

## CHITOSAN AS A MEMBRANE MATERIAL FOR PERVAPORATION SEPARATION OF ISOPROPANOL-WATER MIXTURES

HASHIM HASSAN<sup>1\*</sup> & MOHD GHAZALI MOHD NAWAWI<sup>2</sup>

**Abstract.** Chitosan based pervaporation membranes were prepared from locally available shrimp shells using various chemical treatments. The dried shrimp shells were first grinded and treated with sodium hydroxide aqueous solution and then followed by treating with hydrochloric acid solution to remove the calcium content before chitin is produced. The chitosan membranes were prepared by dissolving a pre-weighed quantity of chitosan into acetic acid solutions. Membranes characteristics and its performance were studied for the pervaporation separation of isopropanol-water mixtures. The homogeneous chitosan membranes showed preferential water sorption and permeation. Results show that the total permeation flux for the homogeneous chitosan membrane decreases while separation increases as the feed isopropanol concentration increases from 10 to 95 wt%. Based on the present study, it is found that the chitosan membranes produced from domestic shrimp shells could be used as the raw material for the production of high water selective membranes.

*Keywords:* Chitosan; membrane; pervaporation; isopropanol-water mixtures

**Abstrak.** Membran pervaporasi yang berasaskan kitosan telah disediakan daripada kulit udang tempatan dengan menggunakan pelbagai kaedah rawatan kimia. Kulit udang kering pada mulanya dikisar dan dirawat dengan larutan akuas sodium hidroksida dan diikuti dengan merawatnya dengan larutan asid hidroklorik bagi mengeluarkan kandungan kalsium sebelum kitin dapat dihasilkan. Membran kitosan dihasilkan dengan melarutkan kuantiti tertentu kitosan ke dalam larutan asid asetik dengan diikuti menuangkannya ke dalam mangkuk petri. Sifat-sifat membran dan prestasinya dikaji dalam pemisahan pervaporasi bagi campuran air-isopropanol. Membran kitosan homogen telah menunjukkan sifat lebih menyerap dan lebih menelap air. Keputusan menunjukkan jumlah fluks tetelap bagi membran kitosan homogen menurun manakala faktor pemisahan pula meningkat dengan peningkatan komposisi isopropanol dari 10 ke 95% berat. Berdasarkan kepada kajian ini, didapati membran yang dihasilkan daripada kulit udang tempatan berpotensi untuk digunakan dalam penghasilan membran selektif kepada air yang tinggi.

*Kata kunci:* Kitosan; membran; pervaporasi; campuran air-isopropanol

---

<sup>1&2</sup>Department of Chemical Engineering, Universiti Teknologi Malaysia, 81310 UTM Skudai, Johor Bahru, Malaysia

\* Corresponding author: Tel: +607-5535522. Email: hashim@fkkksa.utm.my

## 1.0 INTRODUCTION

Chitosan has been one of the promising materials for preparing pervaporation membranes and it has been widely studied [1 – 7]. On the basis of its structural characteristic, chitosan was thought as an ideal dehydration membrane material for pervaporation due to its high affinity to water, having good film-forming properties, functional group that is easy to modify, and having good mechanical and chemical stability in aqueous solutions [8 – 10]. The hydrophilic amino groups in the chitosan molecular structure cannot only cause a preferential interaction with water but chitosan structure can also be easily modified to form a crosslinked-structure using polybasic acids.

Early effort on using chitosan as membrane material for pervaporation dehydration was carried out by Mochizuki [5]. They focused on dehydration of ethanol aqueous solution. The study was then continued for several years by a number of researchers [1 – 19]. Chitosan membranes were also used for pervaporation dehydration of isopropanol with potential applications in the semi-conductors industry [3]. Based on those attractive features, chitosan was chosen as a base material for the development of a highly water permselective pervaporation membranes in this study.

Dehydration of alcohol-water mixture by pervaporation through membranes has received much attention from the chemical industry and so far is the best-developed area of the pervaporation application processes. The technique may provide an economical alternative to distillation for alcohol-water separations and avoids the limitation of osmotic pressure as in reverse osmosis. Pervaporation polymer membranes used in the dehydration of alcohol-water systems should be high water permselective since the size of water molecules is relatively smaller than that of organic molecules so that the rate of diffusion of water molecules is much faster than that of organic molecules even though the solubility is higher for the organics molecules. So, in order to get a high water/organic separation factor for the pervaporation dehydration process, a highly hydrophilic polymer such as chitosan is considered to be a very promising candidate for the selection of membrane material.

In this study membranes were prepared using chitosan available from locally shrimp shells. The chitosan membranes thus prepared were tested for the separation of isopropanol-water mixtures using pervaporation process.

