

CROSSLINKED CHITOSAN MEMBRANES FOR PERVAPORATION SEPARATION OF ISOPROPANOL-WATER MIXTURES

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ABSTRACT

Pervaporation, a membrane process for separating liquid organic mixtures has been regarded as an energy efficient alternative to conventional separation methods especially when involves the separation beyond the azeotropic point. In the present study, pervaporation membranes were developed from chitosan obtained from chitin using the available shrimp shells. Membranes prepared from chitosan were crosslinked with aluminum nitrate solution. The performances of the membranes were investigated in terms of its permeation flux and separation factor in the separation of isopropanol-water mixtures. The crosslinked chitosan membranes showed better performance than that of the uncrosslinked chitosan membranes at high isopropanol in feed composition showing that chitosan membranes has the potential to be used for the dehydration of isopropanol especially at high isopropanol composition in feed mixtures.

Key Words : Pervaporation, Chitosan, Crosslinked, Separation, Isopropanol-water

1.0 INTRODUCTION

Pervaporation has become popular and more attractive especially in the pervaporation separation of alcohol-water mixtures [1] and it has gained more applications in industry [2]. New polymeric materials have been sought and those containing hydrophilic groups in the polymer structure are preferable for preparing the pervaporation dehydration membranes. Among the hydrophilic polymers, chitosan is thought to be an attractive material for the development of pervaporation membranes and are being studied because it shows high permeation flux with rather good separation factor among hydrophilic materials tested for pervaporation dehydration.

Chitosan is the partially deacetylated form of chitin, which is the second most abundant biopolymer found in nature. Chitosan has both reactive amino and hydroxyl groups that can be used for chemical reactions and salt formations. Hydrophilic groups are responsible for the preferential sorption of water molecules, which leads to high flux and high separation factor. The presence of hydrophilic groups sometimes causes the membrane to swell more significantly and due to its plasticization action results in the low separation factor of the membrane [3]. However, it has been recognized that there is a trade off phenomenon between flux and separation factor. That is, improvement in separation factor will result in the decrease in permeation flux and vice-versa.

Hydrophilic materials on the other hand, suffer from some major drawbacks such as excessive swelling properties which has arouse from the interaction between the hydrogen bonding of the hydrophilic functional groups of the polymer and the water molecules, and the water-soluble properties. Chemical crosslinking is usually the simplest technique that can be used to improve the pervaporation performance of the membrane since the degree of crosslinking and thus hydrophilicity/hydrophobicity can be adjusted conveniently by changing crosslinker concentration or crosslinking time. Through

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crosslinking, the swelling of the polymer can be suppressed and making it less soluble in high water content. Hydrophilic membranes such as PVA and chitosan having high water-permeability but suffer from the low separation efficiency in spite of the high total permeation flux because of excessive swelling action of water. This technique was proven to be very successful since the first commercialized pervaporation membrane was produced by GFT. Crosslinking is a widely used technique to achieve high separation factor with reasonable permeation flux as have been reported by several researchers [4-11].

In the present study, locally produced chitosan membranes were crosslinked using aluminum nitrate aqueous solution. The chitosan membranes were investigated for the pervaporation separation of isopropanol-water mixtures. The performance of pervaporation membranes was studied in terms of its permeation flux and separation factor. Effects of crosslinking time were also investigated in order to fully utilize the potential of chitosan as pervaporation membranes.

2.0 MATERIALS AND METHODS

Chitosan used in this study was derived from chitin that was extracted from locally available shrimp shells. Acetic acid and sodium hydroxide were supplied by Merck (Germany), ethanol by Fluka(M), aluminum nitrate by Aldrich(M) and Isopropanol by J.T.Baker(USA).

