Abatement of Heavy Metals and Softening of Hard Water by the $CoAlPO_4$-5/Polysulfone Membrane

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ABSTRACT: To improve the membrane, if $CoAlPO_4$-5 was appropriately added, it could increase the rejection rate of metal ions compared with the PSf membrane. Besides, penetration rate would also increase, and the pressure applied could be lowered when the improved membrane was used. The optimum amount of $CoAlPO_4$-5 added for Co : Al : P = 0.1 : 0.92 : 1.0 is about 5 wt %, while for the Co : Al : P = 0.08 : 0.93 : 1.0, this optimum value would shift toward a higher wt % because the latter has less active sites per unit weight of $CoAlPO_4$-5. The hydrated radius of metal ion had great influence on the rejection rate. The larger the radius, for example, that of the +3 valence cations, the higher the rejection rate would exhibit, and the rate for Cd^{2+} was much lower because its radius was the smallest one. Moreover, although incompatibility existed in the improved membrane and the variation of applied pressure was limited, durability of this membrane under the operating conditions was good. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 2768–2773, 2001

Key words: improved membrane; rejection rate; hydrated radius; optimum wt % of addition

INTRODUCTION

Separation processes via membrane, either in the liquid phase or in the gas phase, has gradually replaced the traditional method of separation because the former needs a lot less energy. Furthermore, in some industrial processes, such as freshening of sea water, treatment of wastewater, recovery of noble metals, with the advantages of simpler construction, smaller space requirement, easier operation and maintenance, etc., there were more and more applications of the membrane process.[1–2]

Recently, for those various separation processes, the thin-film composite membrane was the one used most widely and the most potential method for the synthesis of such membrane was the interfacial polymerization method that had been reported in many works.[3–12] In our previous studies, we also had obtained interesting results about the increase of separation efficiency by improving the membrane via the interfacial polymerization method.

Nevertheless, to further improve the separation efficiency, there were some investigations focused on zeolite–polymer composite membranes for the gas separation[13] and for pervaporation.[14] A zeolite blended membrane could be easily prepared by adding different sizes and shapes of zeolites into the membrane.[15–17] We had even synthesized the $CoAlPO_4$-5/PC membrane to improve efficiency of separation of N_2 and O_2, and

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some interesting results had been reported.[18] Furthermore, because $CoAlPO_4$-5 had the characteristics of a hydrophilic surface, ion-exchange ability, trapping effect of pores, and durability for repeatedly use, we had thus been prompted to study the separation efficiency of metal ions from water by using the $CoAlPO_4$-5/Polysulfone (PSf) membrane.

In this work, the efficiency of separation of some metal ions, such as Al^{3+}, Fe^{2+}, Cd^{2+}, Mg^{2+}, Ca^{2+}, etc., had been tested by using the $CoAlPO_4$-5/PSf membrane with different wt % of $CoAlPO_4$-5 blended and the $CoAlPO_4$-5 with various Co contents in the mother liquor would also be used to study the shift of optimum amount of $CoAlPO_4$-5 in the PSf membrane. Moreover, the effect of the hydrated radius of metal ions on the rejection rate would be discussed.

EXPERIMENTAL

Materials

Udel® Polysulfone P-3500 was obtained from Amoco Performance Products. Chloroform, triethylamine, cobalt acetate, the other salts of various metals, etc., were purchased from Merck Co. All the above-mentioned chemicals were of reagent grade and without further purification.

$CoAlPO_4$-5 Preparation

Two types of $CoAlPO_4$-5 with mol ratios of Co : Al : P in the mother liquor equal to 0.1 : 0.92 : 1.0 and 0.08 : 0.93 : 1.0 were synthesized according to the procedures described by Messina et al.,[19] and these two $CoAlPO_4$-5 will be signified as Co–10 and Co–8, respectively in the following expressions. The $CoAlPO_4$-5 precursors were calcined at 550°C and then characterized by XRD to confirm the right crystal pattern. In addition, with UV/VIS spectrometer measurements, the cobalt species was proven to be in a tetrahedral crystal field.[20] In preparing the membrane, the $CoAlPO_4$-5 added was the sieved particles with sizes below 200 mesh.

