

Pervaporation Properties of Humic Acid-Added Membranes

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ABSTRACT: The saving and recycling of chemical substances, which may be hazardous to human health and ecosystems, constitute a desirable goal worldwide. It is important to use a natural polymer that has a highly specific function and an environmental friendliness. In this study, humic acid was added to a natural polymer, a pectin membrane, and a hydrophobic poly(1-trimethylsilyl-1-propyne) (PMSP) membrane to enhance the affinity for phenol or aniline. Also, the separation performance, based on the membrane materials and methods of addition, was investigated. The effect of the adsorption of phenol and aniline by humic acid was investigated. A high rate of aniline adsorption was observed. The interaction of the humic acids and

the aniline was mainly observed by polar bonding. For the PMSP membrane with humic acid added to the surface, the humic acid exists in a colloidal state. During pervaporation, the permeation of water was prevented by the adsorbed solute. Because the permeability of aniline increased and the permeability of water significantly decreased, the PMSP membrane with humic acid added to the surface had a high permeate aniline concentration, and the permselectivity was improved. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 461–468, 2004

Key words: pervaporation, membranes, recycling, separation techniques, humic acid

INTRODUCTION

Chemical substances, which exist in the environment, may be hazardous to human health and ecosystems. Recently, PRTRs (Pollutant Release and Transfer Registers), constituting a new framework to improve and enhance the management of chemical substances by businesses with the aim of protecting the environment from hazardous chemical substances, have been established. Public understanding about the management, saving, and recycling of chemical substances is desired worldwide to protect not only human life but also aquatic life.

Phenol and aniline are important materials or additives in the chemical industry and laboratory, and are also frequently present in process effluents from petrochemicals and pharmaceuticals. Aquatic life criteria have been developed to protect aquatic life in various countries. Phenol and aniline have been found to be in the aquatic life criteria table because of their toxicity in Japan. Thus the removal of very low concentrations of phenol and aniline (mg/L order) is needed. Because they mix azeotropically with water,¹ effective disposal is expected.^{2,3} Pervaporation is an attractive alternative to traditional methods (e.g., adsorption on acti-

vated carbon, biodegradation, photolysis, and ozonization) for removing low concentrations of organic solvents from wastewater because it has high selectivity, energy-saving features, and produces no toxic decomposed substances.^{4,5} The pervaporation separation process has become an effective process and has been studied for the separation and recovery of liquid solutions such as azeotropic mixtures, close boiling components, thermal decomposition products, and isomeric mixtures in the chemical industries.^{2,3,5–19} Hoshi et al.^{2,3} reported the effective separation of a phenol–water mixture using polyurethane. Park et al.¹³ used a poly(acrylonitrile-co-vinylphosphonic acid) membrane to separate the azeotropic water/pyridine mixture. The permselectivity can be modeled by a sorption–diffusion mechanism.^{11,12,15,17,19} The sorption of the permeate component can be controlled by its affinity for the membrane material.

Natural polymers have been expected to be used and studied as membrane materials because of their environmental friendliness.^{6,7,11,20} Moreover, it is important to use a natural polymer that has a highly specific function.²⁰ Yamada et al.²⁰ reported the endocrine removal by UV-irradiated DNA material. Dissolved humic acids, the main organic carbon-containing components in surface water, ground water, sediment, and soil, are commonly yellowish-brown colloidal substances.^{21–23} They are important components of organic carbon in environmental samples and

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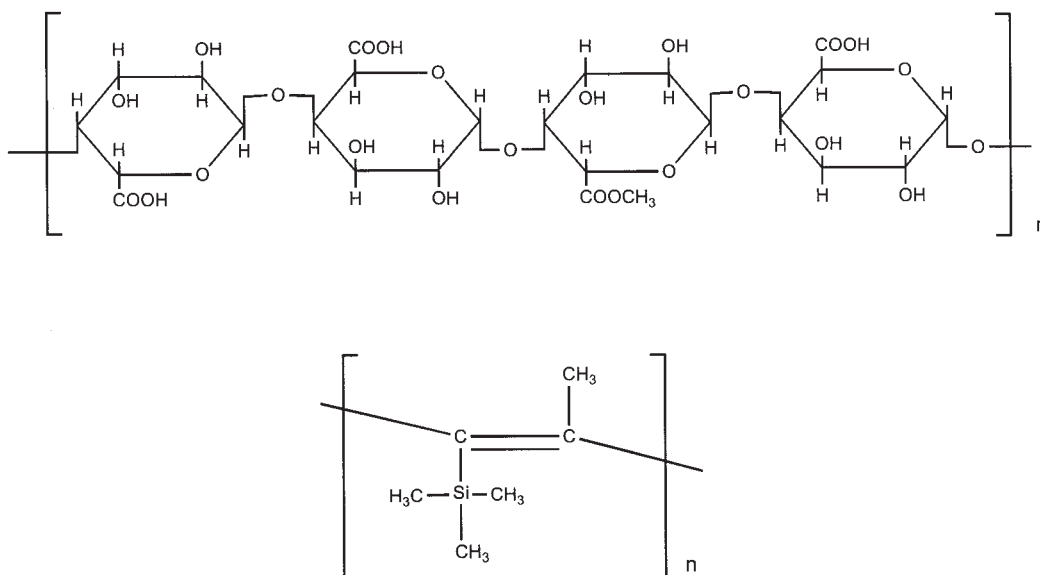