2.1 Chitosan Preparation

First, the dried shells were cut into pieces to about 2-6 mm in size. Then the shells were treated using 2-3 M aqueous solution of sodium hydroxide (NaOH) for protein removal. The treatment was carried out at 80-90°C for 2 hours. After washing with distilled water, the shrimp shells were subsequently treated in 2M hydrochloric acid (HCL) aqueous solution for 24 hours to produce chitin. The chitin was then washed with distilled water and dried under the sun. Chitin thus obtained were further treated with 50% NaOH solution at a temperature of 90-110°C for 3 hours to produce chitosan. Finally, chitosan flakes were washed with distilled and deionized water, dried under the sun for three hours and was further dried at room temperature.

The cast solution was prepared by dissolving chitosan flakes in acetic acid aqueous solution (10 wt %). The concentration of chitosan in the cast solution was controlled at 2.0 wt %. After the chitosan flakes was fully dissolved, the cast solution was filtered to remove impurities and undissolved chitosan to give a clear homogeneous casting solution. The petri dish used was washed carefully with distilled water and ethanol (50 wt %) and dried at room temperature. The resulting casting solution was poured onto a petri dish, allowing the casting solvent to evaporate for 48 hours at room temperature. The formed membrane was peeled off from the plate before being immersed in a coagulation bath containing 3 wt% NaOH, 47 wt% ethanol and 50 wt% water for 24 hours at room temperature, then washed thoroughly with deionized water to remove NaOH and finally was air-dried at room temperature.

2.2 Preparation of Crosslinked Chitosan Membranes

The solution technique was used in the preparation of the crosslinked membranes. Aluminium nitrate ($\text{Al}(\text{NO})_3 \cdot 9\text{H}_2\text{O}$) was used as a crosslinking agent in this study. A

crosslinking solution was prepared at 0.01 wt% of aluminum nitrate. When the crosslinking agent solution was ready, chitosan membranes were immersed in the respective crosslinking bath. The crosslinking time were varied from 5 to 30 minutes for crosslinking with aluminum nitrate solution.

The pervaporation performance of chitosan membranes were investigated for the separation of isopropanol-water mixtures with an effective membrane cell area of 52 cm² that was supported by a sintered stainless steel. The permeate pressure was maintained about 3-5 mmHg by a vacuum pump. The isopropanol solution was stirred well during experiments. Permeates were condensed in a cold trap using liquid nitrogen. The weight of permeates collected in the cold trap was measured using a digital electronic balance and the permeate composition was analyzed by a Kalfisher titration equipment to determine the permeation flux and the separation factor.

The separation factor of the membrane is determined as:

$$\alpha_{A/B} = \frac{y_A / y_B}{x_A / x_B} = \frac{y(1-x)}{x(1-y)} \quad (1)$$

where, y_A and y_B are the weight fractions of components A and B in permeate while, x_A and x_B are the weight fraction of components A and B in feed.

The pervaporation separation index (PSI) is used to evaluate the overall pervaporation membrane. It is defined as the product of permeation flux and separation factor as:

$$PSI = J(\alpha - 1) \quad (2)$$

3.0 RESULTS AND DISCUSSION

Figure 1 shows the effect of crosslinking time on permeation flux for isopropanol weight percent in the feed solution ranging from 50 wt% to 95 wt%. It can be seen that permeation flux of the crosslinked membranes are well below the permeation flux of the uncrosslinked chitosan membranes (0 min) over the entire feed composition.

