box. Kedem and Katchalsky proposed the relation of the volume flux (Jᵥ) and solute flux (Jₐ) through the membrane in the following equations:

\[ Jᵥ = L_p (ΔP − σΔπ) \]  \hspace{1cm}  \ldots (1)

\[ Jₐ = ωΔπ + (1 − σ)C_{ₐw}Jᵥ \]  \hspace{1cm}  \ldots (2)

The fluxes are related to three membrane parameters σ, ω and \( L_p \), namely reflection coefficient,
solute permeability and pure water permeability, respectively. As can be seen from the Eq. (2) the solute flux is the sum of diffusive and convective terms. Solute transport by convection takes place because of an applied pressure gradient across the membrane. A concentration difference on both sides of the membrane causes diffusive transport. Speigler and Kedem\textsuperscript{21} used the above equations and obtained the expression of the rejection rate of the solute related to hydrodynamic flux:

\[
R = \sigma \frac{(1 - F)}{(1 - \sigma F)} \quad \ldots (3)
\]

where,

\[
F = \exp \left( -\frac{(1 - \sigma)}{\omega} J_v \right) \quad \ldots (4)
\]

The parameter $\sigma$ can be determined by using Eq. (5), given below, derived from the Kedem-Katchalsky model\textsuperscript{22}

\[
\frac{1}{R} = \frac{1}{\sigma} + \left( \frac{L_D}{L_p} - \sigma^2 \right) \frac{L_p \pi_1}{\sigma J_v} = A_1 + A_2 \frac{1}{J_v} \quad \ldots (5)
\]

where, $L_D$ represents the osmotic permeability of membrane, $A_1 = 1/\sigma$ and $A_2 = \left( \frac{L_D}{L_p} - \sigma^2 \right) \frac{L_p \pi_1}{\sigma}$.

Plotting the experimental values of $(1/R)$ versus $(1/J_v)$ should confirm the relationship and the intercept permits to calculate $\sigma$. As reported in the literature\textsuperscript{21}, an irreversible thermodynamic model was applied to explain the rejection performance of an uncharged solute and there was no electrostatic interaction between membrane and solute. This is the case when the membrane is uncharged such as RO membrane or when the solute is neutral (organic compounds). Many authors\textsuperscript{2,23,24} extended this model in retention of electrolyte with an NF membrane that is charged. The parameters $\sigma$ and $\omega$ depend on the membrane effective charge and on the solute concentration of feed solution. The present model is more accurate in predicting the performance of a membrane when compared with the two-parameter solution-diffusion model\textsuperscript{12,19}.

**Results and Discussion**

**Membrane permeability**

Before the cadmium salt rejection experiments, the PWP of the membrane using distilled water is measured at 30±1°C. A plot of PWP versus pressure will give a slope $L_p$, known as the PWP coefficient of the membrane. The $L_p$ is found to be 13.29 L/h.m\textsuperscript{2}.atm, which is a typical value of nanofiltration membranes\textsuperscript{2,4,23}. The $L_p$ is considered to be a reference to evaluate cleaning procedure, concentration polarization and fouling of the membrane.

**Effect of feed concentration and applied pressure**

Feed and permeate salt concentrations are measured in terms of conductivity, as is explained earlier\textsuperscript{12}. The range of conductivity of the feed used in the study is 0.033 to 0.9213 mS/cm, for the initial feed concentrations of 10 to 250 ppm, respectively. The rejection percentage obtained by using the conductivity measurement can be calculated by the following relation:

\[
R = \left( 1 - \frac{k_p}{k_F} \right) \times 100 \quad \ldots (6)
\]

where, $k_p$ and $k_F$ are the conductivity of cadmium ions in the permeate and feed samples in mS/cm. As shown in Fig. 2, percentage rejection of cadmium salt increases slightly with increase in permeate flux for different feed concentrations (10 to 250 ppm) with the applied pressure range between 3 to 20 atm. The salt rejection decreases with increase in feed concentration, which is expected, in general, with RO/UF membranes\textsuperscript{4,12,23,25-27}. The maximum rejection efficiency of the metal is found to be 75.76 and 61.47% for the initial feed concentrations of 10 and 250 ppm, respectively. Somewhat similar results were found by Ballet et al\textsuperscript{2} for CdCl\textsubscript{2} salt. According to Garba et al\textsuperscript{4}, in the case of chlorides or nitrates salts of cadmium, the results have shown that when the Cl\textsuperscript{−} or NO\textsubscript{3}\textsuperscript{−} ions concentration is increased, Cd\textsuperscript{2+} retention is decreased. This may be because of the formation of...

Fig. 2 — Flux versus rejection curve for cadmium salt of different concentrations at feed rate 12 L/min
soluble complex CdCl\textsuperscript{+} and a neutral complex CdCl\textsuperscript{o} which might have allowed a decrease in the rejection of cadmium salts\textsuperscript{4}.

Experiments are carried out to study the effect of pressure, ranging from 3 to 20 atm, at pH 6.0±0.2 for cadmium salt rejection. As can be seen from Fig. 3, the permeate flux increases linearly with increasing pressure, which indicates that there is insignificant concentration polarization in the membrane cell. It can also be seen from Figs 3 and 4 that with increasing concentration from 10 to 250 ppm the permeate flux and rejection decreases. The rejection decreases with increase in feed concentration because the cations shield effect on the membrane negatively charged groups became progressively stronger, leading to the decrease of membrane repulsion forces on the anions. It is a typical phenomenon of charged membranes\textsuperscript{28}. It can be seen from Fig. 4 that the cadmium salt rejection increases with pressure. With increasing pressure, convective transport becomes more important and rejection too increases\textsuperscript{23}.