Figure 1 Structures of pectin and PMSP.

play critical roles in metal reduction and transport.^{21–23} Also, they can act as an electron-transfer agent and have chemical interactions with organic compounds.²⁴ In our previous study,²⁵ pervaporation of a model solution with added humic acid was investigated and the affinity of humic acid to various compounds was clarified. It is interesting to add a substance that has an affinity for various compounds to a membrane material. Pectin, added to a membrane, has been studied as a biodegradable natural polymer, environmentally friendly material that has an affinity for humic acid. The poly(1-trimethylsilyl-1-propyne) (PMSP) membrane is hydrophobic and has the highest permeability of all polymeric membranes.²⁶ Therefore, this polymer is expected to have potential utility in industrial applications. In this study, humic acid was added to a natural polymer, a pectin membrane, and a hydrophobic PMSP membrane to enhance the affinity for phenol or aniline. Also, the separation performance, based on the membrane materials and methods of addition, was investigated.

EXPERIMENTAL

Materials

Pectin (Wako Pure Chemical Industries, Osaka, Japan) and the polytetrafluoroethylene (PTFE) filter sheet (Fluoropore[®], FP-060, pore size 0.6 μm , 90 μm thickness; Sumitomo Electric Industries, Tokyo, Japan) were used as received throughout this study. Poly(1-trimethylsilyl-1-propyne) (PMSP; Shin-Etsu Chemical Co., Tokyo, Japan) was also used throughout this study. The pectin and PMSP structures are shown in Figure 1. Humic acid and sodium salt (technical; 50–

60% as humic acid; Acros Organics, Morris Plains, NJ) were used. Phenol and aniline (special grade; Kanto Chemical Co., Tokyo, Japan) were used. An Ultra filter centrifugal filter device (Ultrafree-15[®], 10,000 NMWL; Millipore Corp., Milford, MA) was used.

Membrane preparation

Three kinds of pectin membranes and three kinds of PMSP membranes were prepared. The membrane preparation method is outlined in Figure 2. The pectin was dissolved in water to 10 g/L and poured onto a PTFE filter sheet. The pectin and humic acid were dissolved in water to 10 and 0.5 g/L, respectively, then poured onto a PTFE filter sheet. The pectin was dissolved in water to 10 g/L and poured onto a PTFE filter sheet, and after the membrane dried, the humic acid dissolved in water to 0.5 g/L was poured onto it.

The PMSP was purified by the solution precipitation method using a toluene–methanol solution. The purified PMSP was dissolved in toluene to 10 g/L and poured onto a PTFE filter sheet. The PMSP, dissolved in toluene to 10 g/L, and the humic acid (the weight ratio to PMSP was 5 wt %) were mixed, and then poured onto a PTFE filter sheet. The PMSP was dissolved in toluene to 10 g/L and poured onto a PTFE filter sheet and after the membrane dried, the humic acid dissolved in water to 0.5 g/L was poured onto it.

The cast solution was dried under natural conditions to form a membrane, and then dried in a 40°C oven for 24 h. The obtained membranes were covered by PTFE filter sheets. The thickness of the membranes used in this study was around 220 μm .