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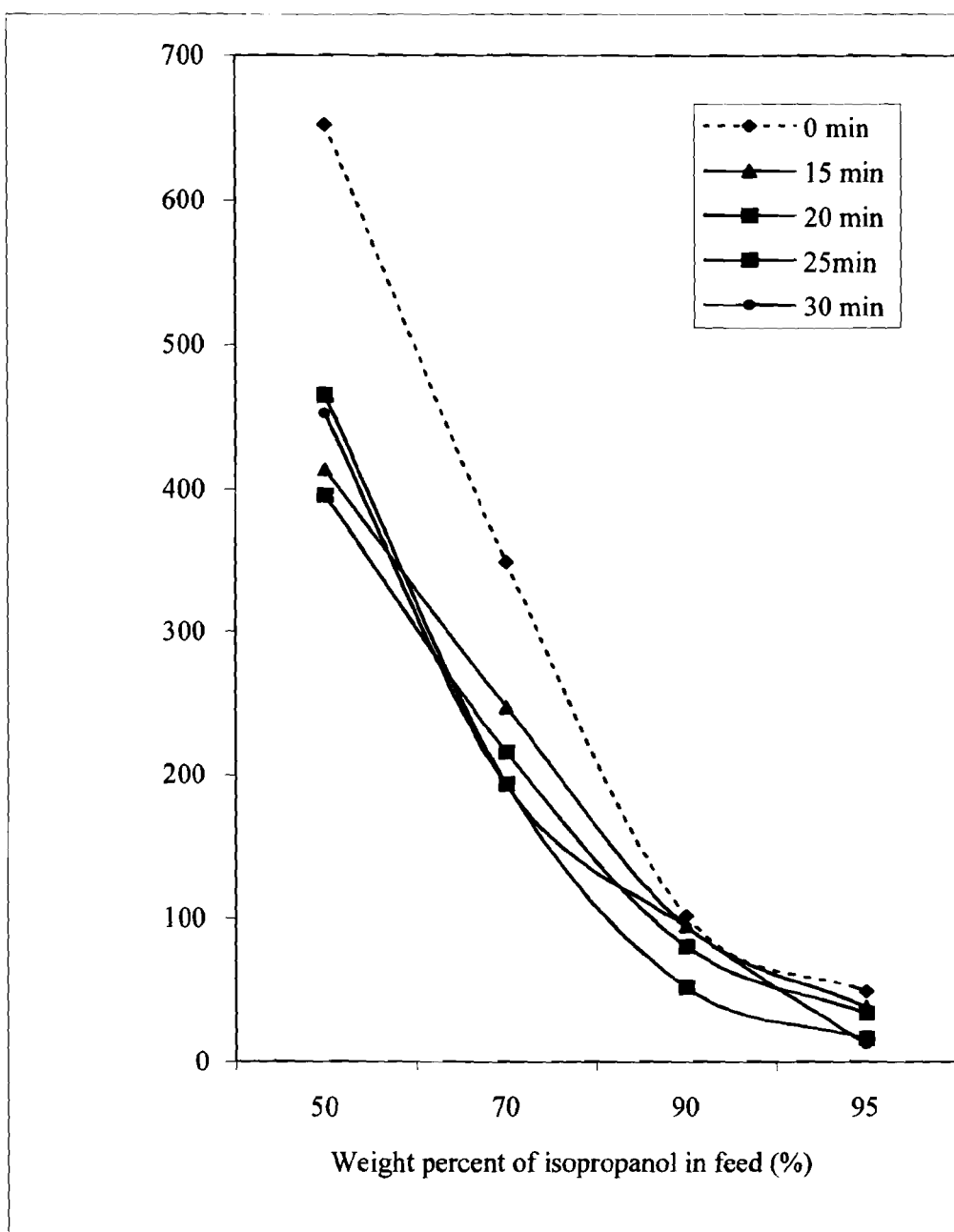


Figure 1 The total permeation flux of membrane for various crosslinking time versus weight percent of isopropanol in the feed.

The change of permeation flux with crosslinking time can be explained in the following way: once the crosslinking took place, the crosslinking density would increase with time to make the zone more compact and rigid so that the transport and reaction crosslinking agent molecules could be more controlled by the diffusion through it. Higher crosslinking degree, the resulting membrane has a more compact network structure and less chain mobility, which makes the solubility and diffusivity of the permeant molecules to decrease. It is found that the solubility of the liquid in the crosslinked membranes decrease due to the formation of more compact structure in the membrane.

Figure 2 shows the effect of crosslinking time on the permeation flux at various isopropanol weight fraction in the feed solution. The permeation flux of membrane decreases with increasing crosslinking time from 0 to 15 minutes. However the difference in permeation flux cannot be seen at high isopropanol weight fraction in feed solution since the permeation flux of the crosslinked and the uncrosslinked differs not so much. It is clear that for the entire feed concentration, the permeation flux of the membrane is almost consistent with increasing crosslinking time from 20 to 30 minutes. It means that the crosslinking reaction is completed at 20-minute crosslinking time.

