Effect of Adding Other Metal Ions on the Removal of Cd^{2+} by the $CoAlPO_4$-5/Polysulfone Membrane

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ABSTRACT: Based on our previous work, performance of separation of Cd^{2+} by the $CoAlPO_4$-5/polysulfone membrane was not as good as that of the other metal ions. This could be significantly improved by the addition of other metal ions into the Cd^{2+} solution. The metal ions added were those with larger hydrated radius than that of Cd^{2+}. When Mg^{2+} and Ca^{2+} were added, the rejection rate of Cd^{2+} could be increased from about 50% ($[Cd^{2+}]$ = 50 ppm) to nearly 100% and the rate would increase with concentration of Mg^{2+} and Ca^{2+}. However, when the added ions were Fe^{2+} and Mn^{2+}, although the performance of Cd^{2+} removal was still high, the rejection rate would inversely decrease with increasing concentration of Fe^{2+} and Mn^{2+}. These phenomena were mainly attributable to the effect of hydrated ion and the effect of lowered pH value induced by the hydrolysis of the solution. As to the addition of Al^{3+}, although the rejection rate would decrease with increasing Al^{3+} concentration up to 100 ppm, an abrupt increase was observed at 150 ppm, which was thought to be attributable to the concentration polarization effect caused by the formation of the high valence $[Al_n(OH)_m]^{(3[supi]n-[supi]m)+}$ complex. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 2172–2177, 2002

Key words: $CoAlPO_4$-5/polysulfone membrane; rejection rate; hydrated radius; hydrolysis; pH value

INTRODUCTION

Separation processes by membrane have found more and more applications with their predominance of less energy, smaller space requirement, and easier operation and maintenance over the traditional method of separation, such as wastewater treatment, seawater freshening, and noble metals recovery.[1,2]

In our previous studies, by use of the interfacial polymerization method, efficiency of membrane separation was significantly increased.[3] Furthermore, based on the investigations about gas separation and pervaporization by the zeolite–polymer composite membrane,[4–8] a $CoAlPO_4$-5/polymer composite (pc) membrane was synthesized to improve performance of separation of N_2 and O_2[9] and a $CoAlPO_4$-5/polysulfone (psf) membrane was used to reduce the concentration of heavy metal ions and soften hard water.[10] Some interesting results were observed and a higher performance of separation than that of the polysulfone membrane was acquired. Concerning the application of the $CoAlPO_4$-5/psf membrane, in particular, we found that not only rejection rates of metal ions but also flow rates of penetrates were greatly improved, except for the removal of Cd^{2+}. According to our studies, the hydrated radii

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of metal ions exerted a significant influence on the rejection rate. We concluded that the larger the hydrated radius (e.g., that of +3 valence cations), the higher the rejection rate. Because the radius of hydrated Cd^{2+} had the smallest value among those of the metal ions tested, the rejection rate of Cd^{2+} was not as high as that of the other metal ions. However, the removal of Cd^{2+} was an important topic, given that Cd^{2+} ions could cause serious health problems and many industrial wastewaters were contaminated by this ion. To further improve the performance of separation of Cd^{2+} and assuming the effect of hydrated radius, we were thus prompted to mix another metal ion, which had larger hydrated radius, with the Cd^{2+} solution to fulfill this purpose.

In this work, various concentrations of Mg^{2+}, Ca^{2+}, Al^{3+}, Fe^{2+}, and Mn^{2+} were added to various concentrations of Cd^{2+} to test the performance of removal of Cd^{2+} by the $CoAlPO_4$-5/psf membrane. In addition, the influence of a decrease of pH value attributed to hydrolysis of solution caused by some metal ions is also discussed.