## 2.0 MATERIALS AND METHODS

### 2.1 Materials

Chitosan used in this study was extracted from domestic shrimp shells. Acetic acid and sodium hydroxide were supplied from Merck (Germany); ethanol from Fluka (Switzerland) and isopropanol from J. T. Baker (USA). Deionized water from the laboratory was also used in this study.

## 2.2 Chitosan Preparation

Chitosan, a deacetylated form of chitin was obtained from shrimp shells by the following procedures. Firstly, protein is removed from ground shells by treating it with sodium hydroxide aqueous solution (NaOH) of 2 – 3 M at temperature of 80 – 90 °C for 2 hours. Then it was thoroughly washed with distilled water. The shrimp shells are subsequently treated in a 2M hydrochloric acid (HCL) aqueous solution overnight to produce a product so-called chitin. The chitin thus obtained is then washed with distilled water and is allowed to dry under the sun. The chitin is subsequently treated using 50 wt% sodium hydroxide aqueous solution at temperature of 90 – 110 °C for 3 hours before chitosan flakes are produced. Finally this chitosan flakes are washed and air-dried and ready to be used for membrane preparation.

## 2.3 Membrane Preparation

A pre-weighed quantity of chitosan is first dissolved in 10 wt% of acetic acid solution at room temperature for 24 hours to produce a casting solution with a 2 wt% of chitosan. Then the casting solution is filtered to remove impurities and undissolved chitosan to give a clear homogeneous casting solution. Membrane in the form of flat sheet is then produced by casting the solution into a petri dish and by allowing the casting solution to evaporate under free air for 2-3 days. The dry membrane is then peeled-off from the petri dish and treated in a coagulation bath containing 3 wt% NaOH, 47 wt% ethanol and 50 wt% water at room temperature for 24 hours. Finally, the membrane is thoroughly washed, air-dried and ready to be used for the next experiments.

## 2.4 Liquid Sorption Experiments

Dry membrane samples were immersed in the isopropanol-water mixtures at different compositions ranging from 0 wt% to 100 wt% isopropanol at room temperature for 72 hours to reach equilibrium sorption. The swollen membranes were removed and subsequently blotted between tissue papers to remove the excess solvent, weighed immediately and quickly placed in a dry glass tube that was connected to a cold trap followed by a vacuum pump. The liquid sorbed by the membranes was then desorbed and collected in the cold trap. During desorption process, the membranes were periodically weighed until their weight remained constant with deviation at  $\pm 5$  % from its initial dry weight. The liquid thus collected in the cold trap was then analyzed to determine its composition.

The degree of swelling is calculated using the following equation:

$$DS = \frac{W_s - W_d}{W_d} \quad (1)$$

where  $W_s$  and  $W_d$  are the weight of the dry and swollen membranes, respectively.

## 2.5 Pervaporation Experiments

A pervaporation equipment used in this study has been reported elsewhere [20]. Membrane with an effective area of 52 cm<sup>2</sup> 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. Kalfisher titration equipment is used to determine the percentage of water in the mixture. The permeation flux is calculated using equation (2).

$$J = \frac{N}{A\Delta t} \quad (2)$$

where  $N$  is the weight of the permeate collected at a time interval  $\Delta t$ , and  $A$  is the effective membrane area.

The separation factor of the membrane is determined from the following equation:

$$\alpha_{A/B} = \frac{y_A / y_B}{x_A / x_B} = \frac{y(1-x)}{x(1-y)} \quad (3)$$

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 [8] as:

