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Dehydration of aqueous pyridine solution through crosslinked chitosan membrane

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SUMMARY

The present study investigates the pervaporation performance of crosslinked chitosan membrane for the dehydration of aqueous pyridine solution. The control of the degree of crosslinking contributes to an improved pervaporation performance of chitosan membranes. The chitosan membrane crosslinked with 4.515 x 10^{-4} (mol/g polymer) glutaraldehyde solution shows the separation factor of 510 and the flux of 140g/m^2hr measured with 93wt% aqueous pyridine solution at 25°C.

INTRODUCTION

Chitosan is the deacetylated product of the alkali treatment of chitin. Chitin is one of the most abundant organic materials which can be easily available in nature. Chitin is insoluble in organic solvents, but chitosan is readily soluble in the dilute aqueous solution of inorganic acids, formic acid, acetic acid, and so on. Chitosan, however, is stable in a basic environment. It is quite useful for industrial and biomedical applications. In recent years, basic and applied researches on the effective applications of chitosan and its derivatives have been actively conducted. Examples are the adsorption of heavy metal ions(1), artificial skin substitutes(2), and functional membranes for dialysis(3), reverse osmosis(4) and pervaporation(5-6).

Pyridine is important solvent in chemical industries. It is miscible with water over the entire composition and the mixture forms an azeotropic system in the compostion of 0.57 weight fraction of pyridine. The dehydration of pyridine aqueous solution is difficult at an azeotropic composition and requires strong drying chemicals. Pervaporation is very effective separation method for azeotropic mixture and is known to be energy-saving processes. Several researchers have been reported about the separation of pyridine aqueous solution(7-11).

In this study, crosslinked chitosan membrane was used for the dehydration of pyridine aqueous solution, since it is highly insoluble in pyridine and very hydrophilic.

EXPERIMENTAL

Materials

Chitosan(Tokyo Kasei Org. Chem., Japan) was used after treatment with 200 mesh sieve.

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Acetic acid, ethanol, pyridine and 25% glutaraldehyde were purchased from Junsei Chem.(Japan) and used without further treatment.

Membrane preparation

2 grams of chitosan, whose degree of deactylation was calculated to be 76% from the amino content, was dissolved in 200 ml of 2wt% aqueous acetic acid solution at room temperature with stirring. The chitosan solution was filtered to remove dirts and undissolved chitosan. The chitosan solution was cast onto an acryl plate and dried at 40°C in a drying oven for a day. The chitosan membrane was immersed into 1N NaOH solution for a day and washed repeatedly with distilled water.

For manufacturing a crosslinked chitosan membrane, the chitosan solution containing the known amount of glutaradehyde(see Table 1) was used.

Table 1. The amount of glutaraldehyde solution to manufacture the crosslinked chitosan membrane

sample	The amount of glutaraldehyde solution [mol / g polymer]
x-chitosan-1	4.515×10^{-5}
x-chitosan-2	9.030×10^{-5}
x-chitosan-3	4.515×10^{-4}

Degree of swelling

Chitosan and crosslinked chitosan membrane samples were dipped into test tubes filled with pyridine/water mixures by weight. The degree of swelling was determined after the test tubes were placed in an incubator kept at 25°C for two days using the following equation,

$$\text{Degree of swelling}(\%) = \frac{W_w - W_d}{W_d} \quad (1)$$

where W_w and W_d represent the weights of the membrane in wet and dry states, respectively.

Pervaporation experiment

The equipment and procedures used to conduct the pervaporation experiments were identical to those described previously by Lee et al.(12). The effective membrane area in contact with liquid was about 25.98m^2. The downstream pressure was maintained at 5 torr.

The separation analysis was carried out by Shimadzu GC-6A equipped with a 3m long column packed with Porapak-Q and with thermal conductivity detector. Separation factor(α) and permeate flux(J) are defined as follows.

$$\alpha = \frac{Y_w / Y_p}{X_w / X_p} \quad (2)$$

$$J = \frac{Q}{A \times t} \quad (3)$$

where Y_i is the weight fraction in permeate and X_i is that in feed. w and p denote water and pyridine, respectively. Q, A and t represent the weight of permeant(g), effective membrane area(m^2) and operating time(hr), respectively.