Figure 3 shows the effect of crosslinking time on separation factors for pervaporation of isopropanol-water mixtures in the range of 50 wt% to 95 wt% of isopropanol weight percent in the feed solution. It can be seen that separation factor show a maximum at 90 wt% of isopropanol in feed solution. The crosslinking degree increases with time resulting in increase of the hydrophilicity of the membrane while the membranes become denser. It can be observed that the separation factor has a maximum at 20 minutes crosslinking time, while the permeation flux decreases with increasing degree of crosslinking. The pervaporation behaviour can be explained by the structure of the crosslinking membrane. That is, as the membrane separation process is mainly occurred in the amorphous region of the membrane according to the conventional solution-diffusion mechanism, the presence of crosslinking causes in the reduction of amorphous region due to the formation of crystallites in the membrane structure. The permeation flux will decrease as the crosslinked membrane becomes less hydrophilic. It is also speculated that the subsequent decrease in the separation factor may resulted from inorganic particles and defects in the membrane matrix. The structure of membrane become looser with the increase in crosslinking time and this allows more isopropanol molecules to penetrate through membrane.

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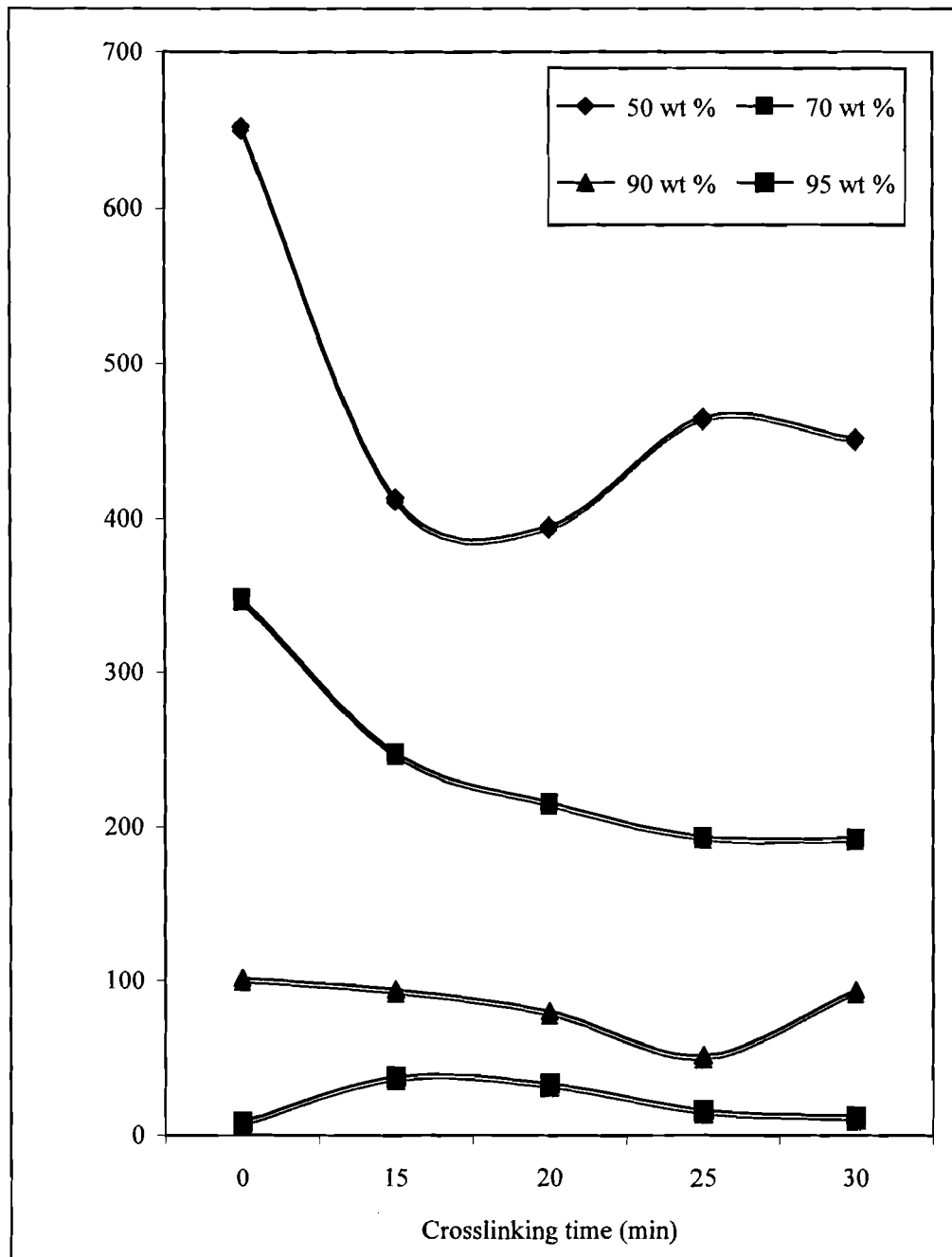