$$PSI = J(\alpha - 1) \quad (4)$$

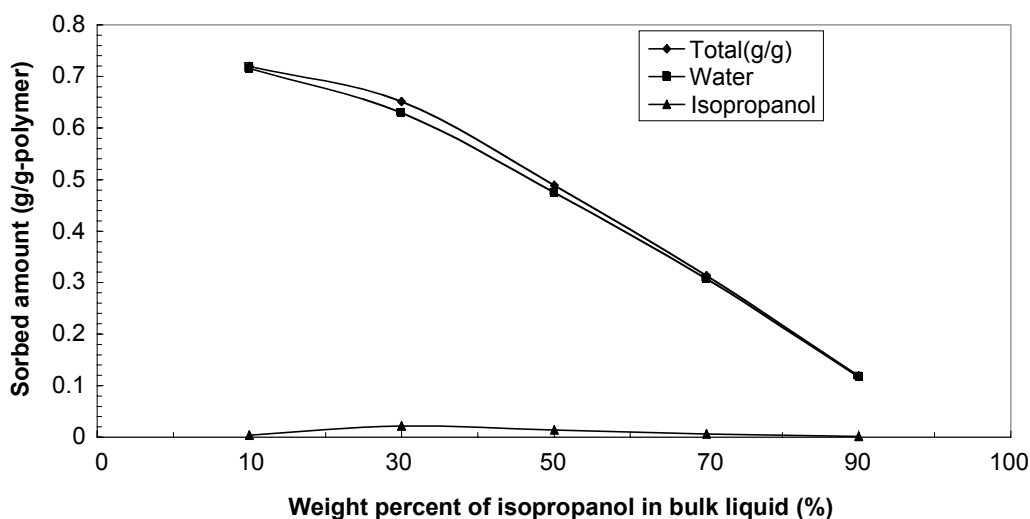
## 3.0 RESULTS AND DISCUSSION

### 3.1 Liquid Sorption Characteristics

The pervaporation transport mechanism can be well interpreted by the solution-diffusion model. Thus, preferential sorption characteristics of the membranes have been explored in the present study. Sorption, namely solubility of the membrane is caused by the interaction between penetrant and polymer. It has long been accepted that the sorption properties are useful in order to properly select the suitable membrane materials and the subsequent chemical treatment needed. This is because the pervaporation properties of the membranes partly depend on the sorption characteristics. However, it must be pointed out first that the sorption data does not always necessarily correspond to the permeability data because the diffusion phenomenon through the membrane also significantly contributes to the permeability.

Some knowledge on the sorption characteristics was obtained through experiments and the results will be discussed.

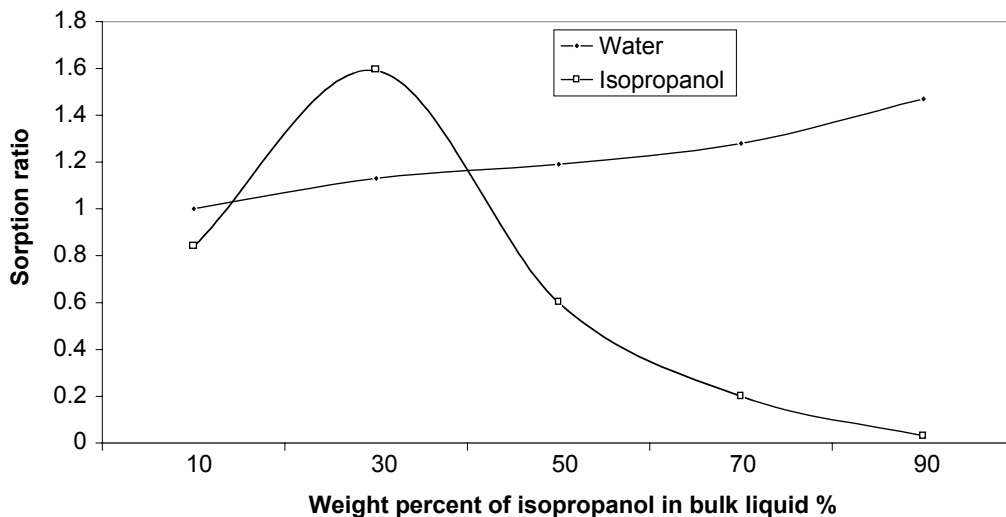
The liquid sorption experiments were carried out for homogeneous chitosan membrane samples in the entire range of feed compositions. The results of the liquid sorption experiments for both isopropanol and water are presented in Figure 1. From the results, it shows that as the concentration of isopropanol in bulk liquid increases, the sorption of isopropanol is increased to a maximum at 30 wt% isopropanol in bulk liquid then decreases. While the water sorption decreases with the increase of isopropanol weight percent. It is also clear that the water uptake is always higher than the isopropanol, suggesting that there are different degrees of interaction between polymer-penetrant and penetrant-penetrant.



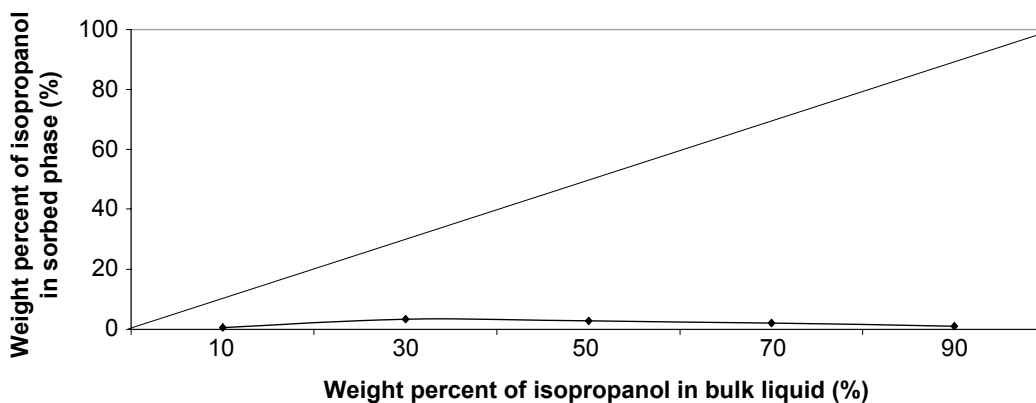
**Figure 1** Sorption data for isopropanol/water mixtures in homogeneous chitosan membranes

