SEPARATION MECHANISM OF MONO- AND DIVALENT IONS BY LOW PRESSURE REVERSE OSMOSIS MEMBRANE

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ABSTRACT

This paper describes an investigation on the rejection of the divalent anions from $ZnSO_4$ using LPROMs, and to establish the effect of operating pressure, feed concentration and temperature on metal removal, then to compare with the monovalent anions, $ZnCl_2$. A bench-scale spiral wound configuration of sulphonated polysulphone low pressure reverse osmosis membrane (LPROM) was used to remove heavy metals at various operating conditions, i.e. operating conditions, solute concentrations and temperature. The results show that the higher the operating pressure the greater will be the permeate flux for heavy metals from both mono- and divalent anions. At low operating pressure however, metals from the divalent anions give a higher permeate flux than did the monovalent anions. Permeate flux in both mono- and divalent anions is shown to be subsequently increased by a decrease of the concentration of feed solution. Regarding metal removal, metals from divalent anions were rejected more effectively than monovalent anions at all levels of feed concentration.

Key words: heavy metals, charged membrane, low pressure reverse osmosis membrane, metal removal, flux.

Introduction Reverse osmosis (RO) is a pressure-driven membrane operation which normally requires more than 690 kPa (100 psig) for effective removal of metal ions from their solvent (Zaini and Anderson, 1996). Low pressure reverse osmosis membrane (LPROM) is relatively not a new concept in membrane technology. In the last few years, LPROM became more significant in its applications, mainly due to the production of improved membrane with high water and solute permeation constants.

Many investigations have been made on the performance of LPROM (Zaini and Anderson, 1996, Sun *et al.* 1995, Urairi *et al.*, 1992). The application of LPROM for heavy metal removal, particularly to differentiate between mono- and divalent ions, however, has not been studied very extensively up to date.

Experimental Design and Methods The objectives of this paper were to study the rejection of the divalent anions from $ZnSO_4$ using LPROMs, and to establish the effect of operating pressure, feed concentration and temperature on metal removal, then to compare with the monovalent anions, i.e. $ZnCl_2$.

The LPROM system as illustrated in Figure 1 consists of a feed tank equipped with a heat exchanger system to maintain the feed solution at a desired temperature, a pH controller, a high-pressure centrifugal pump (50 micrometer in pore diameter), an accumulator (to minimise the pressure pulsations), a pretreatment catridge filter and a LPROM module.

The performance of LPROMs was evaluated by response parameters, i.e. (a) permeate flux, and (b) the percentage of metal removal, under varying experimental conditions such as operating pressure, feed concentration of metal ions, and temperature, at a constant pH and 40 percent recovery.

Preliminary experiments were carried out to establish data on permeate flux decline with time and flux changes in solute rejection with time, using 500 mg/l NaCl at 60 psi (414 kPa), 25^0C and 40 percent recovery.

Results Figure 2 shows the permeate flux as a function of the operating pressure for 1 mM $ZnSO_4$ and 1 mM $ZnCl_2$ feed solutions at 25^0C, 40 percent recovery and pH of 3 to 5. The figure shows a positive correlation between permeate flux and the operating pressure for both mono- and divalent anions. These results suggest that the higher the operating pressure the greater will be the permeate flux. From this figure, however, the effect of valence type was not significant. Regarding metal removal, divalent anions were rejected more effectively than monovalent anions as shown in Figure 3. At 90 psig (621 kPa) for instance, the metal removals were 99.5 and 96.0 percent, respectively for $ZnSO_4$ and $ZnCl_2$.

The effect of feed concentration on metal removal was further analysed and presented in Figures 4 and 5, again, as a function of the operating pressure. Both figures suggest that as the feed concentration increases, the permeate flux and the metal removal from $ZnSO_4$ solution will subsequently increase.

Results presented in Figures 6 and 7 demonstrate the effect of temperature and pressure on permeate flux and metal removal from a divalent anion system. Figure 6 shows the 3-D response surface to demonstrate the positive correlation for temperature and pressure on the

permeate flux of the ZnSO$_4$ system. As can be seen the higher temperature and the operating pressure, the greater will be the permeate flux.

