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APPLICATION OF LOW-PRESSURE REVERSE OSMOSIS MEMBRANE FOR ZN^{2+} AND CU^{2+} REMOVAL FROM WASTEWATER

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ABSTRACT

Reverse osmosis (RO) is a pressure-driven operation which normally requires more than 690 kPa (100 psig) for effective removal of metal ions from their solvents. This paper, however, illustrates the feasibility of using complexation and low-pressure RO membranes for the removal of Zn^{2+} and Cu^{2+} by applying pressures significantly below 690 kPa. The results show that the use of EDTA is a reliable method for increasing the percentage removal of both Zn^{2+} and Cu^{2+} with sulphonated polysulphone RO membranes. The percentage removal of metal ions of Zn^{2+} was slightly greater than that for Cu^{2+}. Copyright © 1996 IAWQ. Published by Elsevier Science Ltd.

KEYWORDS

Low-pressure RO membrane; complexation; metal ions; removal; chelating agents; recovery.

INTRODUCTION

The application of reverse osmosis (RO) as a separation process is considered to be a promising technology for recovering metal ions from various industrial wastewaters containing metals (Zaini and Anderson, 1995). By using this technology, solvents which contain metal ions are transferred through a membrane in such a way that the concentration of some solutes is reduced.

Reverse osmosis has received considerable attention in a number of industries where a high degree of treatment is required, as shown in Table 1. Recently, due to increasing international concern over environmental pollution, the application of RO technology for pollution control has become more widespread, in addition to brackish and sea water desalination (Zaini and Anderson, 1996). For pollution control their application was considered in the 1970s but little progress has been made due to the limited performance of cellulosic membrane materials with an asymmetric structure when treating solutions with a large pH range, at higher temperatures and in other extreme conditions.

Table 1. Selected applications of reverse osmosis

Brackish water and sea water desalination
Production of high-quality-water for:
Electronics industry
Air conditioning plants
Dialysis
Boiler feed make-up
Pharmaceutical industry
Removal of pesticides
Oil/water separation processes
Separation processes in the food industry:
Dairy: cheese whey concentration/dewatering; milk concentration; desalting of salt whey
Beverage: Cold stabilisation of beer; removal of colour from wine; removal of alcohol from beer and wine
Sugar: pre concentration of dilute sugar solutions; maple syrup; recovery of sugar from rinse water
Fruit and vegetables: concentration of fruit and vegetable juice; juice flavour and aroma concentration
General: Concentration of protein solutions; tartar stabilisation
Non-Industrial wastewater treatment and/or reclamation:
Municipal wastewater
Landfill leachate
Surface water and ground water
Aircraft and space stations
Military operations
Industrial wastewater treatment and/or reclamation:
Plating industry
Nuclear industry
Pulp and paper industry
Textile industry
Coal-liquefaction industry
Wool-scouring industry
Abattoir industry
Mining industry
Photographic industry
Food industry
Petrochemical industry
Pharmaceutical industry

The most important reason however, was due to the high cost of operation and maintenance mainly as a result of the requirement to apply high pressures to the system and the need for rigorous pre-treatment. In the late 1980s, the application of RO systems had become most widespread with the introduction of a range of membrane materials which could offer the following characteristics (Brandt *et al.*, 1993):

i) high water flux rates,
ii) high salt rejection,
iii) tolerance to chlorine and other oxidants,
iv) resistance to biological attack,
v) inexpensive,
vi) easy to form into thin films or hollow fibres,
vii) mechanically strong, e.g. tolerate high pressures,

viii) chemically stable, and
ix) able to withstand high temperatures.

Recently special attention has been given to low-pressure membrane separation processes (MSPs), and this effort has led to the production of nanofiltration membranes (with pressures of 690 to 1380 kPa). Research into heavy metal removal from wastewaters so far has been focused mainly on high-pressure RO membranes that require a pressure of more than 1380 kPa, mainly using only a test cell system. Bhattacharya *et al.* (1989) for example, have carried out research using low-pressure RO in which operating pressures were varied in the range of 300 kPa to 1800 kPa using a thin channel flow cell (1.4 cm wide, 0.84 cm in height and 100 cm long) with a membrane area of 140 cm^2.

This present study, however, was concerned with the application of low-pressure composite RO membranes with a spiral-wound configuration in order to improve their economic feasibility. The composite membrane has some advantages when compared to asymmetric membranes. In composite membranes, each layer can be optimised for solvent flux and solute rejection by applying a relatively low pressure, while the porous support layer can be optimised for maximum strength and compression resistance plus minimum resistance to permeate flow (Peterson, 1993). Some composite membranes however, have an anion charge that causes cationic fouling. And because of the high flux rates, fouling rates are higher when compared with asymmetric membranes.

