ULTRAFILTRATION MEMBRANES FROM POLYSULFONE AND SULFONATED POLYSULFONE IN METAL IONS DIALYSIS ENHANCED BY POLYELECTROLYTE

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ABSTRACT

The dialysis of metal ions including Mg(II), Ni(II) and Zn(II) through ultrafiltration membranes made of polysulfone and sulfonated polysulfone was enhanced by sodium salt of poly(acrylic acid) diluted in the receiving compartment. In experiments, concentration of Mg(II), Ni(II) and Zn(II) in the feed solution was equal to 10^{-3} mol/dm^3, concentration of polymer in the receiving solution was equal to 10^{-2} mol/dm^3, and pH = 9. In the presence of complexing polymer, concentration of all metal ions in the receiving solution is higher than 50% for the polysulfone membrane and increases to almost 100% for the sulfonated polysulfone membrane. This effect is due to a cation-exchange property of the sulfonated polysulfone membrane.

Keywords: Polysulfone, Ultrafiltration membrane, Metal dialysis, Polymer-metal complexes

INTRODUCTION

There are numerous applications requiring multivalent ions removal from water solutions. These include clean up of groundwater (elimination of water hardness) and wastewater from metallurgical industry (removal of valuable heavy metals) [1-7]. Dialysis is a traditional membrane process for metal ions removal from water in which the ions move across nonporous ion-exchange membranes in accordance with Donnan equilibrium principle [8]. Dialysis is a diffusion phenomenon which is governed by the difference of metal concentration at the two sides of the membrane. The solute flux is

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stopped when the concentrations are equal in the two compartments. The amount of metal ions crossing the membrane can be increased by modifying their chemical potential in one of the two compartments.

If some complexing polymer is added in the feed compartment, a decrease in free metal ions concentration will lead to a decrease in the transfer rate of metal ions to the receiving compartment [9]. On the contrary, if the complexing polymer is added into the receiving compartment, the interaction of the metal ions with polymer (polymer-metal complex formation) should be responsible for an increase in the amount of metal ions transferred. In the case of a very stable complex formed, it should be possible to recover the total amount of metal ions in the receiving compartment [10].

The aim of this work is to compare two kinds of ultrafiltration membranes: polysulfone and sulfonated polysulfone membranes in Mg(II), Zn(II) and Ni(II) dialysis enhanced by poly(acrylic acid).

EXPERIMENTAL
Materials

Polysulfone (PSU) Udel P-1700 was purchased from Amoco, Co., US. Sodium salt of poly(acrylic acid) (PAA) of average mass molecular weight (M_w) equal to 35,000 g/mole was received from Aldrich Chem. Co. Ltd., England, chlorosulfonic acid (CSA) from BDH Chemicals Ltd., England. Reagent-grade $MgCl_2$, $NiCl_2$, $ZnCl_2$, 1,2-dichloroethane (DCE), and N,N-dimethylformamid (DMF) were obtained from POCH (Gliwice, Poland). The aqueous solutions were prepared with distilled water.

Membranes

Polysulfone was sulfonated using a mixture of chlorosulfonic acid and 1,2-dichloroethane (at room temperature, 2 hours). The polymer concentration of in DCE was 10%-wt.; the initial molar ratio of CSA to PSU was 0.75:1. Porous asymmetric membranes from polysulfone (PSU) and sulfonated polysulfone (SPSU) were formed by the phase-inversion method from a 15%-wt., and 30%-wt. solution in DMF, respectively. Water was a coagulation bath.

Dialysis

The dialysis cell was divided into two identical compartments (35 cm^3) separated by the membrane. One of them contained a metal salt ($MgCl_2$, $NiCl_2$ or $ZnCl_2$) and the other the sodium salt of poly(acrylic acid) (PAA) – Fig. 1.

The concentrations of metal ions in the both aqueous phases were determined by atomic adsorption spectrometry measurements (AAnalyst 100, Perkin-Elmer).
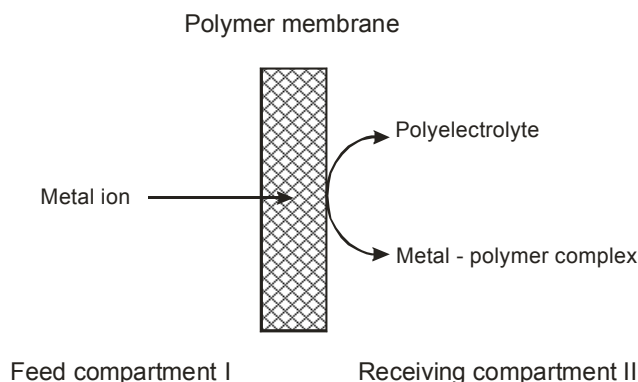
Polymer membrane

Fig. 1. Schematic diagram of the dialysis cell.