RESULTS AND DISCUSSION

We have studied on the application of chitosan and its modified membranes in the dehydration of aqueous ethanol solution through pervaporation and aquired excellent dehydration results due to its considerable water selectivity(6, 13-15). Chitosan is only soluble in acidic solution while it is quite stable in bases. In the present study, since chitosan membrane is hydrophilic and stable in strong base like pyridine, dehydration performance of chitosan membrane was attempted.

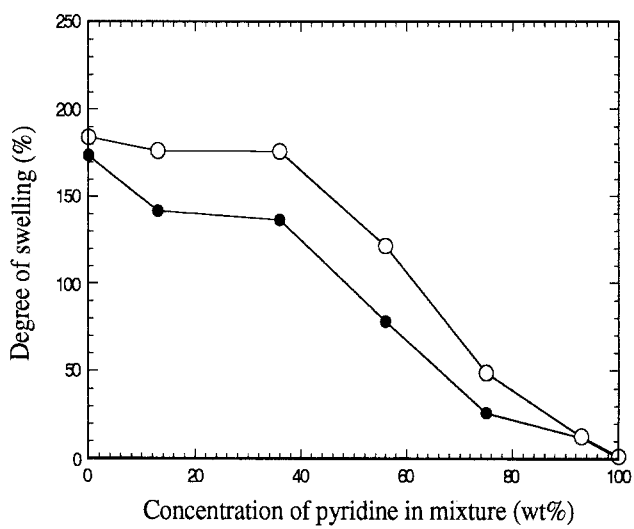

Fig. 1 The results of the degree of swellings of chitosan(○) and crosslinked chitosan(●) membrane.

Fig. 1 shows the results of the degree of swellings of chitosan and x-chitosan-1 membranes. The degree of swelling was comparatively decreased in above 38wt% pyridine concentration in its aqueous solution. The degree of swellings of chitosan membrane in pure water and pyridine were 184.1 and 1.5, respectively. The degree of swelling in pure water is 123 times higher than the that of pure pyridine. Through this result, it was confirmed that chitosan membrane could be applied for the dehydration of pyridine aqueous solution by using pervaporation. However, in pervaporation, an excessive swelling may cause a detrimental effect on selectivity because of the strong effect of absorbed water on the solubility of the organic component(16). Swelling can be reduced through crosslinking. We conducted the crosslinking of chitosan membrane by using glutaraldehyde dilute solution. In Fig. 1, crosslinking restricts swelling of chitosan membrane and therefore the degree of swelling decreased in entire pyridine concentration.

Fig. 2 shows the effect of the concentration of crosslinking agent on the separation factor(α), total flux(J), water flux(J_w) and pyridine flux(J_p) of chitosan membrane measured at 25°C. The concentration of pyridine in feed was 56wt%. While the total flux somewhat decreased, α of chitosan membrane was fairly improved because the crosslinking restricts the swelling of chitosan membrane and the permeation of pyridine. X-chitosan-3 membrane crosslinked with 4.515 x 10^{-4} (mol glutaraldehyde/g polymer) showed the separtion factor of ca. 36 and the J of 831 g/m²hr at 56wt% pyridine solution in the feed.

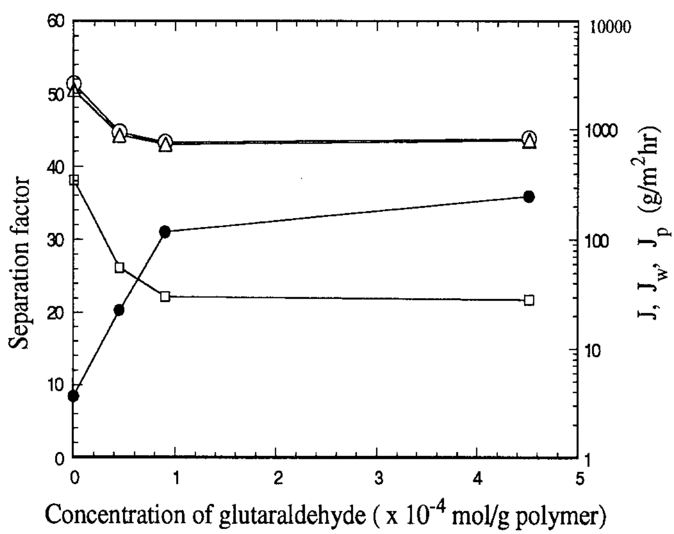

Fig. 2 Effect of the concentration of crosslinking agent on the separation factor(●), J(○), J_w(△) and J_p(□) of chitosan membrane. The operating temperature was 25°C.