COMPLEXATION

A complex is formed when a number of ions or molecules combine with a central atom to form an entity in which the number of atoms directly attached to the central atom exceeds the normal covalence or oxidation charge of this atom. Complexes are known to modify the nature of metals in solution, generally reducing the free metal ion concentration so that the effects and properties which depend on the free metal concentration are altered. These effects include changes in solubility, toxicity and the biostimulatory properties of metals; modification of the surface properties of solids; and the adsorption of metals from solution.

Complexation has been successfully applied as an aid to membrane separation processes (MSPs) in the removal of heavy metals from an aqueous solution, especially in the electroplating industry, using ultrafiltration, charged ultrafiltration, couple membrane transport and high-pressure RO.

Table 2. Specification of the RO unit

Membrane material:	Sulphonated polysulphone
Membrane configuration:	Spiral-wound
Mode of operation:	Continuous
Active surface area:	0.465 m^2
pH range:	2 - 11
Charge:	Negative
Thickness:	150-175 micron (<1 micron active layer)
Expected life span:	3 years

The application of complexation in combination with MSPs is based on reacting various types of ligands with endogenous cations in aqueous metallic constituents to form a metal-containing complex (chelate) and the removal of these metal containing co-ordination complexes by RO. The opposite charges of the ionised ligand and the metal attract each other and form a stable complex. This concept was proposed by Michaels (1968), O'Neil *et al.* (1976), Bulbula *et al.* (1976), Ryan (1976), Bhattacharyya *et al.* (1976 and 1986) and Chaufer and Deratani (1988) for ultrafiltration (UF); and by Hauck and Sourirajan (1972), Kamizawa (1978) and Hopfenberg *et al.*, (1978) for high-pressure RO membranes (i.e. at more than 1380 kPa).

EXPERIMENTAL METHODS

The objective of this study was to establish the removal behaviour of metal ions, i.e. Zn^{2+} and Cu^{2+}, by using complexation in combination with a low-pressure RO membrane. Extensive bench-scale experiments with RO membranes, supplied and manufactured by NWW-Acumem, as shown in Figure 1, were carried out. The specification of the RO membrane is given in Table 2.

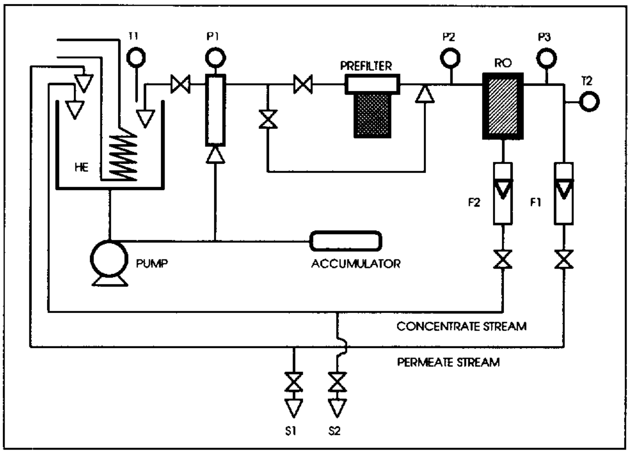

Figure 1. Reverse Osmosis System.

F1	Flow meter 1
F2	Flow meter 2
HE	Heat Exchanger
P1	Pressure Gauge 1
P2	Pressure Gauge 2
P3	Pressure Gauge 3
RO	Reverse Osmosis Unit
S1	Permeate Sampling Point
S2	Concentrate Sampling Point
T1	Temperature Measurement Location 1
T2	Temperature Measurement Location 2

Preliminary experiments

Preliminary experiments were carried out to establish data on flux decline with time and flux changes in solute rejection with time. The data are useful for interpreting the various changes that would take place, especially those due to membrane compaction, hydrolysis or fouling.

Preparation of Zn and Cu-EDTA solutions A known quantity of $ZnCl_2$ and $CuCl_2$ was weighed out before adding to the EDTA solution (disodium salt). The pH was adjusted to be between 3 to 5 by adding NaOH or HCl stock solution under vigorous stirring. The total EDTA to total metal ratio was varied in the range of 0.5 to 2.0.

Experimental procedures The RO membranes were used with distilled water for 24 hours at 414 kPa, 25°C and 40% recovery. After the distilled water flux data had been collected, the RO membranes were emptied and NaCl solutions were used. The RO membranes were washed, rinsed and filled with distilled water and run for a further one hour. The distilled water flux data were used as the reference.

Experiments at 40% recovery The Zn^{2+}-EDTA and Cu^{2+}-EDTA systems were investigated under various pressure conditions at a constant recovery, i.e. 40%, at a constant temperature of 25°C, and with the pH range of feed solutions between 3 to 5. All analytical procedures were carried out according to *Standard Methods* (APHA, 1992).