Figure 2 The total permeation flux versus crosslinking time at various weight per isopropanol in feed solution.

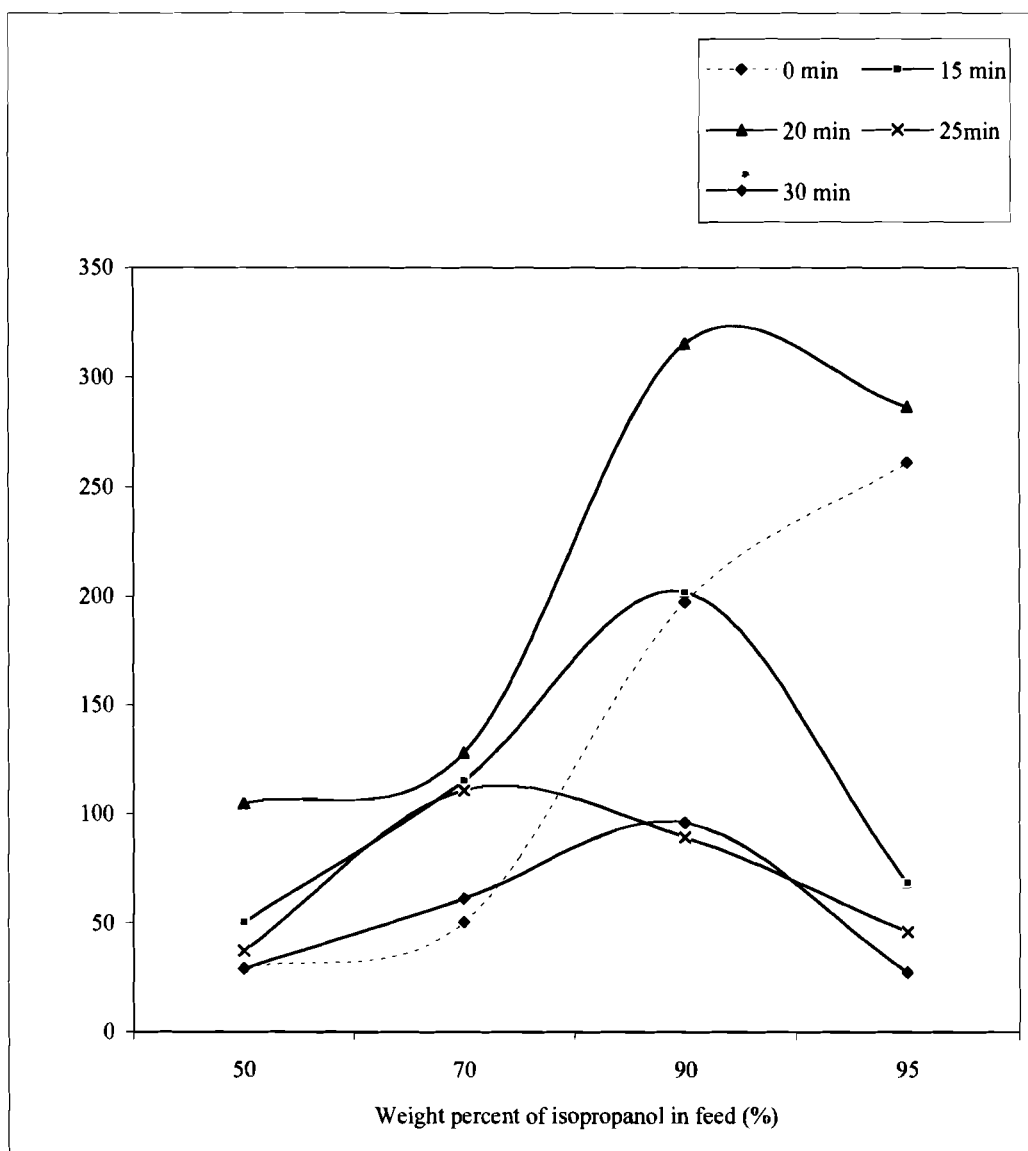


Figure 3 Separation factor of the crosslinked membrane versus weight percent of isopropanol in the feed.

Table 1 shows the pervaporation separation index (PSI) of isopropanol-water mixture at 90 wt% isopropanol in feed for crosslinking time ranging from 15 to 30 minutes. It shows that the 20-minute crosslinking time gives the highest value of PSI. PSI indicates the overall performance of the membrane when there exist a trade-off relationship between permeation flux and separation factor i.e. increasing of permeation flux is followed by a decrease of separation factor and vice-versa. So, the 20-minute crosslinking time is chosen for further investigation of pervaporation performance for the separation of isopropanol-water mixtures.

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Table 1 Pervaporation separation index (PSI) at 90 wt% of isopropanol in the feed for crosslinking time ranging from 15 to 30 minutes of crosslinking time.

Crosslinking Time (min)	Permeation flux (g/m².hr)	Separation Factor	Pervaporation Separation index (PSI)
15	94.4	201.9	18964
20	80.1	315.4	25183
25	51.7	89.4	4570
30	93.9	96	8920

Figure 4 shows the effect of isopropanol concentration in the feed on the permeation flux and separation factor for the 20-minute crosslinking time membrane. Within the investigated range of concentration, the separation factor shows an increasing trend with increasing permeation flux. It attained the highest separation factor at 90 wt% of isopropanol in the feed showing that the membrane has the potential to be used for separation within the azeotropic region of mixture between isopropanol and water.

By comparison, the crosslinked membranes show a higher separation factor but a lower permeation flux than the uncrosslinked membranes for the entire feed composition. In order to compare the performance between the modified and the unmodified membranes, the pervaporation separation index (PSI) was used. The PSI for both membranes is plotted as a function of isopropanol concentration in the feed solution as shown in Figure 5. Membranes with crosslinked structure show a higher PSI value up to 90 wt% isopropanol in the feed. The higher value of PSI was attributed to the increase in separation factor of the crosslinked membranes as compared to the uncrosslinked membranes since the PSI value is a product between the permeation flux and the separation factor. However, the PSI value of the crosslinked membrane was slightly decreased at 95 wt% of isopropanol concentration due to the decrease in the permeation flux and the separation factor.