In addition, the effect of temperature and the operating pressure was observed for the zinc removal in Figure 7. It shows that the percentage of zinc removal was proportional to the increase of the temperature and operating pressure. Throughout this study the combined effect of temperature and the operating pressure on both response parameters, i.e. permeate flux and metal removal, was in agreement with Brandt *el al*. (1993) and Bhattacharyya and Williams (1992) who postulated that temperature affects permeate flux in RO membrane because increases in temperature result in increases in osmotic pressure, and solute and solvent permeability.

General discussion The results suggest that LPROMs more effectively reject metals associated with divalent anions than with monovalent anions. At higher feed concentrations, however, the effect of the charge subsequently decreased. The overall results in this study are a consequence of the electrostatic interaction between a negatively charged membrane and metal ions according to its valence type, as postulated by the Donnan equilibrium and the extended Nernst- Planck models. The Donnan equilibrium model relies on ion-selectivity to retard the transfer of either a cation or an anion across the membrane. In addition, the extended Nernst-Planck model describes the transport of ions across the membrane in terms of diffusion and migration, as a result of concentration and electrical potential gradients, as well as convection caused by the pressure difference across the membrane. The results of this study are also consistent with the results of Urairi *et al*. (1991) and Tsuru *et al*. (1991) which revealed the application of a bipolar RO membrane for separating mono- and divalent ions.

In explaining these results it is also important to understand the nature of negatively charged LPROMs. These membranes have many fixed charged groups that can separate solutes of almost the same size or molecular weight according to their electrical polarity, namely positive, negative or neutral (Jitsuhara and Kimura, 1983; Kimura and Tamano, 1986; and Nakao *et al*., 1988). Positive membranes reject positive ions more than negative ions, and *vice versa*. Neutral membranes, however, do not reject such solutes because their transport mechanism is a "sieve effect" (Urairi *et al*., 1992). It should be noted that most studies on the

effect of valence type in MSPs are in the domain of electrodialysis and ion exchange membranes, and are relatively new to charged RO or ultrafiltration.

Unlike in electrodialysis, where counter-ions pass easily through the negatively charged membrane and co-ions will be rejected, however the negatively charged LPROM repelled co-ions (namely Cl^- and SO_4^{2-}) by an electrostatic force which created a repulsive effect. The electrostatic force surrounds a stationery charged membrane. In addition, counter-ion (namely Zn^{2+}) was rejected by an electroneutrality force which also generated a repulsive effect. The transport mechanism for solvents passing through the membrane can be explained by the preferential sorption of water molecules at the solvent-membrane interface, which is caused by the interaction force working between the membrane-solvent-solute.

Figure 8 schematically shows the rejection mechanism of both co-ions and counter-ions on the surface of a negatively charged LPROM. It is important to mention that the main rejection driving force of an LPROM is the operating pressure, and it causes a volume flux consisting mainly of solvent passing through the membrane. The pore radius of the LPROM is less than 1 nanometre. While solvent water molecules, whose radius is about 0.1 nanometre, can pass through the membrane freely, meanwhile metal ions and most of electrolyte solutes and organic solutes which contain more than one hydrophilic functional group in the molecule, cannot pass through the membrane (Matsuura, 1994). These solutes are either rejected from the membrane surface, or they are more strongly attracted to the solvent water phase than to the membrane surface.

For the negatively charged LPROM, the repulsive effect occurs for co-ions according to the valences of the ions. In this study, the rejection for divalent co-ion (namely SO_4^{2-}) was greater than monovalent co-ion (namely Cl^-). It is suggested that divalent co-ions receive a more repulsive effect than monovalent co-ions. Charged LPROMs have high ion-selectivity according to co-ion valences but a low one according to counter-ion valences. For counter-ions, the attractive effect occurs according to the valences of ions, however the electroneutrality effect is much greater than the attractive effect. As a result, counter-ions were also rejected together with co-ions. This phenomenon illustrates that the rejection

mechanism of negatively charged LPROM was based not only on a "sieve effect" but also a "charge effect".

In this study, sulphonated polysulphone negatively charged LPROMs have been used effectively for the treatment and reclamation of heavy metals. Ideally, these membranes give three major improvements in membrane technology, compared to cellulose acetate, i.e. high chlorine resistance, high permeate flux and high solute rejections to monovalent ions in dilute solutions. In this type of membrane, solute removal decreases with decreasing salinity and increasing operating pressure (higher permeate flux), thus illustrating a very strong Donnan effect in the transport mechanism (Peterson, 1993).

