



PERVAPORATION DEHYDRATION OF ISOPROPANOL-WATER MIXTURES USING CHITOSAN ZEOLITE-A MEMBRANES

MOHD. GHAZALI HJ. MOHD. NAWAWI¹ & LE T. NGOC TRAM²

Abstract. Pervaporation (PV) dehydration of isopropanol (IPA) using modified chitosan membranes was studied. The membranes were prepared from chitosan and modified by using zeolite-A. Pre-weighed amount of zeolite-A was added into acidic solvent and stirred to produce homogeneous solution. Chitosan flakes were then added into the solution and stirred overnight. Various ratios of zeolite-A and chitosan from 1:20 to 1:2 were used to produce the modified chitosan membranes. The chitosan-zeolite A solution was casted on a glass plate and dried at room temperature. The dried membranes were treated with alkaline solution and thoroughly washed in deionized water. The hydrophilicity of the membranes was studied through the swelling test. The test was carried out in a 90 wt% IPA-water mixture. The result showed that the degree of swelling decreased with the increase of the amount of zeolite-A. The mechanical properties of membranes were also tested for the tensile strength and elongation at break. Then, the membranes were investigated for the PV separation of IPA-water mixtures at the permeate pressure of 720 mmHg under vacuum. The feed concentration was varied from 0 to 95 wt% IPA, and the feed temperature was varied from 30 to 70°C. The results showed that the ratio 1:8 of zeolite-A and chitosan produced the best combination to modify the membrane for the separation of water-IPA mixtures. The structural morphologies of the chitosan filled zeolite-A membranes with ratio 1:8 and 1:2 wt zeolite-A/wt chitosan was studied under Scanning Electron Microscopy (SEM). The results showed that the membranes were dense, and no pores were visible. The addition of the zeolite did not alter the structure of the membranes.

Keywords: Pervaporation, dehydration, membrane, chitosan, zeolite-A, isopropanol

Abstrak. Kajian pervaporasi (PV) penyahidratan isopropanol (IPA) menggunakan membran kitosan terubahsuai telah dijalankan. Membran disediakan daripada kitosan dan diubahsuai menggunakan zeolite-A. Zeolit-A yang diketahui beratnya ditambahkan ke dalam pelarut berasid dan diaduk untuk menghasilkan larutan homogen. Kepingan kitosan kemudian ditambahkan ke dalam larutan tersebut dan diaduk semalaman. Pelbagai nisbah zeolit-A dan kitosan daripada 1:20 hingga 1:2 digunakan untuk menghasilkan membran kitosan terubahsuai. Larutan kitosan-zeolit-A dituangkan ke atas plat kaca dan dikeringkan pada suhu bilik. Membran yang dikeringkan kemudian dirawat dengan larutan alkali dan dibasuh di dalam air ternyahion. Sifat hidrofilik membran dikaji melalui ujian pengembangan. Ujian dijalankan dalam campuran 90 wt.% IPA-air. Keputusan menunjukkan bahawa darjah pengembangan berkurangan dengan penambahan zeolit-A. Sifat mekanikal membran dikaji untuk kekuatan tegangan dan pemanjangan pada takat putus. Kemudian, membran tersebut dikaji untuk pemisahan campuran IPA-air pada tekanan 720 mmHg di bawah vakum. Kepekatan suapan diubah daripada 0 hingga 95 wt.% IPA dan suhu suapan diubah daripada 30 hingga 70°C. Keputusan menunjukkan bahawa nisbah 1:8 antara zeolit dan kitosan menghasilkan kombinasi terbaik

^{1&2} Department of Chemical Engineering, Faculty of Chemical & Natural Resources Engineering, Universiti Teknologi Malaysia, 81310 Skudai, Johor, Malaysia.

¹ Corresponding author: Tel: +607 5535593, Fax: +607 5581463, E-mail: g hazali@fkkksa.utm.my

untuk mengubahsui membran bagi pemisahan campuran IPA-air. Struktur morfologi membran kitosan-zeolit-A dengan nisbah 1:8 dan 1:2 berat zeolit-A/berat kitosan dikaji menggunakan *Scanning Electron Microscopy (SEM)*. Keputusan menunjukkan bahawa membran yang dihasilkan adalah padat dan tiada liang dapat diperhatikan. Penambahan zeolit tidak mengubah struktur membran.

Kata kunci: Pervaporasi, penyahidratan, membrane, kitosan, zeolite-A, isopropanol

1.0 INTRODUCTION

Membranes have been used in separation technique for a long time. Almost all membranes are prepared from synthetic materials. Natural polymers are not so many like synthetic but more biocompatible and biodegradable. Besides cellulose and its derivatives, the next most common natural polymer are chitin and chitosan. Chitosan have been used not only in pharmaceutics, ophthalmology, cosmetics, agriculture, and food processing [1-5], but also in membrane separation. Chitosan is insoluble in water but chitosan membrane shows high hydrophilicity. Many researchs investigated separation alcohol-water mixtures using pervaporation system through chitosan membranes and modified chitosan membranes by blending, crosslinking or complex [6-12].