EXPERIMENTAL

The materials used, the $CoAlPO_4$-5 synthesis, the membrane preparation, and the apparatus and experimental procedures for studying separation of metal ions were all shown and described in our previous work.[10] In this study, the $CoAlPO_4$-5 used for the preparation of $CoAlPO_4$-5/psf membrane had a molar ratio of Co : Al : P in the mother liquor of 0.1 : 0.92 : 1.0 and the optimum amount of $CoAlPO_4$-5 (i.e., 6% according to our previous study) was blended with polysulfone solution. Various concentrations of Mg^{2+}, Ca^{2+}, Al^{3+}, Fe^{2+}, and Mn^{2+} were mixed with three concentrations of Cd^{2+}(50, 100, 150 ppm). The residual metal ions in the penetrate were analyzed by atomic absorption spectrometry (GBC-AA-960). The average flow rates of penetrate and rejection rates of metal ions were then calculated.

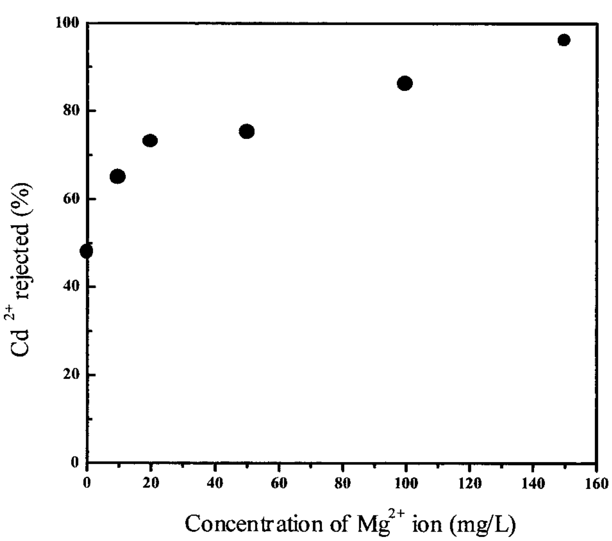

Figure 1 Effect of Mg^{2+} ion concentration on the rejection rate of Cd^{2+}. [Cd^{2+}]: 50 ppm; pressure: 2–3 MPa; temperature: 30°C.

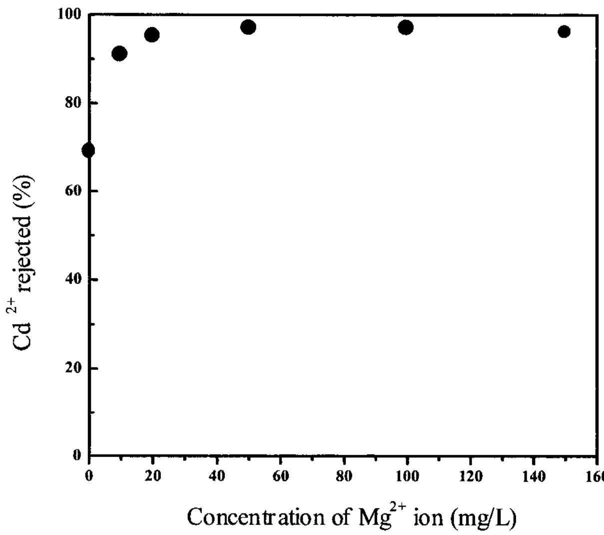

Figure 2 Effect of Mg^{2+} ion concentration on the rejection rate of Cd^{2+}. [Cd^{2+}]: 100 ppm; pressure: 2–3 MPa; temperature: 30°C.

RESULTS AND DISCUSSION

Effect of Adding Mg^{2+} on the Rejection Rate of Cd^{2+}

Figures 1 and 2 show the effect of adding various concentrations of Mg^{2+} on the rejection rate of Cd^{2+} by using the $CoAlPO_4$-5/psf membrane. It was found that addition of Mg^{2+} could greatly increase the rejection rate of Cd^{2+} from about 50% ([Cd^{2+}] = 50 ppm) to as high as 97%. Moreover, at the concentration of Cd^{2+} of 50 ppm, the rejection rate of Cd^{2+} would increase with the concentration of Mg^{2+}, whereas the rejection rate apparently would not vary when the Cd^{2+} concentration was 100 ppm and the Mg^{2+} concentration was higher than 50 ppm. When Mg^{2+} was added,