Sulphonated polysulphone operates best under conditions of a sufficiently high operating pressure to generate permeate fluxes that are higher than normally acceptable in RO installations. Abnormally high fluxes correlate with enhanced membrane fouling or scaling. The superior fouling resistance of this membrane, however, appears to enable a high flux operation.

Conclusions

i)   The higher the operating pressure the greater will be the permeate flux for heavy metals from both mono- and divalent anions. At low operating pressure however, metals from the divalent anions give a higher permeate flux than did the monovalent anions. Permeate flux in both mono- and divalent anions is shown to be subsequently increased by a decrease of the concentration of feed solution. Regarding metal removal, metals from divalent anions were rejected more effectively than monovalent anions at all levels of feed concentration. In this study the following order of metal removal took place:

   1 mM $ZnSO_4$ > 2 mM $ZnSO_4$ > 3 mM $ZnSO_4$ > 4 mM $ZnSO_4$ > 1 mM $ZnCl_2$ > 2 mM $ZnCl_2$.
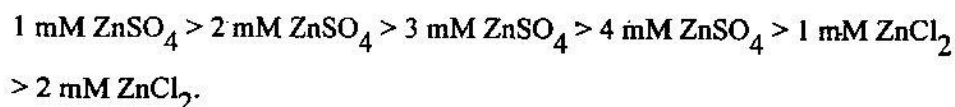
ii)   This study suggests that the permeate flux and the percentage metal removal have in a linear correlation to the temperature and the operating pressure. The permeate flux shows a significant correlation, whereas it was not very significant for metal removal.

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Urairi M., Tsuru T., Nakao S. & Kimura S. (1992). Bipolar reverse osmosis membrane for separating mono- and divalent ions. *J. Membrane Sci.* 70, 153-162.

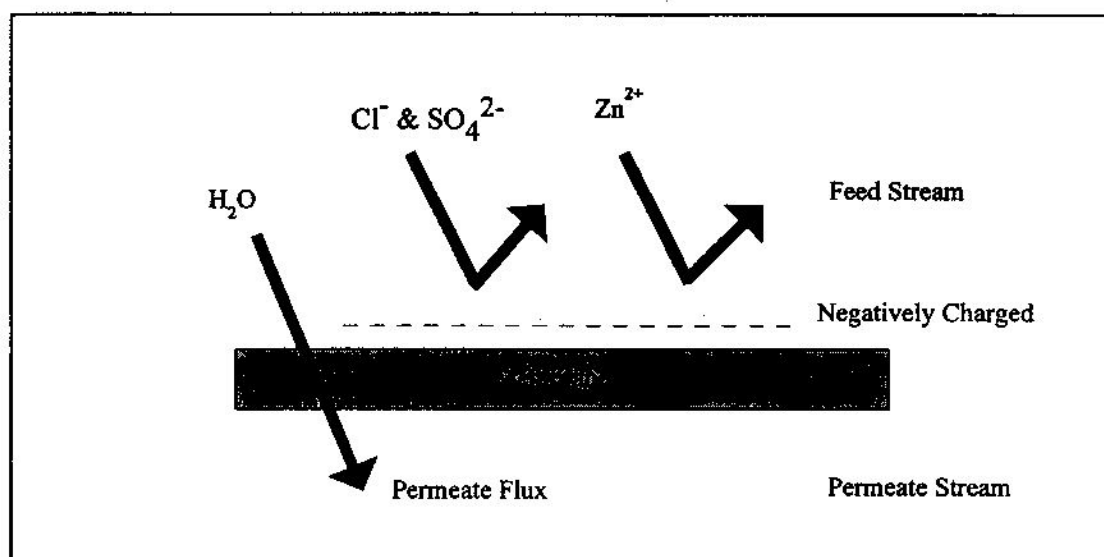Fig.1. Schematic diagram of low pressure reverse osmosis membrane (LPROM) system