Membrane Preparation

PSf and $CoAlPO_4$-5/PSf membranes were prepared from a casting solution of polysulfone in chloroform. Various amount of $CoAlPO_4$-5 according to different wt % design, was added into the solution. Casting the solution onto a glass plate to a predetermined thickness using a Gardner knife at room temperature formed the membranes required for the study. The membranes were dried in vacuum for 24 h before metal ion separation, and water permeation measurements were proceeded.

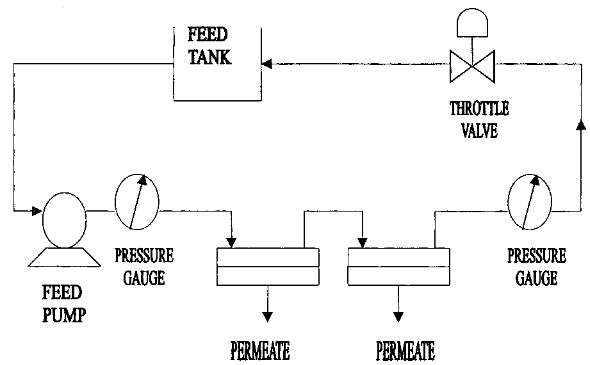

Figure 1 Apparatus for the separation of metal ions.

Metal Ion Separation Measurements

The apparatus used for studying separation of metal ions was shown in Figure 1. Initial concentration of metal ions about 100 ppm was prepared and stored in the feed tank. During tests proceeded, the metal ion solutions were recycled by the feed pump, and the penetrates from membrane 1 and membrane 2 were collected for the measurements of flow rate and rate of penetrate and rejection rate of metal ions.

The flow rates of penetrate from membranes 1 and 2 were then measured separately, and the average value was calculated. The flow rate unit used in this article was mL/h, while it could be divided by the area of the membrane ($\pi \times 10^{-4}$ m^2) to have the unit L/(h · m^2), for example, 0.2 mL/h or 0.64 L/(h · m^2).

RESULTS AND DISCUSSION

Effect of $CoAlPO_4$-5 Content on Rate of Rejection of Metal Ions and on Flow Rate

With various amount of Co-10 added in the membrane, the effect of wt % of $CoAlPO_4$-5 on the rejection rate of various metal ions and on flow rate of penetrate could be seen in the figures from Figure 2 to Figure 8. The results showed that rate of rejection of metal ions had a maximum value as the wt % of blended Co-10 increased. This maximum value appeared at about 5 or 6% of Co-10

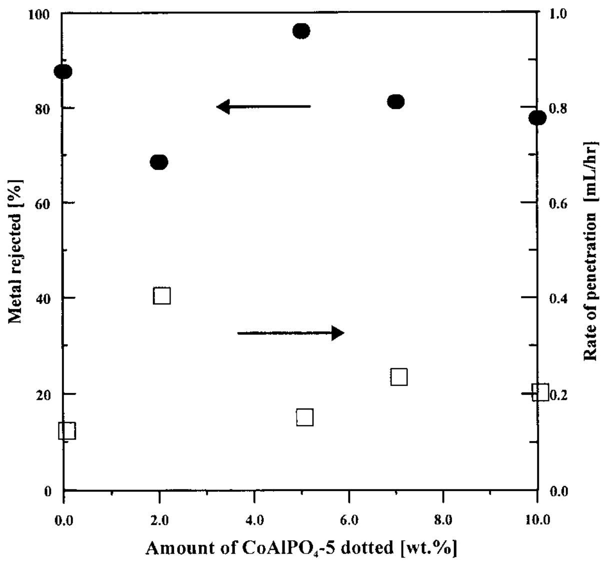

Figure 2 Effect of $CoAlPO_4$-5 content on Mg^{2+} rejection and on rate of penetration. Temp.: 30°C; Co : Al : P = 0.1 : 0.92 : 1.0; Pressure: 0 wt % ~5–6 MPa, others ~2–3 MPa; Initial concentration of metal ion: 100 ppm.