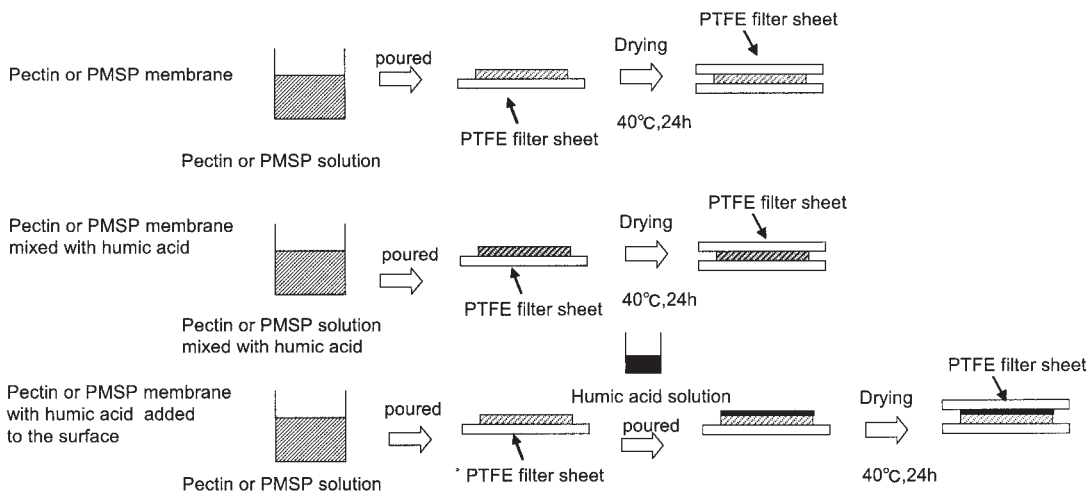


Figure 2 Method of membrane preparation.

Adsorption measurement

To determine the interaction between the permeates and the membrane, the adsorption of phenol and aniline into humic acid was investigated. The humic acid was added to the phenol or aniline/water solution in which the humic acid concentration was 25 mg/L. The solution was then adjusted to around pH 5.6. After 2 h, the solution was filtered through the Ultra filter. The solute concentration in the filtered solution was determined by liquid chromatography using a UV detector (UV-HPLC). The degree of adsorption of the phenol or aniline by the humic acid was measured as

$$\text{Degree of adsorption (\%)} = \frac{C_0 - C_1}{C_0} \times 100 \quad (1)$$

where C_0 and C_1 denote the solute concentrations of the solution with no added humic acid and added humic acid, respectively. The humic acid on the Ultra filter was vibrated in methanol by ultrasonic waves and the extracted phenol and aniline were measured.

Pervaporation experiment

The pervaporation experiments were performed as in a previous study¹⁰ at 40°C, as shown in Figure 3. The feed solution was introduced and stirred in the cell by a magnetic stirring bar. The feed solution flowed in one direction through the cell. The effective membrane area in the cell was 19.6 cm². The pressure on the permeation side was maintained below 10 Torr by

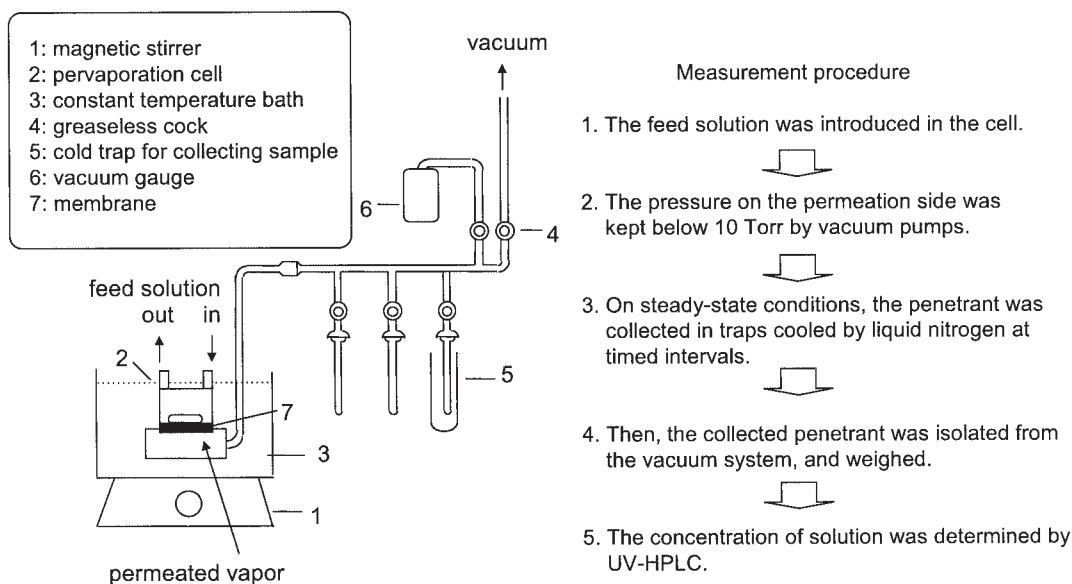


Figure 3 Apparatus and flow diagram of the pervaporation measurement.

TABLE I
Adsorption Data of Phenol and Aniline into Humic Acid^a

Concentration (mg/L)	Adsorption rate (%)		Desorption rate (%)	
	Phenol	Aniline	Phenol	Aniline
2	16	65	78	76
5	56	79	91	81

^a pH 5.6 solution.

vacuum pumps. Upon reaching a steady-state condition, the penetrant was collected in traps cooled by liquid nitrogen (-196°C) at timed intervals. The collected penetrant was then isolated from the vacuum system and weighed. The permeation rate of the solution [i.e., the total flux (J)] was obtained using the following equation:

$$J = Q / At \quad (2)$$

where Q is the amount that permeated during the experimental time interval t , and A is the effective surface area. The solute and water flux were calculated from the total flux, which is the permeation rate of the solution (J) and the permeate composition.