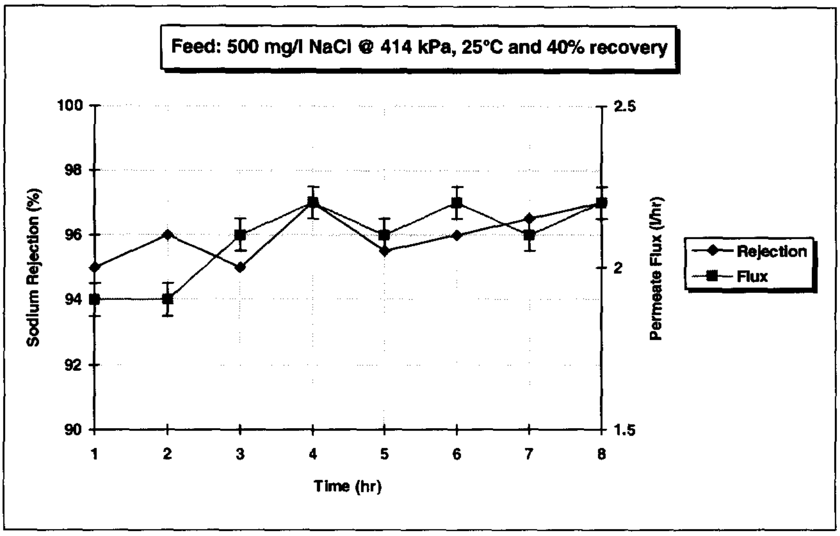

Figure 2. Rejection pattern of sodium chloride permeate flux in RO system.

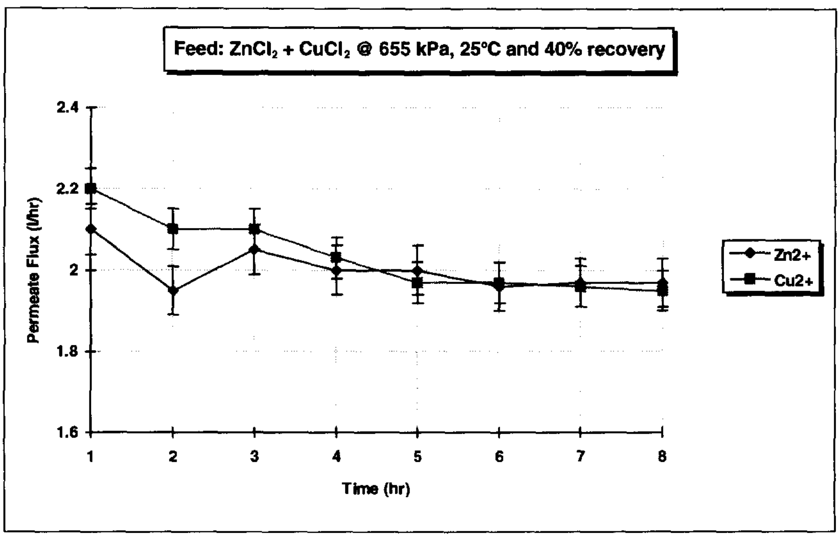

Figure 3. Average permeate flux for Zn^{2+} and Cu^{2+} in RO system.

RESULTS AND DISCUSSIONS

The performance of an RO membrane system can be evaluated by two criteria: permeate flux and rejection of metal ions. Before such evaluations can be made however, the performance of the RO membrane must be predetermined under standard conditions, in this case at 414 kPa, using sodium chloride as a standard to show the degrees of permeate rejection, permeate flux, hydrolysis and compaction. In this study 500 mg/l sodium chloride was used under specific operating conditions, i.e. 414 kPa, 25°C and 40% recovery. Figure 2 shows both permeate flux and rejection of sodium chloride. The permeate flux was relatively low, an average of more than 2 l/h, but the sodium rejection was more than 95%. From this preliminary study it was demonstrated that the RO membrane system was under a stable condition when rejecting sodium (which could represent other inorganic substances) after the first hour of operation. The stable conditions, as shown in Figure 2, are required to illustrate the high performance level of a membrane. An increasing flux however, could indicate hydrolysis of the membrane, while a continuous decline in permeate flux, after an initial decline, if any, would indicate feed-membrane interaction, which alters the micro-structures on the membrane surface.

Figure 3 shows the permeate flux for Zn^{2+} and Cu^{2+} at 25°C, 40% recovery and in the pH range of 3 to 5 for the feed solutions. The permeate fluxes for both metal ions were an average of 2 l/h. In general, these permeate fluxes were relatively low and could be due to a number of factors. One of the most significant is the nature of the spiral-wound configuration. According to Brandt *et al.* (1993), spiral-wound configurations have the major disadvantage of low recovery. Since recovery is the percentage of the feed solution that is converted to permeate, it directly affects the permeate flux. A low recovery means a low permeate flux. In this investigation, few attempts have been made to increase the percentage of recovery, however the highest so far was 40% but the process can produce a high percentage of metal removal as shown in Figures 4 and 5.