The sorption ratio versus liquid composition is shown in Figure 2. Regardless of weight percent of isopropanol in the bulk liquid, the sorption ratio greater than unity is observed for water, indicating positive deviation from ideal sorption. However, the reverse trend is observed for isopropanol. The isopropanol sorption deviates negatively from ideal sorption except at isopropanol weight percent of 30 wt%. At 30 wt% of isopropanol, the sorption of isopropanol is greatly enhanced by the presence of water in the mixture due to coupling sorption phenomenon [21]. The sorption of one component can be increased or decreased in the presence of the other components in the system.

The weight percent of isopropanol in the membrane sorbed phase versus the weight percent of isopropanol in the bulk liquid is shown in Figure 3. For the whole



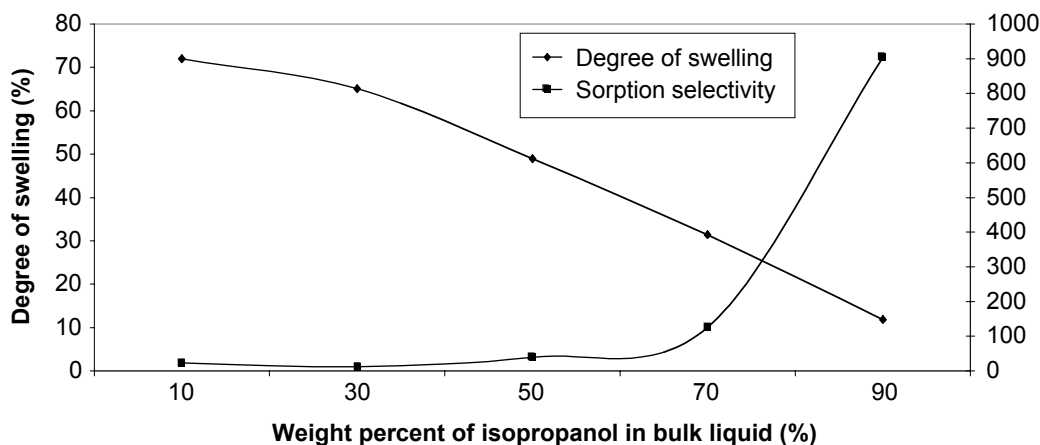
**Figure 2** Sorption ratio versus liquid composition



**Figure 3** Weight percent of isopropanol in membrane sorbed phase versus weight percent of isopropanol in bulk phase. Atmospheric pressure, temperature of 30 °C

concentration range, water is sorbed preferentially; the concentration of water is always higher than that of isopropanol concentration in the membrane sorbed phase. The transport in pervaporation process takes place according to the solution-diffusion mechanism. The permeation rates of components depend on both solubility and diffusivity [21 – 24]. The preferential sorption of the components may have an influence to the permeation rates. Either the preferential sorption will lead to preferential permeation or not will be confirmed and discussed later.

Figure 4 shows a trade-off trend between degree of swelling and sorption selectivity. Membrane swelling decreases while the sorption selectivity on the other hand increases with increasing isopropanol concentration in the bulk liquid. As the chitosan polymer



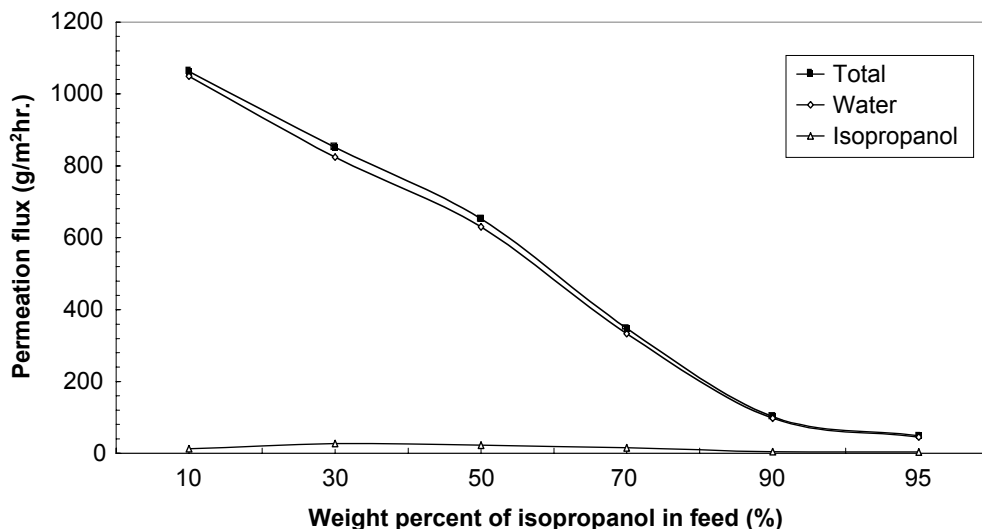
**Figure 4** Degree of swelling and sorption selectivity versus weight percent of isopropanol in bulk liquid