The concentrations of solute in the feed and permeate solutions were determined by UV-HPLC. The separation factor during the pervaporation α_{pv} was calculated as

$$\alpha_{pv} = [Y(1 - X)] / [(1 - Y)X] \quad (3)$$

where X and Y denote the concentrations of the solute in the feed and permeate solutions, respectively, and their concentration units are weight percentage (wt %).

RESULTS AND DISCUSSION

Adsorption of solutes into humic acid

The interaction between the permeates and membrane was investigated using the adsorption measurement of phenol and aniline by the humic acid in a pH 5.6 solution. The results of the adsorption and desorption of phenol and aniline by humic acid are shown in Table I. The phenol and aniline were adsorbed by the humic acid in the pH 5.6 solution. The adsorption of the phenol was observed at a low rate ($>16\%$); however, the adsorption of the aniline was observed at a high rate ($>65\%$). The phenol and aniline adsorbed by the humic acid were extracted using methanol and the desorption rate was 76–91%. The interaction between the solute and humic acid was weakened by the solvent, and the solute could be extracted. The dissociation constants of phenol (pK_a) and aniline (pK_b) at

40°C are 9.8 and 9.1, respectively. During the pervaporation, the effluent of the feed solution from the pervaporation cell is around pH 5.6. The degree of dissociation of the phenol and aniline at pH 5.6 are 0.7×10^{-4} and 0.2, respectively. It is postulated that the phenol is not dissociated in the pH 5.6 solution, whereas the aniline is dissociated. Nanny et al.²⁴, using NMR, reported that the adsorption of phenol by humic acid increased with an increase in the hydrophobicity at the lower pH values, and two modes of interaction between the pyridine and humic acid involve binding with the lone pair of electrons on pyridine's nitrogen and a π - π interaction. Haitzer et al.^{27,28} reported that Hg(II) mainly binds to the oxygen and sulfur functional groups of the humic substances.²⁴ It is postulated that the interaction of humic acid and the aniline mainly involved a polar bond. Phenol is considered to interact with humic acid by a weak aromaticity. These sorption and desorption interactions with humic acid have been used for other new techniques such as the sol-gel matrix.²⁹ The sorption performance of humic acid can be used for various techniques.

Pervaporation through the humic acid-added pectin membranes

The effects of the humic acid addition methods on the flux and the separation performance for the phenol or aniline/water mixture during pervaporation through the humic acid-added pectin membranes were investigated. The water and phenol fluxes, as a function of the phenol concentration in the feed solution, are shown in Figure 4 for the humic acid-added pectin

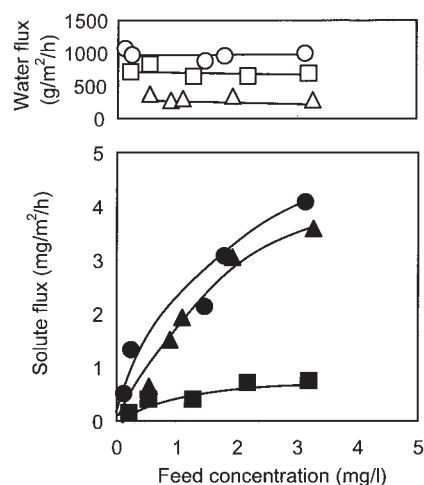


Figure 4 Water and phenol flux as a function of the feed phenol concentration during pervaporation through the humic acid-added pectin membranes: (□) pectin membrane mixed with humic acid; (△) pectin membrane with humic acid added to the surface; (○) pectin membrane, open: water flux; closed: phenol flux.

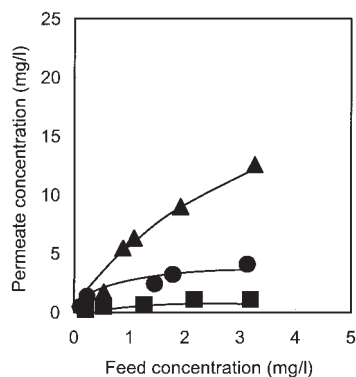


Figure 5 Relationships between the phenol concentration in the feed and permeate during pervaporation through the humic acid-added pectin membranes: (■) pectin membrane mixed with humic acid; (▲) pectin membrane with humic acid added to the surface; (●) pectin membrane.

membranes. The water flux was constant with the feed concentration for the pectin membrane, the pectin membrane with mixed humic acid, and the pectin membrane with humic acid added to the surface. With regard to the humic acid-mixed pectin membrane, the water and phenol fluxes were low compared with those of the pectin membrane. The water and phenol permeations were prevented by the interaction between the pectin and humic acid. Pectin is a polymer with many carboxylic groups. It is thought that because of the hydrogen bond and the polar bond between carboxylic groups, amino groups, and so forth, of the humic acid^{21-24,27,28,30} and pectin, the penetration of a substance was obstructed and the fluxes of water and phenol decreased. With regard to the pectin membrane with humic acid added to the surface, although the flux of water was significantly low compared with that of the pectin membrane, the flux of phenol was almost the same. Because phenol was adsorbed into the colloidal humic acids on the surface of the membrane, the permeation of water was prevented by the adsorbed phenol.