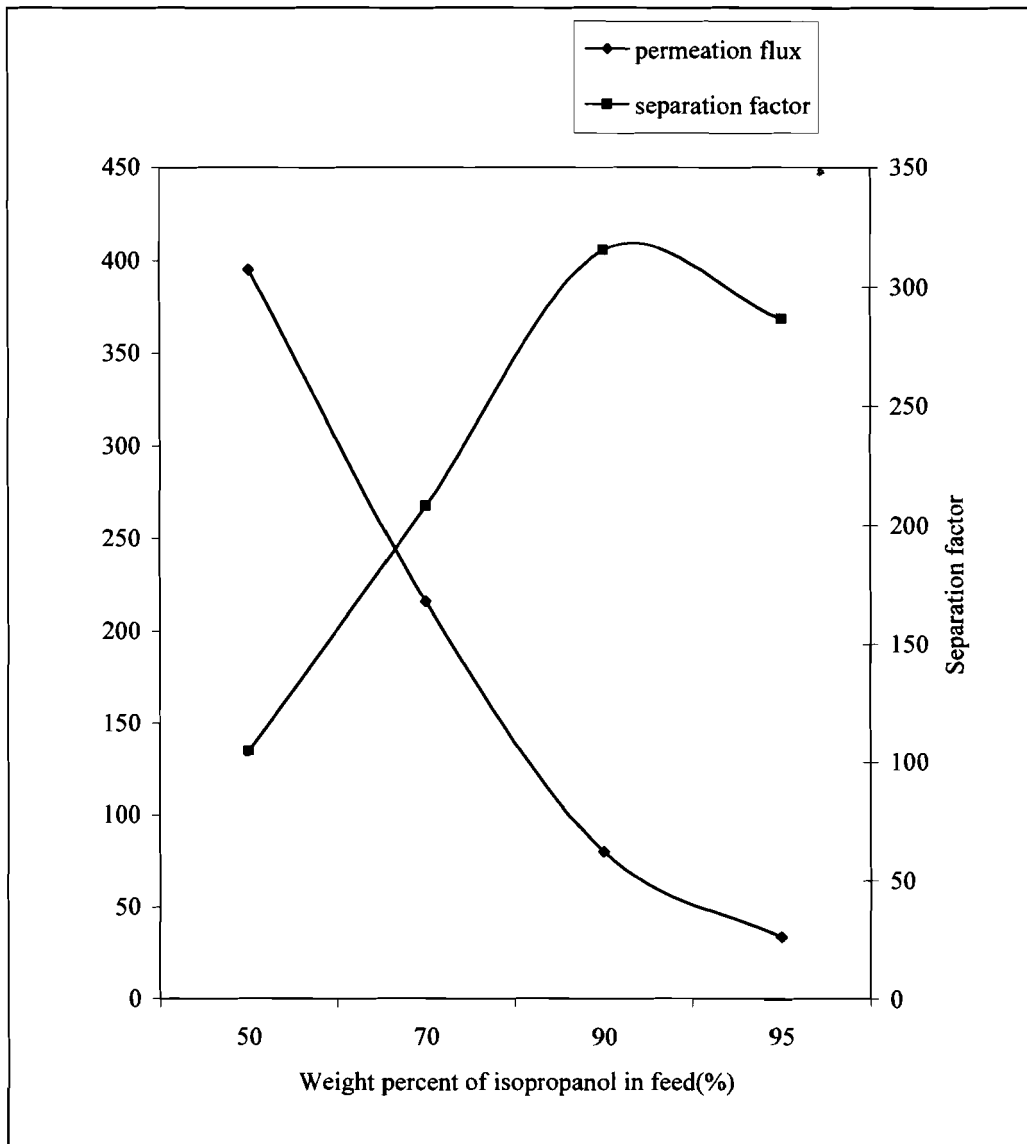


Figure 4 Relationship between permeation flux and separation factor for a 20-minute crosslinked membrane at 90 wt% of isopropanol in the feed.