is highly hydrophilic, swelling is increased with increasing water concentration. Being highly hydrophilic, chitosan is significantly swollen in water but the presence of isopropanol reduces the swelling degree of the membrane [10, 25]. The swollen polymer causes more isopropanol molecules to be sorbed together through the so-called coupling sorption thus decreases the sorption selectivity.

### 3.2 Pervaporation

Pervaporation experiments of the homogeneous chitosan membranes were carried out at 30 °C and at permeate pressure of 0.67 kPa in order to study the effect of feed concentration on the pervaporation performance (permeation flux and separation factor). Feed concentration ranges from 10 wt% to 95 wt% of isopropanol in isopropanol-water mixtures. The analysis of the data for pervaporation separation is presented in terms of its permeation flux and separation factor. To study the permeation mechanism, the observed fluxes are separated into their respective water and isopropanol components, so that each component flux could be plotted against its feed concentration. This separated flux is known as partial or individual flux.

The total and partial permeation fluxes for pervaporation dehydration of isopropanol-water mixtures are shown in Figure 5. As the isopropanol weight percent in the feed increases, the permeation flux for water decreases more significantly than isopropanol resulting in the decrease of the total permeation flux. The decrease of water concentration in the feed had produced stronger inter-and intra-molecular interactions in the polymer, narrowing the transport channels for water and also isopropanol. As a result, with this decrease there is a decrease of the total permeation flux and an increase of the separation factor since kinetic diameter of isopropanol is

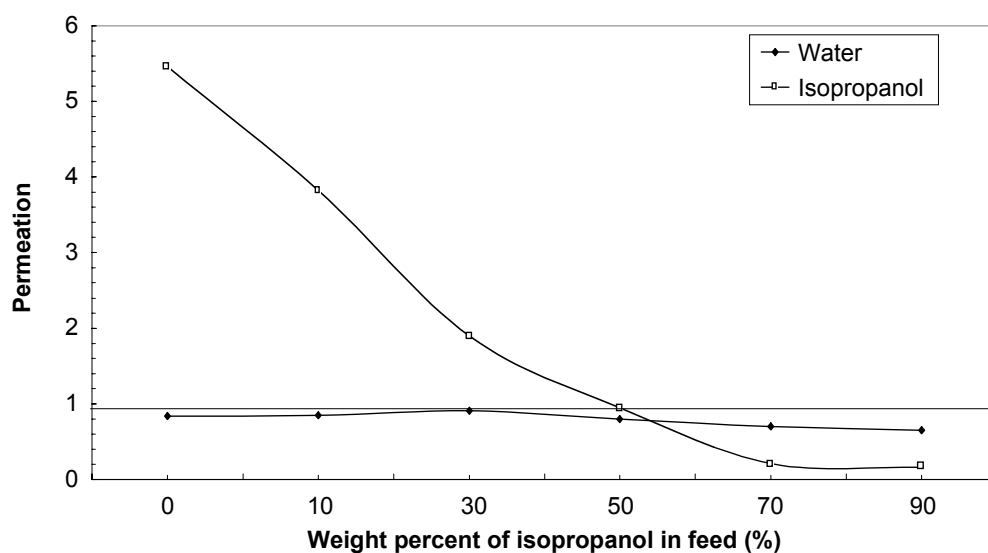


**Figure 5** The total and partial permeation fluxes at different isopropanol weight percent in the feed for homogeneous chitosan membrane