The permeate phenol concentration, as a function of the feed phenol concentration, is shown in Figure 5 for the humic acid-added pectin membranes. Because the penetration of phenol was significantly prevented in the pectin membrane mixed with humic acid, the permeate phenol concentration was lower than that of the feed solution. However, the pectin membrane with humic acids added to the surface had a significantly lower water flux by prevention of the water penetration, as shown in Figure 4. The pectin membrane with humic acids added to the surface had a high permeate phenol concentration.

The water and aniline fluxes, as a function of the aniline concentration in the feed solution, are shown in Figure 6 for the humic acid-added pectin membranes. The water flux was constant with the feed

aniline concentration for the pectin, the pectin membrane mixed with humic acid, and the pectin membrane with humic acid added to the surface. With regard to the pectin mixed with the humic acid membrane, the water and aniline fluxes were relatively low compared with those of the pectin membrane. The water and aniline permeations were prevented by the interaction between the pectin and humic acid. Because of the hydrogen bond and polar bond between the carboxylic groups, amino groups, and so forth, of the humic acid^{21-24,27,28,30} and pectin, the penetration of a substance was obstructed and the fluxes of water and aniline decreased. With regard to the pectin membrane with humic acid added to the surface, although the flux of water was low, the flux of aniline was almost the same compared with that of the pectin membrane. Because the humic acid was in a colloidal state and the aniline was adsorbed onto it, the penetration of water was prevented. The permeate aniline concentration, as a function of the feed aniline concentration, is shown in Figure 7 for the humic acid-added pectin membranes. Because the penetration of water and aniline was prevented, the permeate concentration was at the same level in the pectin membrane with mixed humic acid compared with that in the pectin membrane. However, because of the decrease in water penetration, the pectin membrane with humic acid added to the membrane surface had a high permeate aniline concentration, and the permselectivity was improved; the permselectivity of aniline was higher than that of phenol. The aniline with the lone pair of nitrogen electrons was adsorbed well into the membranes compared with the hydrophobic phenol.

Because humic acid in the pectin membrane could not become colloidlike, the mixed humic acid was not

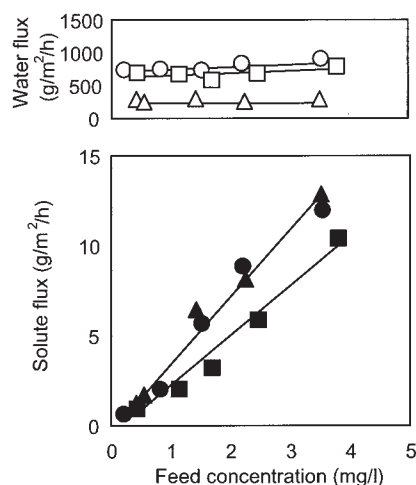


Figure 6 Water and aniline flux as a function of the feed aniline concentration during pervaporation through the humic acid-added pectin membranes: (□) pectin membrane mixed with humic acid; (△) pectin membrane with humic acid added to the surface; (○) pectin membrane, open: water flux; closed: aniline flux.

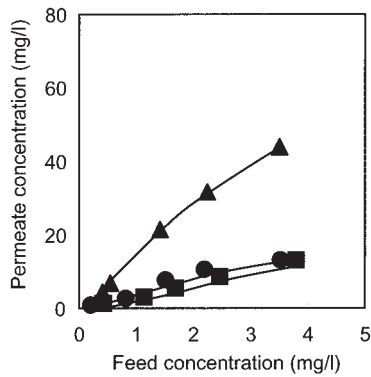


Figure 7 Relationships between the aniline concentration in the feed and permeate during pervaporation through the humic acid-added pectin membranes: (■) pectin membrane mixed with humic acid; (▲) pectin membrane with humic acid added to the surface; (●) pectin membrane.

able to improve the permselectivity for phenol or aniline. However, for the pectin membrane with humic acid added to the surface, the water permeability was prevented and the solute permselectivity was improved.