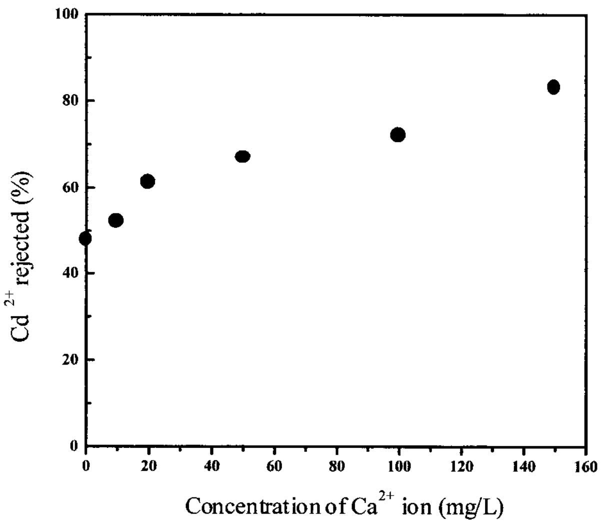

Figure 3 Effect of Ca^{2+} ion concentration on the rejection rate of Cd^{2+}. [Cd^{2+}]: 50 ppm; pressure: 2–3 MPa; temperature: 30°C.

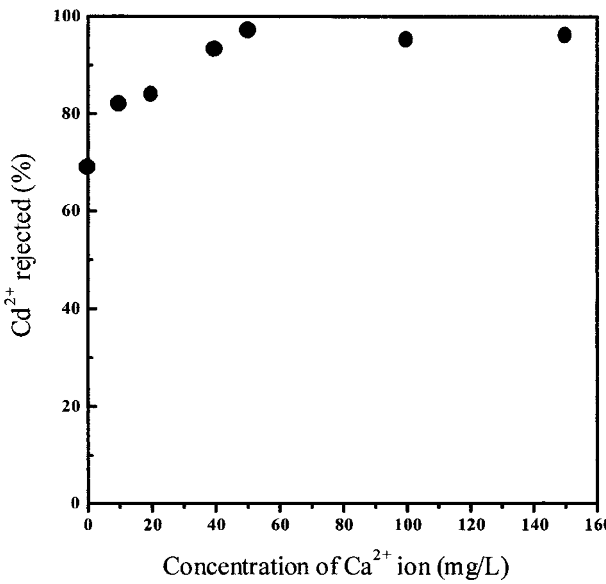

Figure 4 Effect of Ca^{2+} ion concentration on the rejection rate of Cd^{2+}. [Cd^{2+}]: 100 ppm; pressure: 2–3 MPa; temperature: 30°C.

the hydrated Mg^{2+} complex ($[Mg(H_2O)_n]^{2+}$) would be formed and gather near the surface of the membrane. The concentration polarization and the plugging of membrane pores (mainly the pinholes of polysulfone matrix and micropores of $CoAlPO_4$-5) would hinder the penetration of Cd^{2+}, such that the rate of rejection was increased. Furthermore, because those pinholes or micropores of membrane blocked by hydrated Mg^{2+} would increase with Mg^{2+} concentration, it was reasonable that the rejection rate would increase, as shown in Figure 1. As to the higher rejection rate in Figure 2, under the same operating conditions, the penetrating flux of Cd^{2+} was limited. Then, if the initial concentration of Cd^{2+} was greater, its rejection rate would also be higher. Similar results had also been observed in our previous work.[10] In addition, if the Mg^{2+} concentration was higher than 50 ppm, because the rate was nearly 100%, there was little room for improvement.