However, concentration polarization will also increase with increase in pressure, which results in decrease in rejection. The counteracting contribution of increased convective transport and increased concentration polarization result in nearly constant rejection in the pressure range 10 to 20 atm for low feed concentrations, confirming the results of Mehiguene \textit{et al}\textsuperscript{23}. A high diffusive transport of salts through the membrane compared to convective transport may be the reason for low retention at low pressure and high feed concentrations\textsuperscript{23,29}. The overlapping nature for concentrations 200 and 250 ppm (Figs 2 and 4) may be due to the reason that beyond 200/250 ppm feed concentration the membrane performance may have reached a limit.

\textbf{Effect of feed flowrate}

Figure 5 shows the rejection percentages with change in pressure at different feed flowrates in the range of 8-16 L/min at 250 ppm feed concentration. It can be seen from Fig. 5, that increase in feed flowrate leads to an increase in the retention. Similar results are found for the Ni ion by Ahn \textit{et al}\textsuperscript{30} and for the Zn ion by Frares \textit{et al}\textsuperscript{31}. When the flowrate is lower, the interactions between membrane and solution would be more facilitated. The streaming forces in the pores become stronger than the surface forces and the retention decrease quickly. On the other hand, when the flowrate is high, the surface forces become more effective than the streaming forces and the retention increases significantly\textsuperscript{28}. According to Murthy \textit{et al}\textsuperscript{27}, at constant feed pressure and concentration, the mass transfer coefficient increases with increase in feed flowrates which in turn reduces the concentration polarization and increase the rejection.
Determination of membrane transport coefficients and single salt flux distribution

The transport parameters $\sigma$ and $\omega$ are obtained by Eq. (4) using experimental data. The linear relationship of Eq. (5) is in agreement with experimental findings shown in Fig. 6, where $1/R$ is plotted against $1/J_v$ for different feed concentrations (10, 50, 100, 150, 200 and 250 ppm) of cadmium salts. In the present study, the effect of concentration on retention is measured and corresponding values of parameters are given in Table 1. It can be seen from the Table 1 that the reflection coefficient $\sigma$ decreases with the increase in concentration of solute in feed solution, while the solute permeability $\omega$ increases with the solute concentration. Ballet et al.\textsuperscript{2} and Mehiguene et al.\textsuperscript{23} investigated the effect of the nature of co-ion on the retention, they found that the reflection coefficient $\sigma$ for each salt increases with co-ion valency, while the salt permeability $\omega$ decreases with co-ion valency. Nakao et al.\textsuperscript{32} analyzed the dependence of the membrane parameters, reflection coefficient and solute permeability in the system of an organic electrolyte and a negatively charged NF membrane and observed that increase in the solute concentration which results in a decrease in the ion reflection coefficients and increase in their permeability. Similar results were obtained by Tanimura et al.\textsuperscript{33} for the separation of alcohol aqueous solutions by using RO membrane. Estimated salt retentions based on these transport parameters are compared with experimental data and shown in Fig. 7. It can be seen from the Fig. 7 that the model predictions are in good agreement with the experimental results.

### Conclusions

Recently, NF has been widely used to separate solutes from dilute solutions where only medium rejection of the solute is required. In the present work performance of NF-300 membrane has been studied to separate cadmium salt from dilute synthetic wastewaters at different operating conditions. It is observed that the rejection of cadmium ions increases with increase in feed pressure and decreases with increase in feed concentration at constant feed flowrates. The maximum rejection efficiency of the metal is found to be 75.76 and 61.47% for an initial feed concentration of 10 and 250 ppm, respectively. Irreversible thermodynamics model (Spiegler-Kedem) is used to estimate membrane transport parameters. The values of rejection and flux estimated using membrane transport parameters are in good agreement with experimental results.

### Acknowledgements

One of the authors (ZVPM) acknowledges the financial support from the Ministry of Human Resources Development, Government of India, New Delhi, India, under the TAPTEC Research Grant (No.F.27-1/2002. TS.V). Thanks are due to Mr. V.Y.
Jose, Director, Permionics Limited, Vadodara, India, for providing the Perma-TFC-NF-300 membranes.

Nomenclature

- $C_{\text{Aln}}$: Logarithmic average of solute and solvent concentration across membrane
- $F$: Flow parameter defined in Eq. (4)
- $J_A$: Solute flux through membrane (mol m$^{-2}$ s$^{-1}$)
- $J_V$: Solvent flux (L m$^{-2}$ h$^{-1}$)
- $k_F$: Conductivity of feed (mS cm$^{-1}$)
- $k_P$: Conductivity of permeate (mS cm$^{-1}$)
- $L_D$: Osmotic permeability of membrane (cm s$^{-1}$ atm$^{-1}$)
- $L_P$: Hydraulic permeability of membrane (cm s$^{-1}$ atm$^{-1}$)
- $\Delta P$: Pressure difference across the membrane (atm)
- $R$: Salt rejection coefficient
- $\sigma$: Reflection coefficient; 0 for no rejection; 1 for total rejection
- $\Delta\pi$: Osmotic pressure difference across membrane (atm)
- $\omega$: Salt permeability (L h$^{-1}$ m$^{-2}$)

References