Pervaporation through the humic acid-added PMSP membranes

The effects of the humic acid addition methods on the flux and separation performance for the phenol or aniline/water mixture during pervaporation through the humic acid-added PMSP membranes were investigated. The water and phenol fluxes, as a function of the phenol concentration in the feed solution, are shown in Figure 8 for the humic acid-added PMSP membranes. The water flux was constant with the feed concentration for the PMSP, the PMSP membrane with mixed humic acid, and the PMSP membrane with humic acid added to the surface. With regard to the humic acid-added PMSP membranes, the water and phenol fluxes were low compared with those of the PMSP membrane. The humic acid in the hydrophobic PMSP was only slightly affected by polar interaction. However, it could be considered that the humic acid near the surface of the PMSP was dissolved in the water and became colloidal. The permeation was prevented by the adsorbed phenol. With regard to the PMSP membrane with humic acid added to the surface, the flux of water was significantly low. Because the humic acid exists in a colloidal state, the permeation of water was prevented by the adsorbed phenol. The permeate phenol concentration, as a function of the feed phenol concentration, is shown in Figure 9 for the humic acid-added PMSP membranes. Because the penetration of water and phenol was prevented, the permeate concentration was the same level in the PMSP membrane with the mixed humic acid

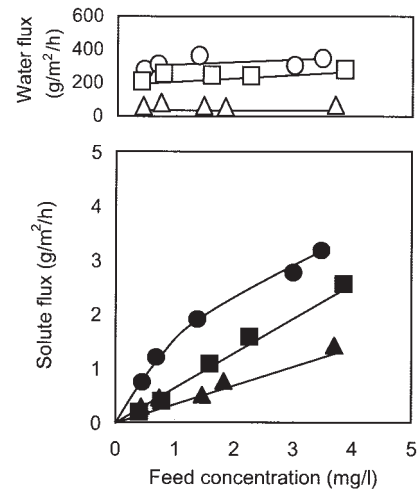


Figure 8 Water and phenol flux as a function of the feed phenol concentration during pervaporation through the humic acid-added PMSP membranes: (□) PMSP membrane mixed with humic acid; (△) PMSP membrane with humic acid added to the surface; (○) PMSP membrane, open: water flux; closed: phenol flux.

compared with that of the PMSP membrane. However, the PMSP membrane with humic acid added to the surface had a high permeate phenol concentration, and the permselectivity was improved by the prevention of water penetration.

The water and aniline fluxes, as a function of the aniline concentration in the feed solution, are shown in Figure 10 for the humic acid-added PMSP membranes. The water flux was constant with the feed aniline concentration for the PMSP membrane, the PMSP membrane mixed with humic acid, and the PMSP membrane with humic acid added to the surface. With regard to the PMSP mixed with the humic acid membrane, the water flux was relatively low and the aniline flux increased compared with those of the

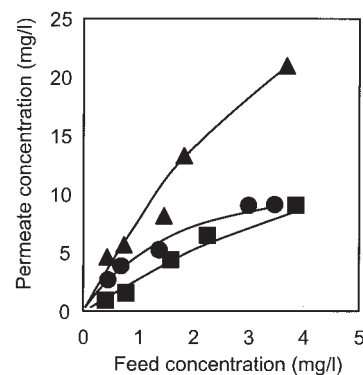


Figure 9 Relationships between the phenol concentration in the feed and permeate during pervaporation through the humic acid-added PMSP membranes: (■) PMSP membrane mixed with humic acid; (▲) PMSP membrane with humic acid added to the surface; (●) PMSP membrane.

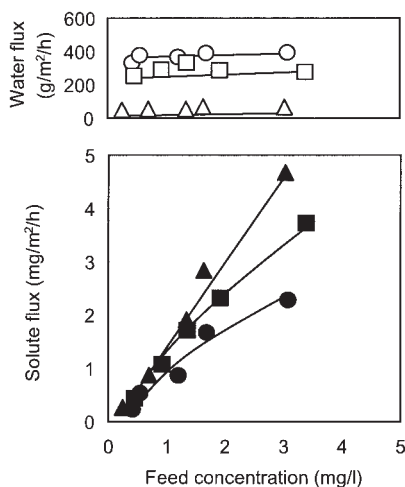


Figure 10 Water and aniline flux as a function of the feed aniline concentration during pervaporation through the humic acid-added PMSP membranes: (□) PMSP membrane mixed with humic acid; (△) PMSP membrane with humic acid added to the surface; (○) PMSP membrane, open: water flux; closed: aniline flux.