The diffusion coefficient of metal ions, D, was calculated from the equation [11]:

$$D = \frac{2.303 \cdot tg\alpha \cdot V \cdot d}{2 \cdot S \cdot t} \quad \left[cm^2 \cdot s^{-1} \right] \qquad (1)$$

$$tg\alpha = \log(C_0/C_0\text{-}2C_t) \qquad (2)$$

where C_0 and C_t are the initial concentration of Mg(II), Zn(II) or Ni(II) in the feed and in the receiving compartment at time t, respectively; V is the volume of each compartment; d is the membrane thickness; S is the active membrane surface.

RESULTS AND DISCUSSION

Polysulfone with good thermal, mechanical, biological, and chemical stability is the most frequently used polymer for ultrafiltration membrane preparation. Ionic groups can be introduced into the polymer by chemical modification [12].

$$X = -SO_3^-$$
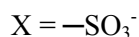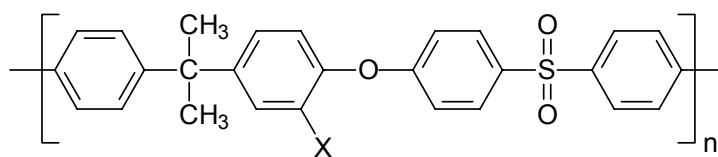
Porous structure of PSU and SPSU membranes is similar (average pore size about 35 nm, flux of water under 0.1 MPa transmembrane pressure about 150 dm^3/m^{2}h) but in the SPSU membrane the concentration of sulfonic groups is equal to 45%-mol.

Ultrafiltration membranes can remove (from water) particles of a size ranging from 2 to 100 nm and average molecular weight larger than 500 g/mole (polymers, colloids) [13]. The dialysis of a feed solution which

contains sodium salt of poly(acrylic acid) (10^{-2} mole/dcm^3) with our ultrafiltration membranes shows that only 3% of the polymer is found in the receiving solution after 24 hours. This means that the polymer cannot cross the ultrafiltration membranes due to the great difference between an average pore size of our membranes (35 nm) and the average molecular weight of the polyelectrolyte (35,000 g/mole). Therefore, the porous structure of PSU or SPSU membranes is suitable for this process.

The metal flux depends on the molar concentration ratio of the polymer to the cation and on the pH of the receiving phase [10]. In our experiments, the concentrations of Mg(II), Ni(II), and Zn(II) in the feed solution were equal to 10^{-3} mole/dm^3, the concentration of polymer in the receiving solution was equal to 10^{-2} mole/dm^3 and pH = 9 (the average pKa for carboxylic groups is around 5).

Dependence of metal ions concentration in feed and receiving compartments on dialysis time is presented in Figs 2-4.
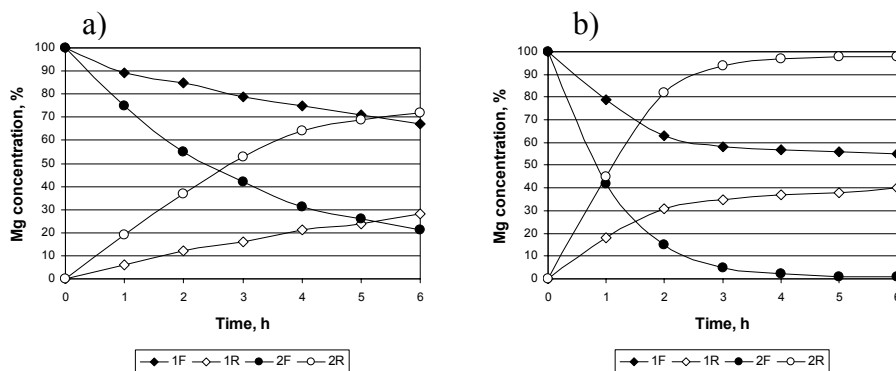

Fig. 2. Evolution of Mg(II) concentration in the feed and receiving compartment in absence (1F and 1R) and presence (2F and 2R) of polyelectrolyte:
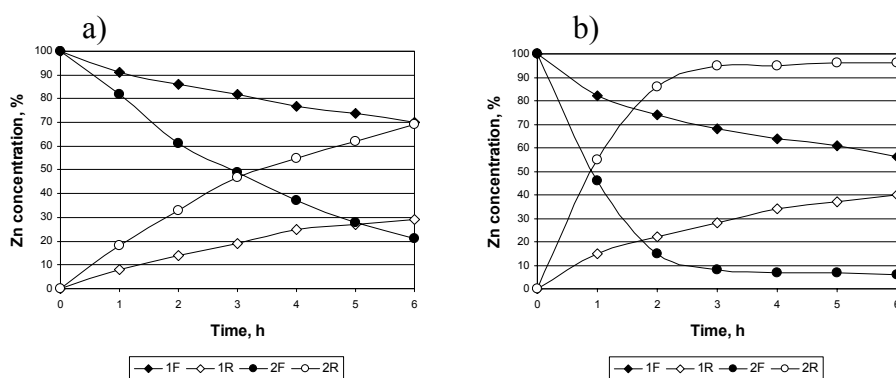a) PSU membrane, b) SPSU membrane.