Effect of Adding Ca^{2+} on the Rejection Rate of Cd^{2+}

Because the ion added to the Cd^{2+} solution was Ca^{2+}, it can be seen that Figures 3 to 5 showed results similar to those of Figure 1 and Figure 2, that is, the rejection rate of Cd^{2+} increased with increasing concentration of Ca^{2+}. Nevertheless, when we compared Figures 1 and 2 with Figures 3 to 5, we found that addition of Mg^{2+} exhibited somewhat higher performance because the hydrated radius of Mg^{2+} (0.8 nm) was larger than that of Ca^{2+} (0.6 nm). Besides, when the concentration of Ca^{2+} was less than 50 ppm, we could see that the rejection rate, when the concentration of Cd^{2+} was 150 ppm, was lower than that when the Cd^{2+} concentration was 100 ppm. This was supposed that, when the Cd^{2+} concentration

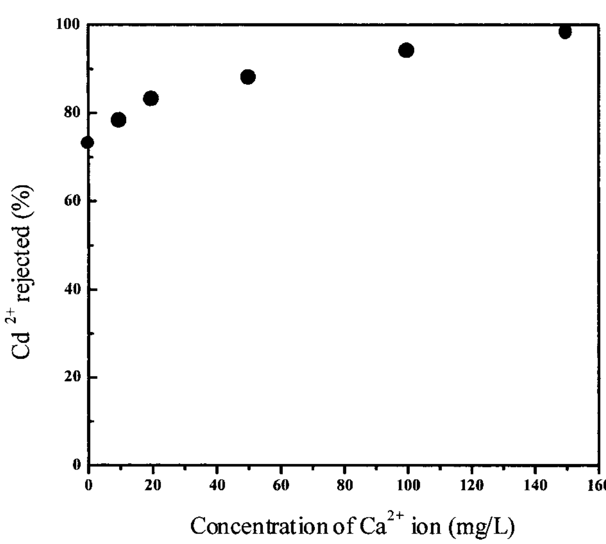

Figure 5 Effect of Ca^{2+} ion concentration on the rejection rate of Cd^{2+}. [Cd^{2+}]: 150 ppm; pressure: 2–3 MPa; temperature: 30°C.

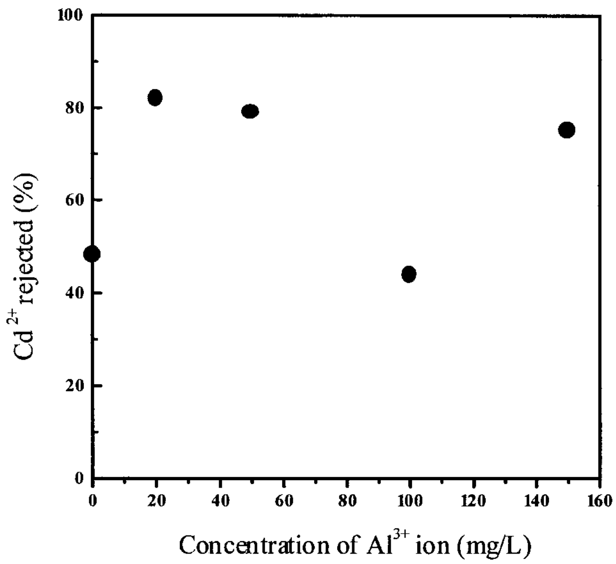

Figure 6 Effect of Al^{3+} ion concentration on the rejection rate of Cd^{2+}. [Cd^{2+}]: 50 ppm; pressure: 3–4 MPa; temperature: 30°C.