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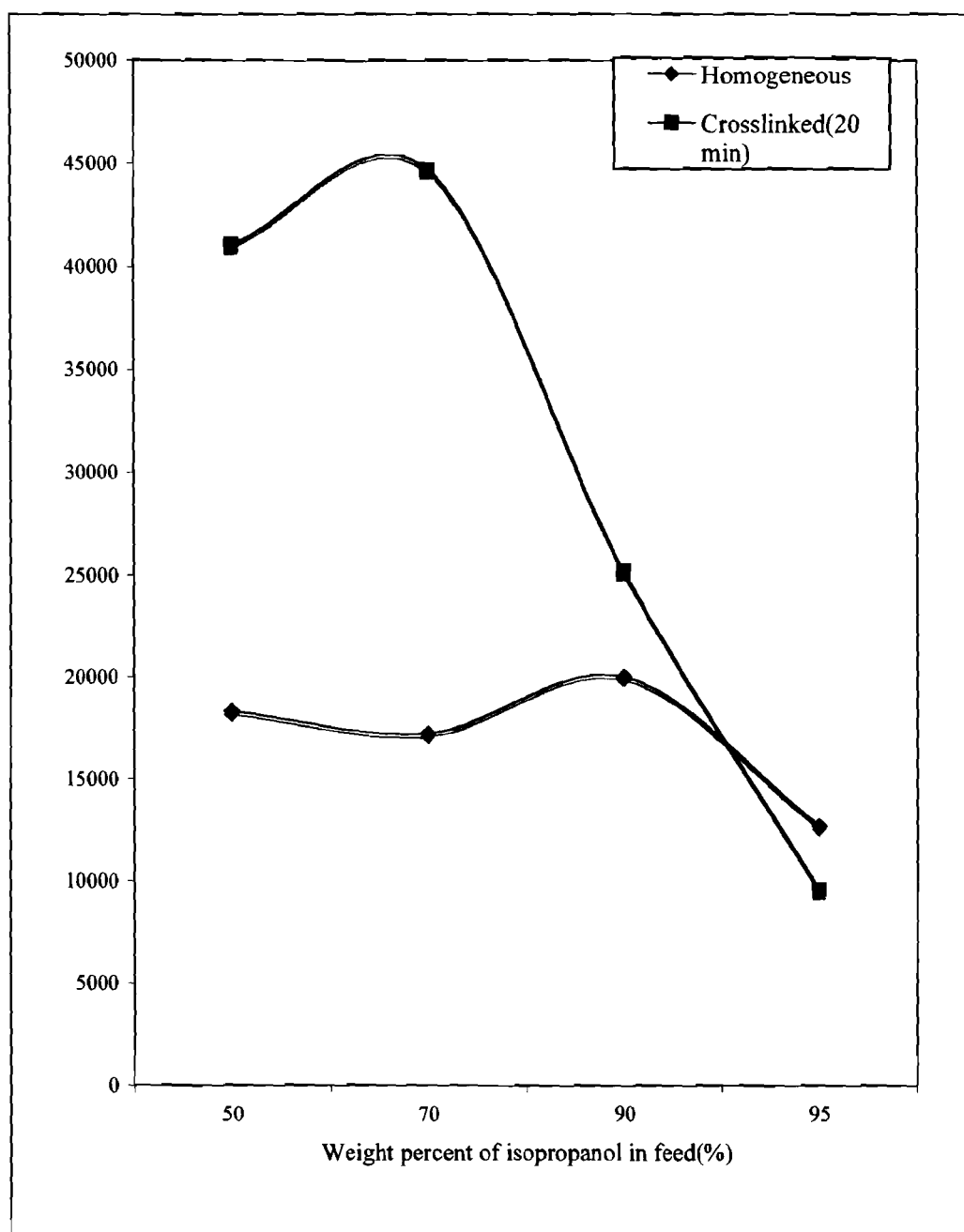


Figure 5 Pervaporation separation index (PSI) of the uncrosslinked and crosslinked membranes versus isopropanol weight percent in the feed.

4.0 CONCLUSIONS

Homogeneous chitosan membranes and crosslinked-chitosan were prepared in this study and were investigated for the pervaporation separation of isopropanol-water mixtures. The following conclusions can be drawn from this study. Membrane crosslinked with aluminum nitrate (20 minute crosslinking time) shows the highest separation factor and was chosen for further investigation. Membranes crosslinked with aluminum nitrate, however show promising results especially at higher isopropanol concentrations in the feed in the range of 70 wt% up to 90 wt%. The result shows that

chitosan membranes crosslinked with aluminum nitrate solution has the potential to be used for the pervaporation separation of isopropanol-water systems at high isopropanol compositions in feed solution (beyond the azeotropic point).

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