relatively larger than that of water [26]. However, the permeation flux for isopropanol increases to a maximum at 30 wt% isopropanol in the feed corresponding to a maximum isopropanol sorption and then decreased gradually. The maximum in isopropanol permeation flux is achieved at 30 wt% isopropanol in the feed. It is also seen that the total permeation flux is mainly constituted by the water permeation flux, and the water permeation flux is almost proportional to the water concentration of feed. These are the characteristics of highly hydrophilic membrane. Due to its high hydrophilicity, chitosan membrane has a great affinity to water. At high water weight percent in the feed, the amorphous region of the membrane swells more significantly resulting in the polymer chain to become more flexible, thus decreasing the energy required for diffusive transport through the membrane. As a result, the water permeation flux increases with an increase in water weight percent in the feed. This increase of permeation flux with increasing water content was a natural result as expected from the fact that this membrane preferentially permeated water. Further explanation on the increase of water flux at increasing water content can be attributed to the sorption mechanism. According to this mechanism, sorption occurs at liquid-membrane interface. The activity of the components of the mixture may vary more with the feed composition depending on the chemical nature of the mixture. Normally one can postulate that the higher the content of the component that has strong interaction with polymer, the better the swelling is. Higher swelling means higher sorption capacity and higher fractional free volume of the polymer-sorbate system. As a result, the permeation flux of this component is increased with its concentration in the feed mixture. The permeation ratio was used to measure the deviation of the

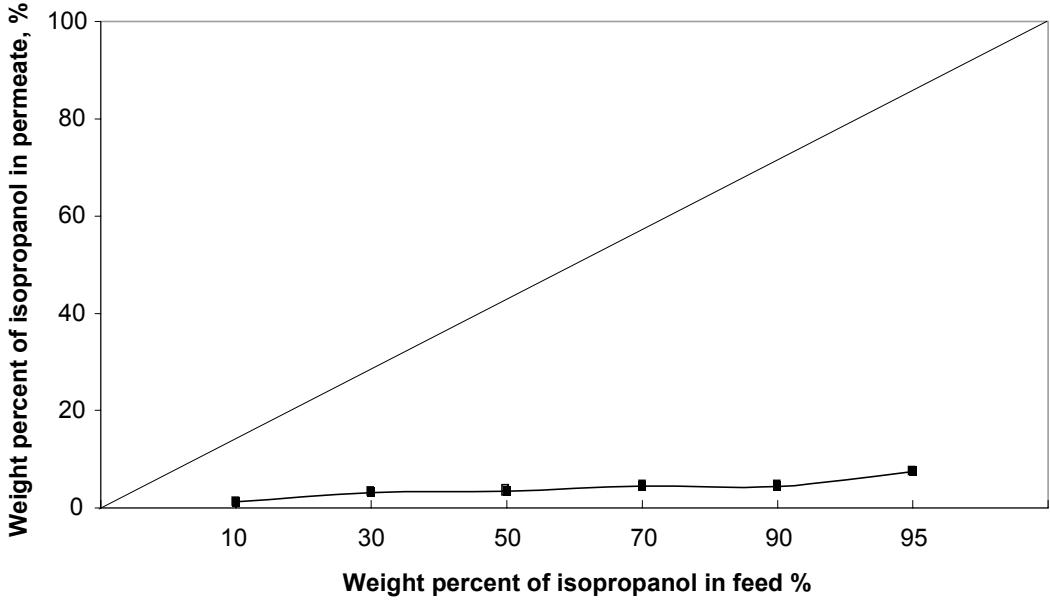


actual permeation rate from ideal permeation rate. The permeation ratio as a function of isopropanol weight percent in the feed is shown in Figure 6. It is interesting to note that at isopropanol concentration below 50 wt%, the isopropanol permeation deviates from its ideal permeation positively. While at isopropanol weight percent in the feed above 50 wt%, the permeation ratio of isopropanol is well below unity indicating that isopropanol deviates negatively from ideal permeation. However, a different trend is observed for water permeation. For the whole range of weight percent of isopropanol in the feed, water permeation deviates negatively from ideal permeation. It means that the presence of isopropanol impaired the permeation of water. By comparing Figure 2 and Figure 6, it is seen that there exists a different trend between sorption ratio and permeation ratio for water. The sorption ratio seems to deviate positively from ideal sorption while permeation ratio deviates negatively from ideal permeation suggesting that the preferential sorption does not necessary give rise to the preferential permeation. These results are attributed to the fact that the feed concentration affects the mobilities of different permeating molecules to a different degree, as was normally observed [27].