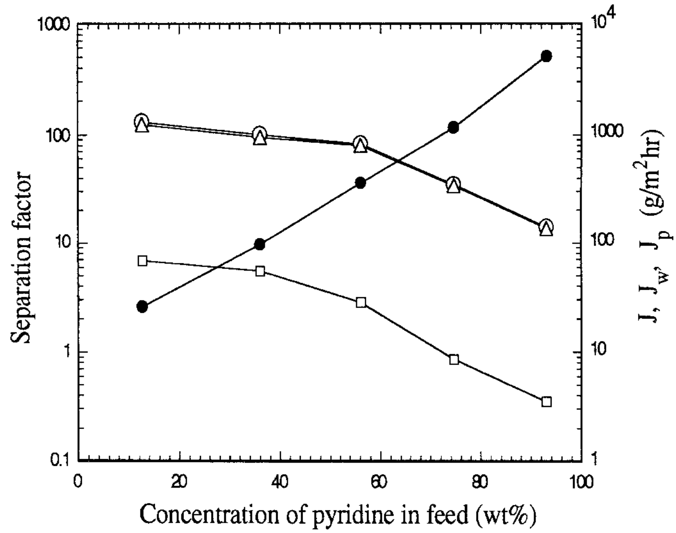

Fig. 3 Effect of the concentration of pyridine in feed on the separation factor(●), J(○), J_w(△) and J_p(□) of crosslinked chitosan membrane. The operating temperature was 25℃ and the membrane thickness was 29 μm.

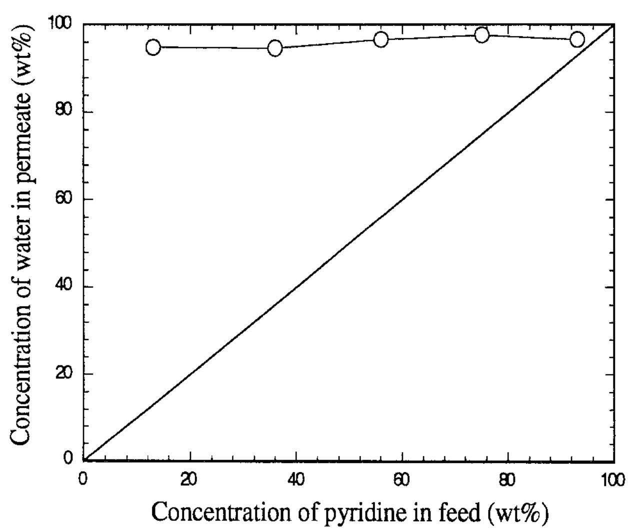

Fig. 4 The X-Y graph of the result of pervaporation through x-chitosan-3 membrane.

Fig. 3 illustrates the effect of the concentration of pyridine in feed on the pervaporation performance through x-chitosan-3 membrane. The J gradually decreased and the α steeply increased because the shrinkage of chitosan membrane occured in higher concentration of pyridine in feed as shown in swelling behavior(see Fig. 1). X-chitosan-3 membrane had the α of 2.6 ~ 508.7 and the J of 139.8 ~ 2342.1 g/m^2hr. In entire concentration of pyridine in feed, the J_W showed similar values with the J and J_W was about 17 ~ 39 times higher than J_P.

Fig. 4 shows the X-Y graph of the result of pervaporation through x-chitosan-3 membrane. In most cases, the concentration of water in permeate ranges above 96wt%. The current crosslinked chitosan membrane turns out to be an efficient dehydration membrane using pyridine as a feed.

CONCLUSION

The degree of swelling of chitosan in pure water is 123 times higher than that of pure pyridine. The separation factor of chitosan membrane was fairly improved by crosslinking. The crosslinking restricted the swelling of chitosan membrane and the permeation of pyridine. In pervaporation result, the J gradually decreased(from 2343 to 140g/m^2hr) against the concentration of pyridine in the feed and the separation factor steeply increased(from 2.6 to 510) because the shrinkage of chitosan membrane occured in higher concentration of pyridine in feed as shown in swelling behavior.

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