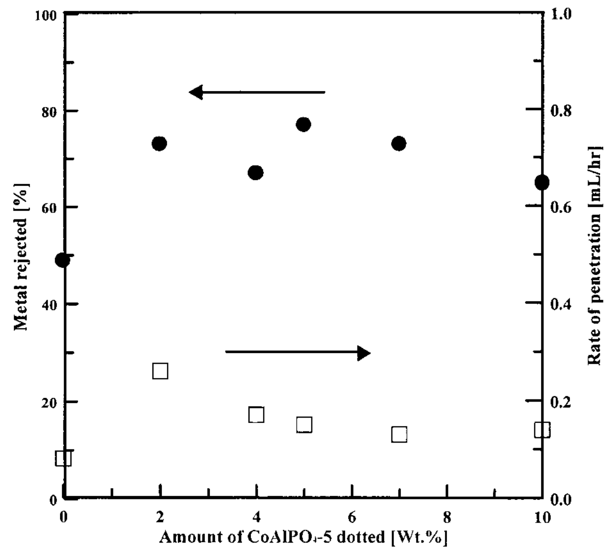

Figure 4 Effect of $CoAlPO_4$-5 content on Fe^{2+} rejection and on rate of penetration. Temp.: 30°C; Co : Al : P = 0.1 : 0.92 : 1.0; Pressure: 0 wt % ~5–6 MPa, others ~2–3 MPa; Initial concentration of metal ion: 100 ppm.

added, and was higher than that of pure membrane (0 wt %) for all the metal ions tested.

The results mentioned above may be illustrated as follows. Because surface of $CoAlPO_4$-5 was hydrophilic, and this property was mainly due to the active sites, i.e., the Co species in the tetrahedral structure of $CoAlPO_4$-5, it would be more hydrophilic on the surface of the membrane as the amount of blended $CoAlPO_4$-5 increases. And there would be more metal ions in the bulk solution concentrated near the surface, thus caused the phenomenon of concentration polarization. This concentration polarization would hinder further approach of the metal ions in the

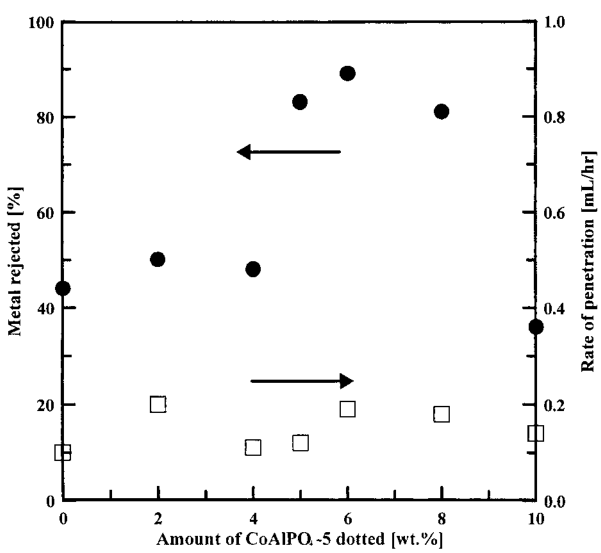

Figure 3 Effect of $CoAlPO_4$-5 content on Ca^{2+} rejection and on rate of penetration. Temp.: 30°C; Co : Al : P = 0.1 : 0.92 : 1.0; Pressure: 0 wt % ~5–6 MPa, others ~2–3 MPa; Initial concentration of metal ion: 100 ppm.