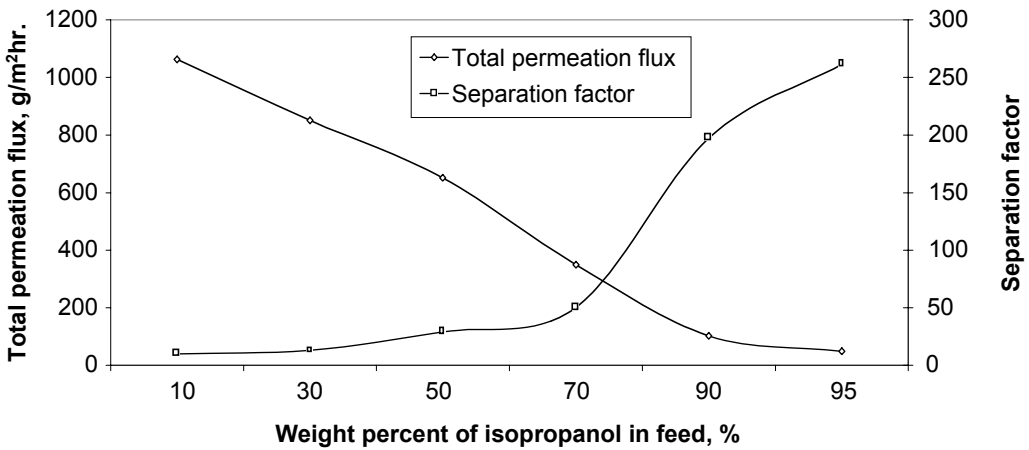
**Figure 6** Permeation ratio versus weight percent of isopropanol in the feed. Permeate pressure of 5 mmHg, operating temperature of 30 °C

The corresponding data for the weight percent of isopropanol in permeate versus the weight percent of isopropanol in feed are presented in Figure 7. It is clear that water is enriched in the permeate product over the entire range of concentration showing that water permeates preferentially. A good interaction between hydrogen bonding of chitosan and water and with the fact that water has a smaller molecular size than isopropanol has resulted the chitosan membrane to be water-selective.



**Figure 7** Weight percent of isopropanol in permeate versus weight percent of isopropanol in feed

Figure 8 shows the effect of feed concentration on the total permeation flux and separation factor at 30 °C. By looking at this figure, it is clear that there is a trade-off relationship between the total permeation flux and the separation factor that is normally encountered in the pervaporation process. Interestingly, high separation factors are observed at high feed isopropanol concentrations. It is clear that the



**Figure 8** The total permeation flux and separation factor for the homogeneous chitosan membranes versus weight percent of isopropanol in the feed

separation factor increases with the increase of isopropanol in the feed. At low isopropanol concentrations, the membrane would be comparatively more swollen than at high concentrations, and this would enable the non-preferential component that is isopropanol to penetrate the polymer matrix and diffuse through the membrane. It can be pointed out that the decrease in separation factor not only results from swelling of the membrane but also from the coupled transport between isopropanol and water. In this study, the coupled transport is unfavourable for the pervaporation dehydration of isopropanol.

#### 4.0 CONCLUSIONS

Based on the present study, it is found that the chitosan membranes produced from domestic shrimp shells could be used as the raw material for the production of high water selective membranes. The membrane produced in this study exhibits a preferential permeation to water. The separation factor of the membrane increases with the decrease of water content in the feed. The preferential permeation was affected, but not determined by preferential sorption from the liquid phase. The preferential sorption of water component for the chitosan membranes does not give rise to the preferential permeation over the whole range of feed solution.

#### ACKNOWLEDGEMENT

The financial support by the Ministry of Science, Technology and Environment of Malaysia through IRPA grant under vot 72163 for funding this research is gratefully acknowledged.

#### REFERENCES

- [1] Zhang, S. and E. Drioli. 1995. Pervaporation Membranes. *Separation Science and Technology*. 30(1): 1-31.
- [2] Shieh, J. J. and R. Y. M. Huang. 1997. Pervaporation with Chitosan Membranes. II. Blend Membranes of Chitosan and Poly (acrylic acid) and Comparison of Homogeneous and Composite Membrane Based on Polyelectrolyte Complexes of Chitosan and Poly(acrylic acid) for the separation of Ethanol-Water Mixtures. *Journal of Membrane Science*. 127: 185-202.
- [3] Nawawi, M. G. M. and R. Y. M. Huang. 1997. Pervaporation Dehydration of Isopropanol with Chitosan Membranes. *Journal of Membrane Science*. 124: 53-62.
- [4] Zikakis, J. P. 1984. *Chitin, Chitosan and Related Enzymes*. Academic Press Incorporation.
- [5] Mochizuki, A., Y. Sato, H. Ogawara and S. Yamashita. 1989. Pervaporation Separation of Water-Ethanol Mixtures Through Polysaccharide Membranes: The Permselectivity of Neutralized Chitosan Membrane and the Relationships Between Its Permselectivity and Solid State Structure. *Journal of Applied Polymer Science*. 37: 3385-3398.
- [6] Wu, L. G., C. H. Zhu and M. Liu. 1994. Study of a New Pervaporation Membrane. Part 2: Performance Test and Analysis of a New Membrane. *Journal of Membrane Science*. 90: 207-212.
- [7] Ge, J., Y. Cui, Y. Yan and W. Jiang. 2000. The effect of Structure on Pervaporation of Chitosan Membrane. *Journal of Membrane Science*. 165: 75-81.
- [8] Feng, X. and R. Y. M. Huang. 1996. Pervaporation with Chitosan Membranes. I. Separation of Water From Ethylene Glycol by a Chitosan/Polysulfone Composite Membrane. *Journal of Membrane Science*. 116:67-76.