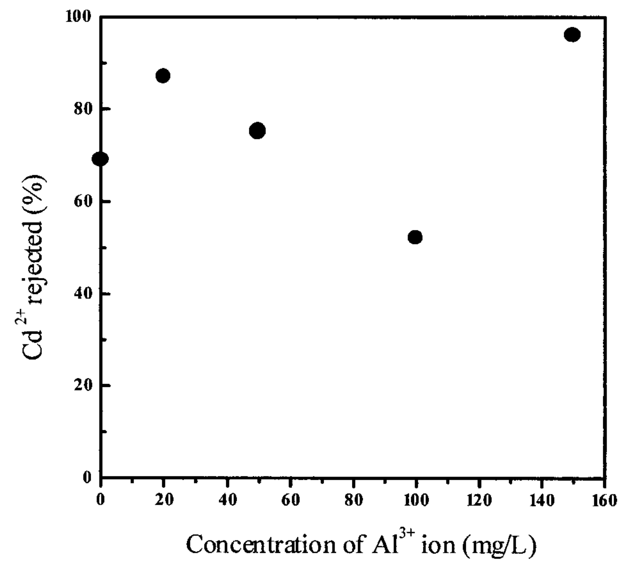

Figure 7 Effect of Al^{3+} ion concentration on the rejection rate of Cd^{2+}. [Cd^{2+}]: 100 ppm; pressure: 3–4 MPa; temperature: 30°C.

was 150 ppm and the Ca^{2+} concentration was lower than 50 ppm, perhaps the Cd^{2+} ions would have greater concentration predominance over the Ca^{2+} ions to gather near the membrane surface, thus leading to more Cd^{2+} ions penetrating the membrane; thus, a lower rejection rate would be observed.

Effect of Adding Al^{3+} on the Rejection Rate of Cd^{2+}

Given that the hydrated radius of Al^{3+} (0.9 nm) was larger than that of either Mg^{2+} or Ca^{2+}, it was first predicted that the rejection rate of Cd^{2+} in the case of Al^{3+} added would also be higher. However, as can be seen in Figures 6 to 8, we obtained a lower rejection rate of Cd^{2+} when the ion added was Al^{3+}. In some cases, it was even lower than that of any without Al^{3+} added ([Cd^{2+}] = 50, 100 ppm; [Al^{3+}] = 100 ppm). Furthermore, we found that the rejection rate would decrease with increasing Al^{3+} concentration from 20 to 100 ppm, whereas it abruptly increased at the concentration of 150 ppm. Moreover, in contrast to the results of Ca^{2+}, the rejection rate increased with Cd^{2+} concentration. These phenomena can be illustrated as follows.

The capability of hydrolysis by the Al^{3+} was much greater than that of Mg^{2+} and Ca^{2+}. Given that the hydrolysis of the aqueous solution occurred in the presence of metal ions, the pH value would be lowered. Thus the pH value of solution with Al^{3+} added should be lower than that with Mg^{2+} and Ca^{2+} added. It can be seen in Figure 9, as the Al^{3+} was added, the pH value was the lowest, decreasing with increasing concentration of Al^{3+}. It was reported in Kawamura et al.[11] that the form of Cd^{2+} ions was greatly influenced by the pH value of solution; that is, it had a greater

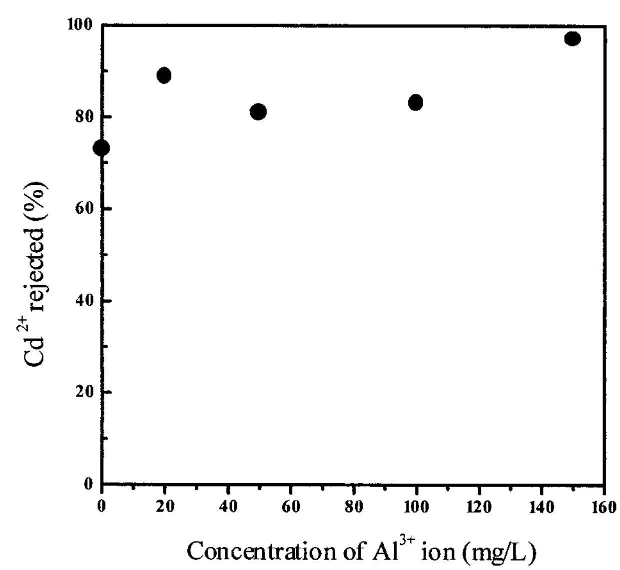

Figure 8 Effect of Al^{3+} ion concentration on the rejection rate of Cd^{2+}. [Cd^{2+}]: 150 ppm; pressure: 3–4 MPa; temperature: 30°C.