Fig. 8. Schematic rejection model for co-ions and counter-ions by
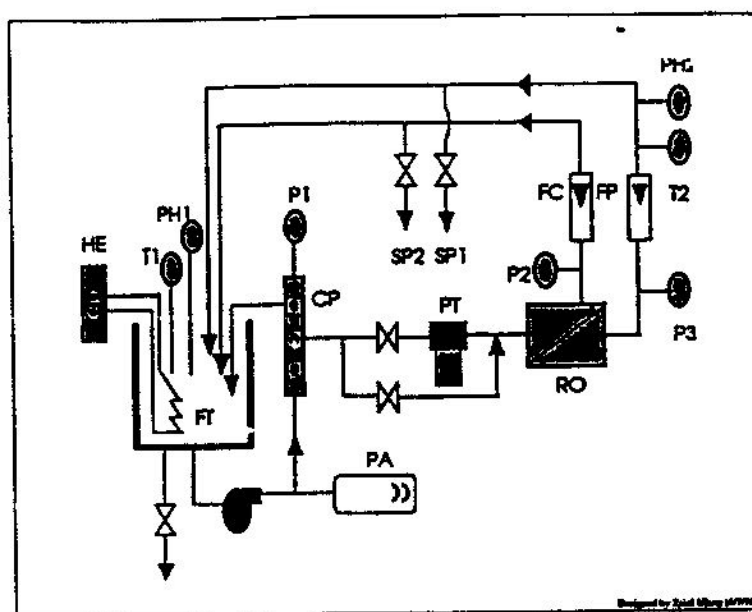negatively charged LPROM

Fig.1 Low pressure reverse osmosis membrane (LPROM) system

Notation

CP	Control panel
FC	Concentrate flow meter
FP	Permeate flow meter
FT	Feed tank
HE	Heat exchanger
P1	Pressure gauge at control panel
P2	Pressure gauge at concentrate stream
P3	Pressure gauge at permeate stream
PA	Pressure accumulator
PH1	pH meter at feed tank
PH2	pH meter at permeate stream
PT	Pretreatment (filter cartridge)
SP1	Sampling point for permeate
SP2	Sampling point for concentrate
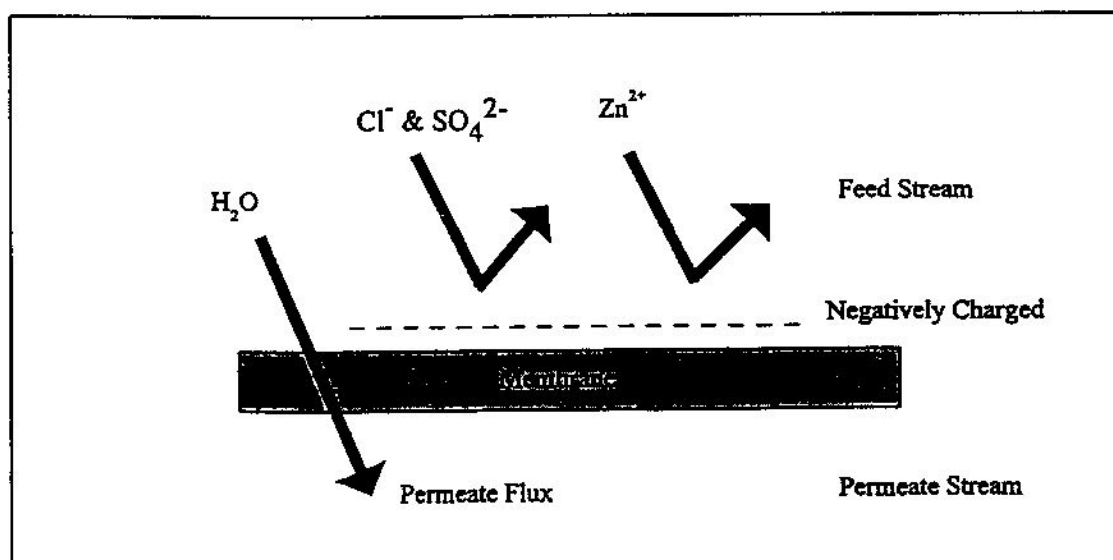
Fig. 8. Schematic rejection model for co-ions and counter-ions by negatively charged LPROM
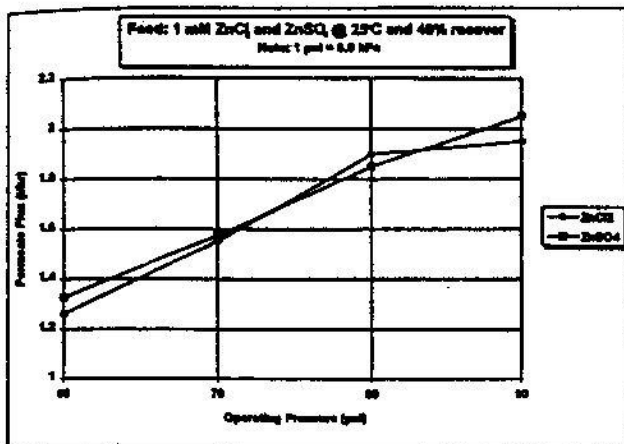
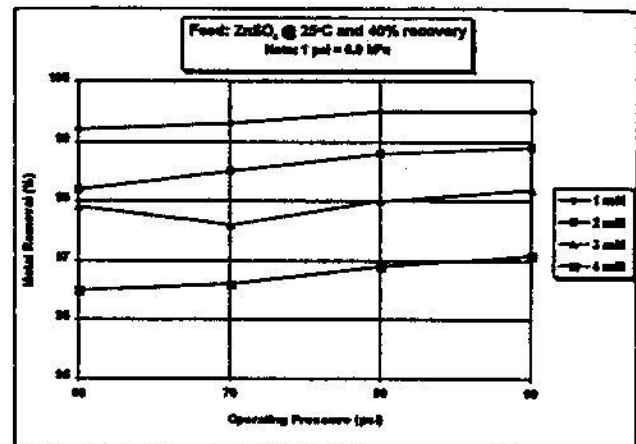Fig.2. Permeate flux of ZnCl$_2$ and ZnSO$_4$ at various pressures