- [9] Kubota, N. 1997. Note: Permeability Properties of Chitosan-Transition Metal Complex Membranes. *Journal of Applied Polymer Science*. 64: 819-822.
- [10] Nawawi, M. G. M. 1997. *Pervaporation Dehydration of Isopropanol-Water Systems Using Chitosan Membranes*. Ph.D. Thesis. University of Waterloo.
- [11] Uragami, T. and K. Takigawa. 1990. Permeation and Separation Characteristics of Ethanol-Water Mixtures through Chitosan Membranes by Pervaporation and Evaporation. *Polymer*. 31: 668-672.
- [12] Uragami, T. and H. Shinomiya. 1992. Concentration of Aqueous Dimethyl Sulfoxide Solutions through a Chitosan Membranes by Permeation with a Temperature Difference. *Journal of Membrane Science*. 74: 183-191.
- [13] Uragami, T., T. Matsuda, H. Okuno and T. Miyata. 1994. Structure of Chemically Modified Chitosan Membranes and their Characteristics of Permeation and Separation of Aqueous Ethanol Solutions. *Journal of Membrane Science*. 88: 243-251.
- [14] Yu, Y., W. Li and T. Yu. 1990. Crosslinking Chitosan Membranes for Pervaporation of Alcohol-Water Mixtures. *Polymer Communications*. 31: 319-321.
- [15] Qunhui, G., H. Ohaya and Y. Negishi. 1995. Investigation of the Permeability of Chitosan Membranes Used in Pervaporation Separation. II. Influences of Temperature and Membrane Thickness. *Journal of Membrane Science*. 98: 223-232.
- [16] Volkov, V., V. D. Skirda, E. N. Vasina, S. A. Korotchkova, H. Ohaya and K. Soontarapa. 1998. Self-Diffusion of Water-Ethanol Mixtures in Chitosan Membranes Obtained by Pulsed-Field Gradient Nuclear Magnetic Resonance Technique. *Journal of Membrane Science*. 138: 221-225.
- [17] Li, B-B., Z. L. Xu, Q. T. Alsahy. 2006. Chitosan-PVA/PAN Composite Membranes for the Separation of Ethanol-Water Solutions. *Desalination*. 193: 171-181.
- [18] Veerapur, R. S., K. B. Gudasi and T. M. Aminabhavi. 2007. Pervaporation Dehydration of Isopropanol using Blend Membranes of Chitosan and Hydroxypropyl Cellulose. *Journal of Membrane Science*. 304: 102-111.
- [19] Sun, H., L. Lu, X. Chen and Z. Jiang. 2008. Pervaporation Dehydration of Aqueous Ethanol Solution using H-ZSM-5 filled Chitosan. *Separation and Purification Technology*. 58: 429-436.
- [20] Pervaporation Separation of Isopropanol-Water Mixtures using Crosslinked Chitosan Membranes. *Jurnal Teknologi*. Volume 39. Disember 2003.
- [21] Huang, R. Y. M. and J. W. Rhim. 1991. Separation Characteristics of Pervaporation Membrane Separation Processes. In: Huang, R. Y. M. ed. *Pervaporation Membrane Separation Processes*. The Netherlands: Elsevier. 111-180.
- [22] Mulder, M. H. V. and C. A. Smolders. 1986. Pervaporation, Solubility Aspects of the Solution Diffusion Model. *Separation and Purification Methods*. 15(1): 1-19.
- [23] Kang, Y. S., S. W. Lee, U. Y. Kim and J. S. Shim. 1990. Pervaporation of Water-Ethanol Mixtures through Crosslinked and Surface-Modified Poly (vinyl alcohol) Membrane. *Journal of Membrane Science*. 51: 215-226.
- [24] Chan, W. H., C. F. Ng, S. Y. Lam and X. He. 1999. Water-Alcohol Separation by Pervaporation through Chemically Modified Poly(amidesulfonides). *Journal of Membrane Science*. 160: 77-86.
- [25] Feng, X. and R. Y. M. Huang. 1994. Concentration polarization in Pervaporation Separation Process. *Journal of Membrane science*. 92: 201-208.
- [26] Crank, J. and G. S. Park. 1968. *Diffusion in Polymers*. New York, NY: Academic Press.
- [27] Sferazza, R. A., R. Escobosa and C. H. Goding. 1988. Estimation of Parameters in a Sorption-diffusion Model in Pervaporation. *Journal of Membrane Science*. 35: 125-134.