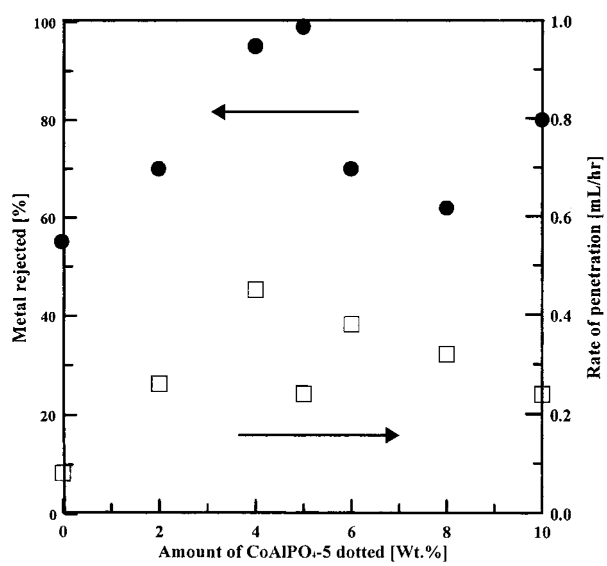

Figure 5 Effect of $CoAlPO_4$-5 content on Mn^{2+} rejection and on rate of penetration. Temp.: 30°C; Co : Al : P = 0.1 : 0.92 : 1.0; Pressure: 0 wt % ~5–6 MPa, others ~2–3 MPa; Initial concentration of metal ion: 100 ppm.

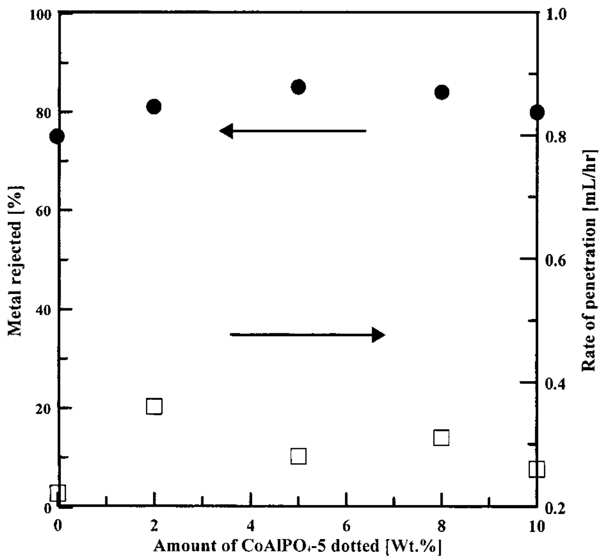

Figure 6 Effect of CoAlPO$_4$-5 content on Co^{2+} rejection and on rate of penetration. Temp.: 30°C; Co : Al : P = 0.1 : 0.92 : 1.0; Pressure: 0 wt % ~5–6 MPa, others ~2–3 MPa; Initial concentration of metal ion: 100 ppm.

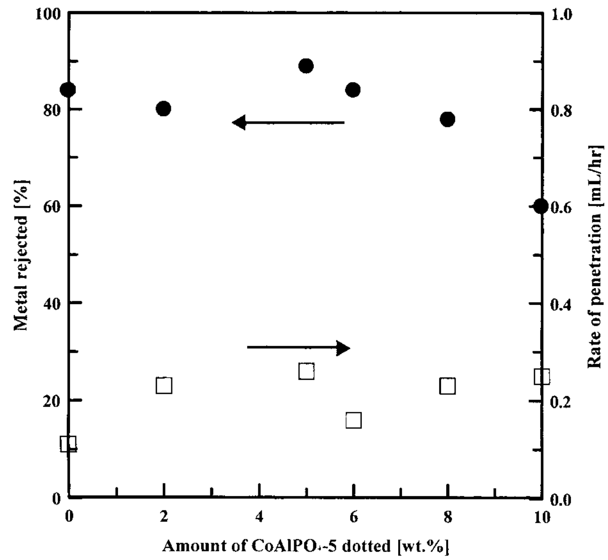

Figure 8 Effect of CoAlPO$_4$-5 content on Fe^{3+} rejection and on rate of penetration. Temp.: 30°C; Co : Al : P = 0.1 : 0.92 : 1.0; Pressure: 0 wt % ~5–6 MPa, others ~2–3 MPa; Initial concentration of metal ion: 100 ppm.