Recently, zeolite filled membranes were studied. Yong *et al.* [13] studied zeolite filled polyimide membrane containing 2,4,6-triaminopyrimide for gas separation. Boom *et al.* [14] studied rubbery polymer EPDM, Viton, and Estane with zeolite X and Fajitsu. The addition of hydrophilic zeolite X and hydrophobic zeolite silicate led to an increase in methanol flux, and a decrease in toluene flux through membranes. Gao and Li [15] used composite hydrophilic membranes polyvinyl alcohol PVA with zeolite KA, NaA, CaA, and NaX. With KA zeolites, the flux rised with increasing zeolite content and the separation factor is maintained upon the addition of zeolite until 11.1%, and then decreased. The flux increased with decreasing zeolite particle size and the separation factor unchanged at low zeolite content, and decreased at high zeolite content. The addition of zeolites to polymer improved the flux of membranes. With larger alcohol molecules like IPA, the separation factors of the majority of A-type zeolite filled membranes were improved markedly. Nawawi *et al.* [16] used chitosan with zeolite 13X. The total permeation flux improved but the separation factor decreased compared to the homogeneous chitosan membranes. Pervaporation Separation Index gave the highest value at 0.1 wt.% zeolite. In this research, chitosan filled zeolite-A membranes were studied to determine the effect of zeolite-A concentration to dehydrate IPA.

2.0 MATERIALS AND EXPERIMENTS

2.1 Materials

Chitosan powders were supplied by Chitochem company (Malaysia) with the average molecular weight (MW) = 50,000-100,000. Molecular sieves (zeolite), 4Å with the average

particle size $\sim 5 \mu\text{m}$ and the pore diameter approximately 4\AA , was purchased from Sigma-Aldrich (M). 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 Membranes Preparation

Zeolite-A was added in the acetic acid 10 wt.% to produce homogeneous solution. The concentration of zeolite-A in the solution was varied from 0.1 wt.% to 1 wt.% of the solvent (equivalent to the ratio of zeolite A:chitosan =1:20 to 1:2). Pre-weighed chitosan was stirred in this solution overnight. The casting solution consisted of 2 wt.% chitosan. After the impurities and undissolved chitosan were removed, the solution was casted onto glass plates and evaporated at room temperature. The membranes were peeled off from the plates and treated with the alkaline solution. Then, the membranes were washed with deionized distilled water to remove the trace of alkaline completely, and dried at room temperature.

2.3 Membrane Characterization

All types of chitosan membranes were tested for their tensile strength, elongation, and Young's modulus at the dry states by using INSTRON 5567.

The hydrophilicity of the membranes was studied through the swelling test. The weight of the dry chitosan membranes was measured. The membranes were then immersed in 90 wt.% IPA at room temperature for 3 days. The membranes were picked out and weighed after the surface liquid was quickly removed with tissue papers. Then, the membranes were put in the sample tube to desorb the liquid absorbed using the vacuum pump. The desorption apparatus was shown in Figure 1.

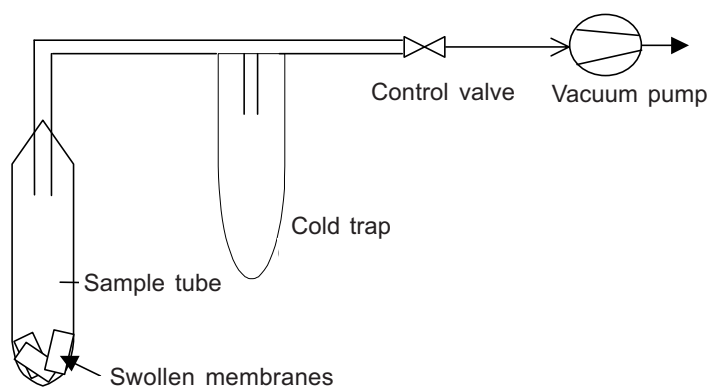


Figure 1 The desorption apparatus to determine the composition of the mixture absorbed in swollen membranes

The liquid sorbed from the membrane was condensed in the cold trap with liquid nitrogen. The liquid collected in the cold trap was analyzed to determine its composition. The degree of swelling is calculated from:

$$DS(\%) = \frac{\text{The weight of swollen membrane}}{\text{The weight of dry membrane}} = \frac{W_s - W_d}{W_d} \times 100 \quad (1)$$