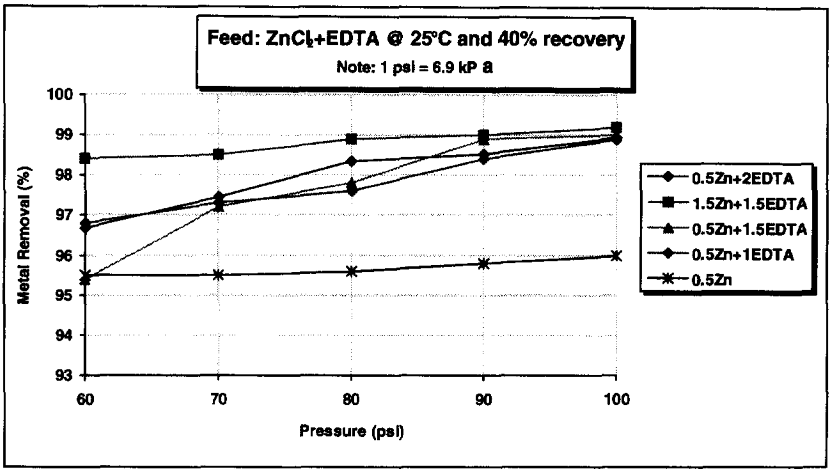

Figure 4. Metal removal of zinc chloride plus EDTA feed solutions in RO system.

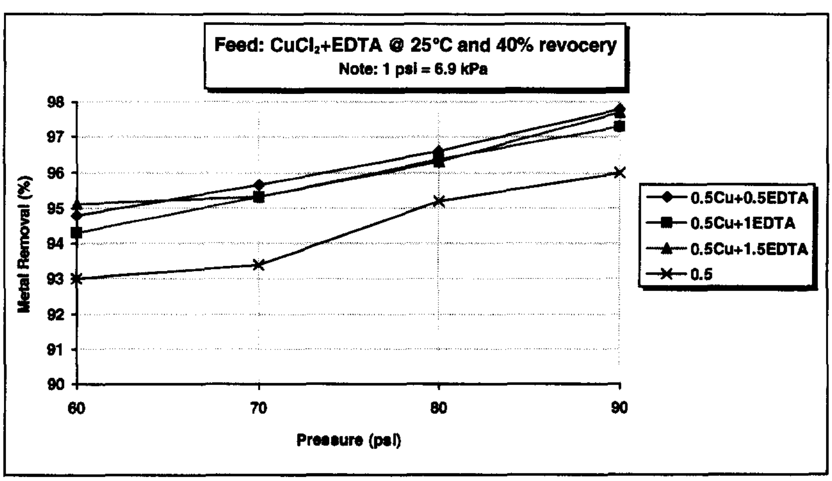

Figure 5. Metal removal of $CuCl_2$ plus EDTA feed solutions in RO system.

Figures 4 and 5 also show that the key parameter in the operation of an RO system is the applied pressure on the membrane surface. At applied pressure from 414 to 690 kPa, the system does not achieve the optimum level of metal ions removal. At applied pressure below the optimum level, the rejection of metal ions or specific constituents should increase in direct proportion to the increase in applied pressure. The effects of complexation on the behaviour of Zn^{2+} and Cu^{2+} removal by low-pressure RO membranes can also be evaluated from Figures 4 and 5. In all cases in this study, the overall rejection of Zn^{2+} and Cu^{2+} was observed to be above 95% at a pressure of 450 kPa, 25°C, a feed pH between 3 to 5, and a 40% recovery with the presence of EDTA as the chelating agent. Without adding EDTA, the feed solutions of $ZnCl_2$ and $CuCl_2$ show a relatively lower degree of metal ions removal, i.e. between 93 to 96% under the above conditions. Overall, metal ion removal was higher for Zn^{2+} compared with Cu^{2+} in the order of ZnEDTA > CuEDTA > $Zn^{2+} \gg Cu^{2+}$.

CONCLUSIONS

Low-pressure composite RO membranes can be successfully used for the removal of the metal ions, i.e. Zn^{2+} and Cu^{2+}. An optimum removal of up to 99% can be achieved by adjusting the appropriate operating parameters, especially the pressure applied, the molar ratio of EDTA to $ZnCl_2$ or $CuCl_2$, the concentration of the metal feed solution at constant temperature of 25°C, 40% recovery and in the pH range of 3 to 5.

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