bulk solution to the surface of the membrane as to the injection rate increasing. In addition, with those effects of adsorption and trapping of the metal ions in the pores of CoAlPO$_4$-5, penetration of metal ions through the membrane would be reduced further. On the other hand, as the CoAlPO$_4$-5 added increased, the incompatibility

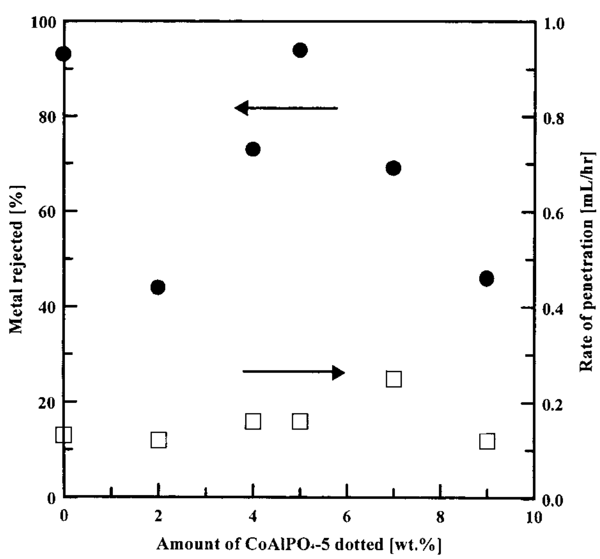

Figure 7 Effect of CoAlPO$_4$-5 content on Al^{3+} rejection and on rate of penetration. Temp.: 30°C; Co : Al : P = 0.1 : 0.92 : 1.0; Pressure: 0 wt % ~5–6 MPa, others ~2–3 MPa; Initial concentration of metal ion: 100 ppm.

in the CoAlPO$_4$-5/PSf membrane would also increase, and there would be more pinholes in the membrane, thus decreasing the rate of the separation of the metal ions.[19,22] This incompatibility could also be shown by the decrease of T_g of the membrane, as could be seen in our previous studies.[19] With the interaction of the above phenomena, we thus had the maximum rate of rejection as the wt % of CoAlPO$_4$-5 added increased.

As to the effect of content on the flow rate, although it was not regular, we could find that most CoAlPO$_4$-5/PSf membranes had a higher rate than the pure PSf membrane, and in some cases, it was even several times higher. Furthermore, although there were some tests that showed lower penetration rate for the improved membrane, we could observe that the pressure applied for the pure PSf membrane (50–60 atm) was much higher than that for the improved membrane (20–30 atm). This was due to the significant increase of hydrophilic property and pinholes on the surface of the CoAlPO$_4$-5/PSf membrane. Besides, the irregular relationship between the wt % and the penetration rate may be caused by the difficulty of uniform preparation of the membrane.

Effect of Co : Al : P in the Mother Liquor on the Rate of Rejection of Metal Ions

When the CoAlPO$_4$-5 added was now the Co–8, then because the active sites per unit weight of

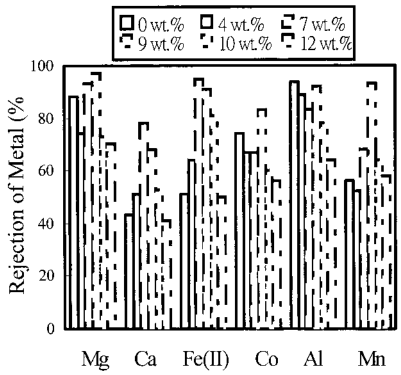

Figure 9 Rejection of metal ions by the $CoAlPO_4$-5 blended membrane with the Co : Al : P of $CoAlPO_4$-5 equals 0.08 : 0.93 : 1.0. Temp.: 30°C; Initial concentration of metal ion: 100 ppm.

$CoAlPO_4$-5 was lower, we found that the optimum rate of rejection was shifted towards a wt % higher than 5%, as can be seen in the Figure 9. This result may further prove our previous proposal of the competing effect of the hydrophilic properties of active sites and the incompatibility between $CoAlPO_4$-5 and the membrane on the rejection rate.