PMSP membrane. With regard to the PMSP membrane with humic acid added to the surface, the water flux was low and the aniline flux significantly increased. The affinity of humic acids is high for aniline. We consider that because the humic acid exists in a colloidal state, the adsorption of aniline was high and the affinity of the membrane for aniline improved. Moreover, for that reason, it is thought that the penetration of water was prevented. The permeate aniline concentration, as a function of the feed aniline concentration, is shown in Figure 11 for the humic acid-added PMSP membranes. Because the penetration of aniline increased and the permeability of water decreased, the separation performance of the PMSP membrane mixed with humic acid increased. More-

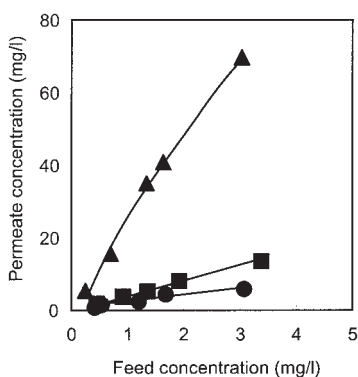


Figure 11 Relationships between the aniline concentration in the feed and permeate during pervaporation through the humic acid-added PMSP membranes: (■) PMSP membrane mixed with humic acid; (▲) PMSP membrane with humic acid added to the surface; (●) PMSP membrane.

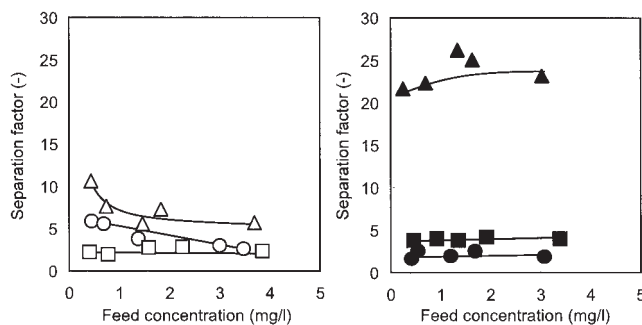


Figure 12 Dependency of the separation factor (α_p) on the feed concentration during pervaporation through the humic acid-added PMSP membranes: (□) PMSP membrane mixed with humic acid; (△) PMSP membrane with humic acid added to the surface; (○) PMSP membrane, open: phenol; closed: aniline.

over, with regard to the PMSP membrane with humic acid added to the surface, the penetration of aniline significantly increased and the permeability of water significantly decreased. The PMSP membrane with humic acid added to the surface had a high permeate aniline concentration, and permselectivity was improved. The permselectivity of aniline was higher than that of phenol. The aniline that has an affinity for humic acid was well adsorbed into the membranes compared with the phenol.

Because humic acid in the PMSP membrane could not become colloidal, the permselectivity for phenol or aniline was not enhanced very much for the PMSP membrane with the mixed humic acid. We consider that because humic acid exists in a colloidal state, the adsorption of aniline was high and the affinity of the membrane for aniline improved for the PMSP membrane with humic acid added to the surface. Therefore, the penetration of water was prevented. The separation factor, as a function of the feed concentration, is shown in Figure 12 for the PMSP membranes with humic acid added to the surface. The separation factor of aniline for the humic acid-added membrane was excellent because of the polar bond between aniline and humic acid. In particular, the permselectivity for aniline by the PMSP membrane with humic acid added to the surface was significantly high.

The change in the separation performance for aniline solution was observed after several cycles of the aniline solution and deionized and distilled water during pervaporation through the most improved membrane, the PMSP membranes with humic acid added to the surface. The flux and separation factor, as a function of the operation time, are shown in Figure 13 for the PMSP membranes with humic acid added to the surface. The total fluxes increased after 200 h of operation. Although the separation factor decreased after 200 h of operation of the aniline solution, it did not decrease until 268 h of operation in deionized and

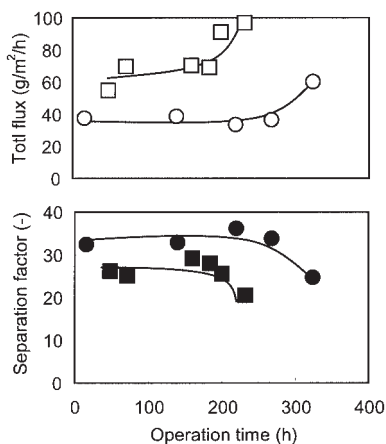


Figure 13 Flux and separation factor (α_p) as a function of the operation time during pervaporation through the PMSP membrane with humic acid added to the surface: (□) after operation of aniline solution; (○) after operation of deionized and distilled water, open: total flux; closed: separation factor.

distilled water. During the membrane preparation, the cast solution was dried under natural conditions to produce a membrane, and then dried in a 40°C oven for 24 h. The separation efficiency decreased as a result of a fouling effect rather than by an ageing effect. The appropriate operating conditions would keep the separation efficiency independent of the fouling.

CONCLUSION

In this study, humic acid was added to a natural polymer, a pectin membrane, and a hydrophobic PMSP membrane to enhance the affinity for phenol or aniline. Also, the separation performance, based on the membrane materials and methods of addition, was investigated.

The effect of the adsorption of phenol and aniline by humic acid was investigated, and a high aniline adsorption rate was observed. It is postulated that the interaction of humic acids and the aniline is mainly observed by polar bonding.