Fig. 3. Evolution of Zn(II) concentration in the feed and receiving compartment in absence (1F and 1R) and presence (2F and 2R) of polyelectrolyte:
a) PSU membrane, b) SPSU membrane.

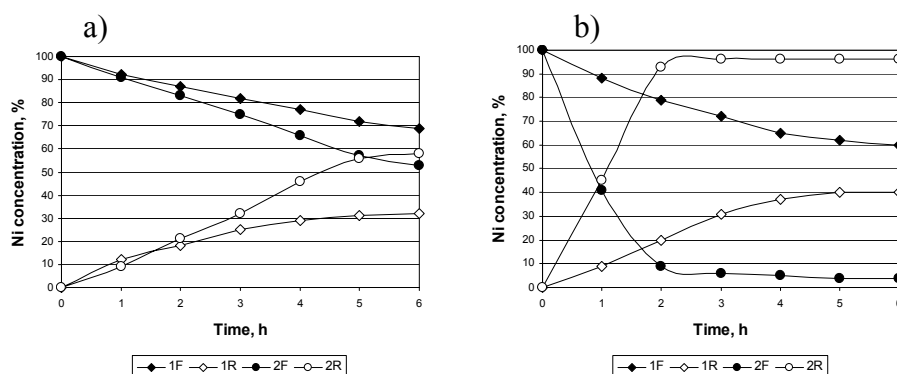a)   b)

Fig. 4. Evolution of Ni(II) concentration in the feed and receiving compartment in
absence (1F and 1R) and presence (2F and 2R) of polyelectrolyte:
a) PSU membrane, b) SPSU membrane.

For the experiments performed without a polyelectrolyte, natural dialysis of metal ions is observed; the concentrations of Mg (II), Zn(II), and Ni(II) in the receiver are lower than 50% (curves 1R). Transport of all investigated metal ions is about 10% higher in the case of sulfonated polysulfone membrane (Figs 2b, 3b and 4b) than in the case of polysulfone membrane (Figs 2a, 3a and 4a). This effect is due to the cation-exchange property of sulfonated polysulfone membrane.

Interaction of metal ions with poly(carboxylic acid) is mainly due to electrostatic forces and the formation of coordinating bonds - Fig. 5. Hence, in the presence of the polyelectrolyte, the concentrations of all metal ions in the receiving solution (curves 2R) are higher than 50% for PSU membrane (Figs 2a, 3a and 4a) and increase to almost 100% for SPSU membrane (Figs 2b, 3b and 4b).
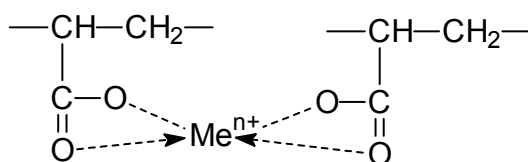

Fig. 5. Structure scheme of carboxylic –metal complexes.

The comparison of Mg(II), Zn(II), and Ni(II) transport shows that the best results can be obtained for SPSU membrane with added polyelectrolyte (PAA). However, transport of the investigated metal ions across SPSU membranes goes with various rates; metal concentration in the receiver

reaches maximum after 4, 3 and 2 hours of dialysis for Mg(II), Zn(II) and Ni(II), respectively (Figs 2b, 3b and 4b - curves 2R). It may result from the differences in the rates of bonding between the polyelectrolyte and the investigated metal ions for which electrochemical potential is equal to: -2.38 V for Mg(II), -0.76 V for Zn(II) and -0.22 V for Ni(II).

The same dependence is observed for the diffusion coefficients of these metals during dialysis with the addition of sodium salt of poly(acrylic acid) (PAA) using SPSU membrane. In the case of the dialysis without PAA, the diffusion coefficients are independent of a kind of investigated metal ions because a polymer-metal complex is not formed (Tab. 1).

Table 1. The diffusion coefficients of investigated metals

SPSU membrane	$10^5 D \ [cm^2 s^{-1}]$		
	Mg(II)	Zn(II)	Ni(II)
Without PAA	0.3	0.3	0.4
With PAA	2.2	2.7	4.1

PAA - sodium salt of poly(acrylic acid)

The application of porous membranes for dialysis is more advantageous compared with solid membranes mainly from the transport rate point of view. The diffusion coefficient of metal transport through porous ultrafiltration membranes is about 100 times higher than through nonporous dialytic membranes [11,14].

CONCLUSIONS

The dialysis of metals through polysulfone ultrafiltration membranes can be enhanced by means of sodium salt of poly(acrylic acid) which is able to bound metal cations.

Properties of porous cation-exchange membranes made of sulfonated polysulfone enable the 100% transfer of metals to the receiver.

Diffusion rate during the polyelectrolyte-enhanced dialysis through sulfonated polysulfone membranes depends on the electrochemical potential of a transported metal.

ACKNOWLEDGEMENTS

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