Fig. 3: Metal removal of ZnCl$_2$ and ZnSO$_4$ at various pressures

Fig.4.Permeate flux of ZnSO$_4$ system at various pressures

Fig.5. Zinc removal from ZnSO$_4$ system at various pressures
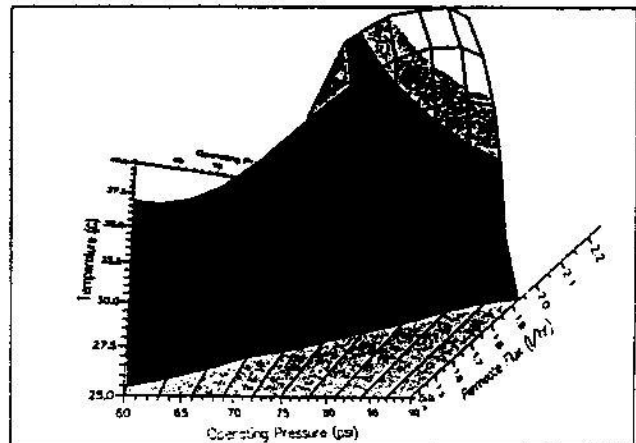
Fig.6.Effect of pressure and temperature on permeate flux

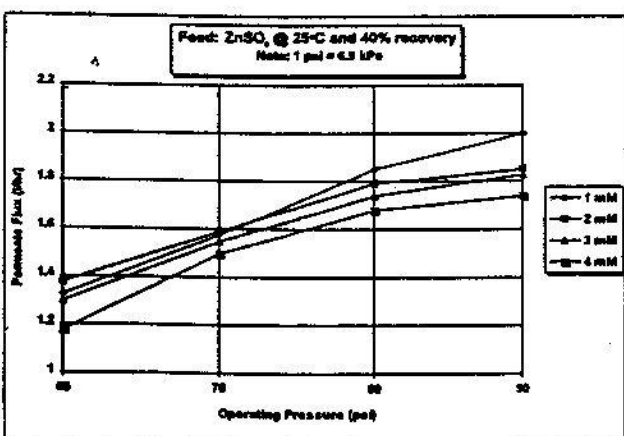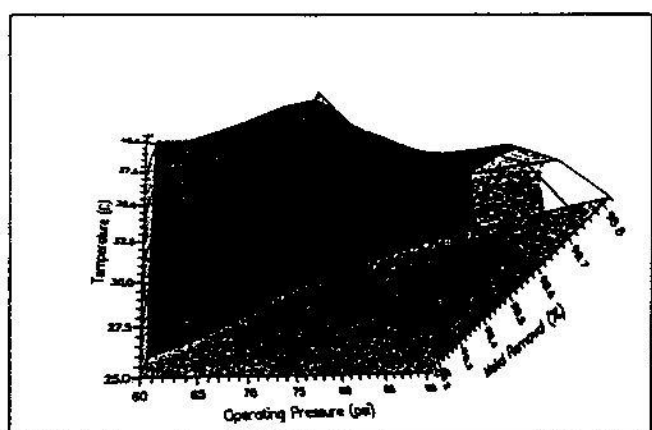
Fig.7. Effect of pressure and temperature on zinc removal

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