For the separation performance of the pectin membrane with mixed humic acid, because the penetration of a substance was prevented by a hydrogen bond and a polar bond between the pectin and humic acid, the fluxes of water, phenol, and aniline decreased. With regard to the pectin membrane with humic acid added to the surface, because the humic acid was in a colloidal state and the phenol and aniline were adsorbed onto it, the penetration of water was prevented. The humic acid in the hydrophobic PMSP was not significantly affected by a polar interaction. Because humic acid in the PMSP membrane could not become colloidal,

the permselectivity for phenol or aniline was not significantly enhanced. With regard to the PMSP membrane with humic acid added to the surface, because the humic acid exists in a colloidal state, the permeation of water was prevented by the adsorbed solute. Moreover, because the permselectivity of aniline increased and the penetration of water significantly decreased, the PMSP membrane with humic acid added to the surface had a high permeate aniline concentration, and the permselectivity was improved.

References

1. The Merck Index, English ed.; Merck & Co. Inc.: Rahway, NJ, 1968.
2. Hoshi, M.; Ieshige, M.; Saitoh, T.; Nakagawa, T.; J Appl Polym Sci 1999, 71, 439.
3. Hoshi, M.; Kogure, M.; Saitoh, T.; Nakagawa, T. J Appl Polym Sci 1997, 65, 469.
4. Matsutani, M. Regulation and Treatment of Environmental Water and Waste Water; IPC Ltd.: Tokyo, 1994 (in Japanese).
5. Yamahara, S.; Nakao, S.; Membrane 1993, 18, 69.
6. Yoshikawa, M.; Masaki, K.; Ishikawa, M. J Membr Sci 2002, 205, 293.
7. Yoshikawa, M.; Yoshioka, T.; Fujime, J.; Murakami, A. J Appl Polym Sci 2002, 86, 3408.
8. Aminabhavi, T. M.; Naik, H. G.; J Appl Polym Sci 2002, 83, 273.
9. Aminabhavi, T. M.; Naik, H. G. J Appl Polym Sci 2002, 83, 244.
10. Yamaguti, T.; Suzuki, T.; Kai, T.; Nakao, S. J Membr Sci 2001, 194, 217.
11. Toti, U. S.; Kariduraganavar, M. Y.; Soppimath, K. S. J Appl Polym Sci 2002, 83, 25.
12. Mishima, S.; Nakagawa, T. J Appl Polym Sci 2000, 75, 773.
13. Park, C. H.; Nam, S. Y.; Lee, Y. M. J Appl Polym Sci 1999, 74, 83.
14. Yeom, C. K.; Kim, H. K.; Rhim, J. W. J Appl Polym Sci 1999, 73, 601.
15. Sun, Y.; Lin, C.; Chen, Y. J Membr Sci 1997, 134, 117.
16. Fang, Y.; Pham, V. A.; Matuura, T.; Santerre, J. P.; Narbaitz, R. M. J Appl Polym Sci 1937 1994, 54.
17. Dotremont, C.; Brabants, B.; Geeroms, K.; Mewis, J.; Vandecasteele, C. J Membr Sci 1995, 104, 109.
18. Schauer, J. J Appl Polym Sci 1994, 53, 425.
19. Goethaert, S.; Dotremont, C.; Kuijpers, M.; Michels, M.; Vandecasteele, C. J Membr Sci 1993, 78, 135.
20. Yamada, M.; Kato, K.; Nomisu, M.; Ohkawa, K.; Yamamoto, H.; Nishi, N. Environ Sci Technol 2002, 36, 949.
21. Kujawinski, E. B.; Hatcher, P. G.; Freitas, M. A. Anal Chem 2002, 74, 413.
22. Scott, M. J.; Jones, M. N.; Woof, C.; Simon, B.; Tipping, E. Environ Int 2001, 27, 449.
23. Yamada, E.; Doi, K.; Okano, K.; Fuse, Y. Anal Sci 2000, 16, 125.
24. Nanny, M. A.; Maza, J. P. Environ Sci Technol 2001, 35, 379.
25. S.; Mishima, T. Nakagawa, J Membr Sci 2004, 228, 1.
26. Nakagawa, T. Membrane 1995, 20, 156.
27. Haitzer, M.; Aiken, G. R.; Ryan, J. N. Environ Sci Technol 2003, 37, 2436.
28. Haitzer, M.; Aiken, G. R.; Ryan, J. N. Environ Sci Technol 2002, 36, 3564.
29. Laor, Y.; Zolkov, C.; Armon, R. Environ Sci Technol 2002, 36, 1054.
30. Diallo, M. S.; Simpson, A.; Gassman, P.; Faulon, J. L.; Johnson, J. H., Jr.; Goddard, W. A., III; Hatcher, P. G. Environ Sci Technol 2003, 37, 1783.