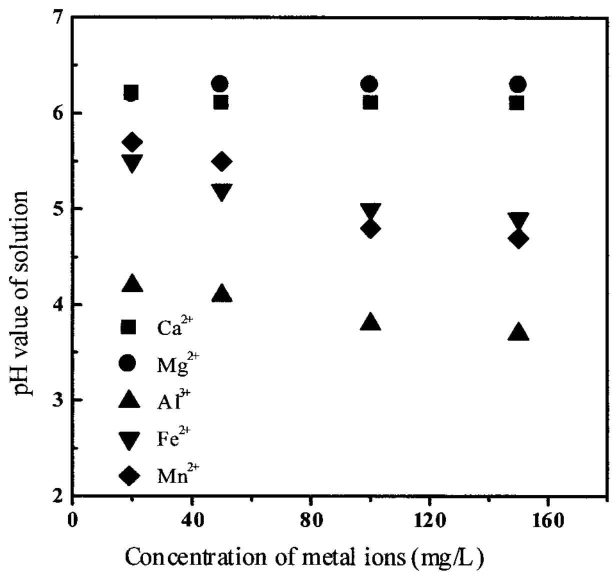

Figure 9 Effect of metal ion concentration on the pH value of solution. [Cd^{2+}]: 100 ppm; temperature: 30°C.

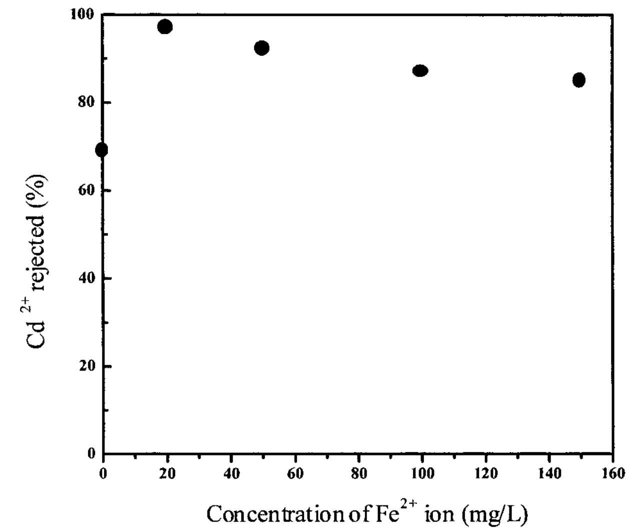

Figure 10 Effect of Fe^{2+} ion concentration on the rejection rate of Cd^{2+}. [Cd^{2+}]: 100 ppm; pressure: 2–3 MPa; temperature: 30°C.

tendency to remain the simple ion form, but not the hydrated ion form, because the pH value was low enough. Then, because addition of Al^{3+} would decrease the pH value, some aquo-ligand might detach from the hydrated Cd^{2+} ion ($[Cd(H_2O)_n]^{2+}$) and the average hydrated radius would be reduced, thus leading to a lower rejection rate. Besides, because there were more simple-form Cd^{2+} ions remaining at higher Al^{3+} concentration and lower pH value, the rate should decrease with increasing Al^{3+} concentration. As to the abrupt increase of Al^{3+} at 150 ppm, it was supposed that some high valence polynuclei hydroxyl aluminum complex ($[Al_n(OH)_m]^{(3n-m)+}$) had been formed under such a high concentration of Al^{3+}, and it was the concentration polarization effect of this high charge complex that caused the unusual result. In contrast to Al^{3+}, the degree of hydrolysis by Mg^{2+} and Ca^{2+} was negligible. Thus the pH value was near that of natural water and apparently would not change with the concentration. It was the hydrated ions of Mg^{2+} and Ca^{2+} that predominantly affected the rejection rate. For the phenomenon of increasing rejection rate with increasing Cd^{2+} concentration, it was deduced that, because Al^{3+} had a higher valence, the concentration predominance was not so apparent when the Cd^{2+} concentration was 150 ppm and the Al^{3+} concentration was lower than 50 ppm. Thus, under the limited penetrating rate of Cd^{2+}, the rejection rate would increase with initial Cd^{2+} concentration, different from the case with Ca^{2+} added.