Effect of Hydrated Radii on the Rate of Rejection of Metal Ions

Table I compared the relationship between the hydrated radii of various metal ions[21] and the rate of rejection. As could be seen, the hydrated radius had significant influence on the rate of rejection. Of the metal ions tested, the Cd^{2+} ion had the lowest rejection rate because its hydrated radius was the smallest (0.5 nm). According to this radius, the Cd^{2+} would have more freedom to transport through the pore of $CoAlPO_4$-5 (0.8 nm), and would penetrate the pinholes easily. In the future study, to increase the rate of Cd^{2+} rejected, some ligands should be used to have a complex of Cd^{2+} with a bigger radius. As to the results of +3 valence cations and the Mg^{2+}, we found their rates were much higher because their hydrated radii were bigger. For the other cations with +2 valence, though the average hydrated radii were all 0.6 nm, the rates of rejection were somewhat different, and this may be due to the different stability of the hydrated metal ions that would lead to a different extent of detach of the ligand H_2O under the compression of the operating pressure. Thus, there were different ratios of smaller hydrated ions in the bulk solution.

Effect of Other Operating Conditions on the Rate of Rejection and on the Flow Rate

We also have tested the influence of initial concentrations of metal ions on the rate of rejection, and it was concluded that the higher the initial concentration, the higher the rejection rate would be. However, as the concentration of metal ions of penetrate was calculated, we found it was not lower for the case of higher initial concentration. For example, for rejection of Fe^{3+}, as the initial concentration was 500 ppm, the rate could be as high as about 96% while for that with initial concentration of 100 ppm, it was just about 91%. Although, it could be deduced that the former case has a higher concentration of Fe^{3+} in the penetrate.

Besides, the effect of applied pressure had also been studied. Limited by the moderate strength of the improved membrane due to the incompatibility and limited by the measure of penetrate (thus, the pressure applied should not be too low to have enough amount of penetrate), the range of operating pressure could not be varied too much. It should be further improved for the preparation of the membrane, for example, blending finer $CoAlPO_4$-5 or less wt % of high Co content $CoAlPO_4$-5 was used to increase the compatibility of the $CoAlPO_4$-5/PSf membrane.

In addition, durability of the improved membrane was also tested, and because it could be used repeatedly without apparent degradation of the properties, we concluded that under the

Table I Relationship between Rejection Rate and Hydrated Radii of Metal Ions

Metal Ion	Mg(II)	Ca(II)	Fe(II)	Fe(III)	Cd(II)	Mn(II)	Co(II)	Al(III)
Rejection rate (%)[a]	97	89	77	91	69	98	85	94
Hydrated radius (nm)[b]	0.8	0.6	0.6	0.9	0.5	0.6	0.6	0.9

[a] Data of 5 wt % $CoAlPO_4$-5 (0.1 : 0.92 : 1.0) added.
[b] Data from ref. 21.

present operating conditions, this $CoAlPO_4$-5/PSf membrane had good durability.

CONCLUSION

The $CoAlPO_4$-5 blended membrane was prepared by adding $CoAlPO_4$-5 into the PSf membrane. It was found that the optimum rejection rate of metal ions was achieved as about 5% of the $CoAlPO_4$-5 (Co-10) was added, while this optimum value would shift to a higher wt % as the $CoAlPO_4$-5 added was Co-8. Furthermore, the rejection rate was apparently affected by the hydrated radius of the metal ions. The ions with higher radii, such as Fe^{3+}, Al^{3+}, and Mg^{2+}, would get a higher rejection rate, but the rate of Cd^{2+} was much lower, because it has a smaller radius. Flow rate of the improved membrane tested was mostly higher than that of the pure PSf membrane, and the applied pressure of the former was also much lower than the latter. With the advantages mentioned above and with durability of the membrane, we concluded that this $CoAlPO_4$-5/PSf membrane was a suitable one for the abatement of the metal ions.

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