Effect of Adding Fe^{2+} and Mn^{2+} on the Rejection Rate of Cd^{2+}

To further verify the effect of pH value and because there were some other metal ions present in the industrial wastewater, the effect of adding Fe^{2+} and Mn^{2+} on the rejection rate of Cd^{2+} was also tested. The results are shown in Figures 10 and 11. Similar to results of Al^{3+}added, we found a decreasing rejection rate with increasing concentration of Fe^{2+} and Mn^{2+}, although not so

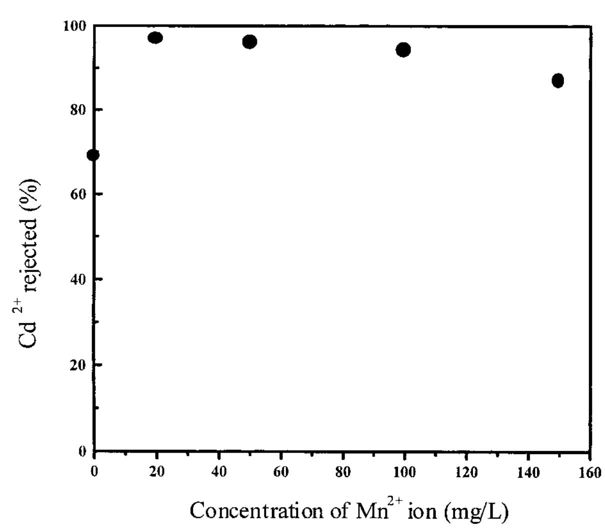

Figure 11 Effect of Mn^{2+} ion concentration on the rejection rate of Cd^{2+}. [Cd^{2+}]: 100 ppm; pressure: 2–3 MPa; temperature: 30°C.

appreciably. If we checked the results of Figure 9, we could find apparent hydrolysis of solution caused by these two ions. The pH value was also lowered and it decreased as the metal ions concentration increased. This explained the results of Figures 10 and 11. Moreover, because the formation of a polynuclei complex of Fe^{2+} and Mn^{2+} was not as easily achieved as that of Al^{3+}, the abrupt increase of the rejection rate at 150 ppm for the case of Al^{3+}added would not be observed because the ions added were Fe^{2+} and Mn^{2+}.

Finally, in this study, we also found that the rejection rate of another ion mixed with Cd^{2+} and the flow rate of the penetrate were about the same as the results of our previous work. Furthermore, the operating conditions, especially the pressure, was also about the same as that applied in our previous study. The membrane continued to exhibit good durability.

CONCLUSIONS

The addition of other metal ions with larger hydrated radius to the Cd^{2+} solution could significantly increase the rejection rate of Cd^{2+}. If the ions added were Mg^{2+} and Ca^{2+}, the rejection rate would increase with concentration of Mg^{2+} and Ca^{2+}, whereas if the ions added were Fe^{2+} and Mn^{2+}, the rejection rate would inversely decrease with their concentration. The former was attributed to the plugging of pores of the improved membrane by the hydrated ions and the latter was attributed to the lowered pH value caused by the hydrolysis of the solution. Concerning the addition of Al^{3+}, the rejection rate would first decrease with Al^{3+} concentration up to 100 ppm, although an abrupt increase was observed at 150 ppm of Al^{3+}. This was deduced to be caused by the formation of $[Al_n(OH)_m]^{(3n-m)+}$. Furthermore, with the addition of another metal ion, the flow rate of the penetrate and the rejection rate of this added ion would not vary significantly compared with results of our previous work.

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