W_s : the weight of swollen membrane

W_d : the weight of dry membrane

2.4 Pervaporation

The membrane performance was investigated through the effect of zeolite concentration and the feed temperature to dehydrate IPA solution. The effect of zeolite concentration was carried out from 0.1 to 1 wt.% in the solvent (or the ratio zeolite A:chitosan = 1:20 to 1:2). The feed concentration was 90 wt.% IPA. The membrane thickness was 25 μm . The permeate pressure was kept at 720 mmHg under vacuum. The membrane effective area was 52.81 cm^2 . The feed temperature was studied from room temperature to 70°C. The pervaporation apparatus has been described elsewhere [16]. The permeation flux was calculated from the amount of permeate collected in a given period time:

$$J = \frac{Q}{A} \quad (2)$$

where Q : the weight of permeate in a given period (g/h)

A : the effective membrane area (m^2)

The permeation composition was determined by using Refractometer. The permeation flux of each component was defined from the total permeate and the permeation composition. The separation factor α was calculated from:

$$\alpha = \frac{Y_w / Y_{IPA}}{X_w / X_{IPA}} \quad (3)$$

where Y, X : the weight fraction of water and IPA in the permeate side, and the weight fraction of water and IPA in the feed mixture.

The pervaporation separation index PSI was calculated from:

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

3.0 RESULTS AND DISCUSSION

3.1 The Membrane Characterization

Mechanical testing gives a good indication of the membrane physical properties. Figure 2 shows the tensile strength, elongation, and Young’s modulus of all types of membranes. With the increase of zeolite-A, the tensile strength and Young’s modulus also increase but the percentage of elongation declines. It was suggested that the interaction between chitosan and zeolite molecules was stronger than the interaction among the chitosan molecules. Therefore, the more zeolite added in the membrane, the stronger the modified membranes will resist the deformation. The polymer chain of chitosan has plasticity while zeolite-A has the crystalline structure. The addition of zeolite A made chitosan membranes broke their interactions among the chitosan molecules, which reduced the plasticity. Therefore the increase of zeolite content made the chitosan membranes more brittle. In general, the higher the zeolite content in the chitosan membranes, the stronger but more brittle the membranes will be.

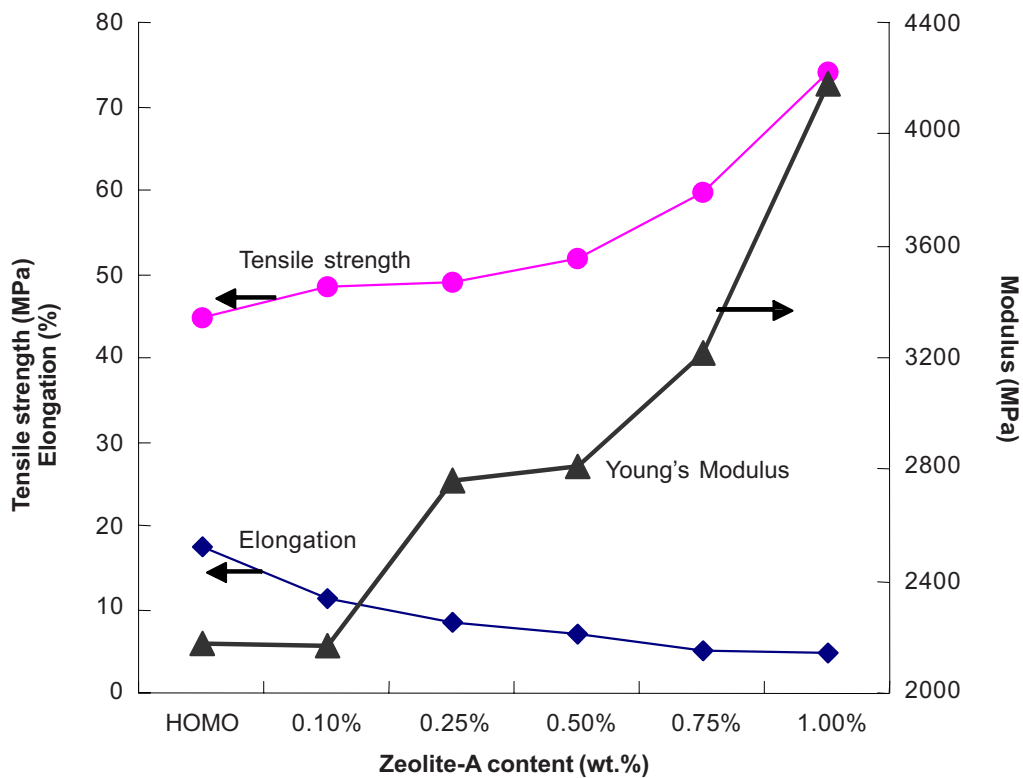


Figure 2 The tensile strength, elongation and Young’s Modulus

3.2 The Hydrophilicity of Membranes

The degree of swelling and the sorption selectivity are shown in Figure 3. The degree of swelling decreased with the increase of the zeolite. When the zeolite concentration increased, the chitosan content will decrease. The chitosan membranes have free volume segments while zeolite adsorbed through its pore size. As suggested above, the interactions between the chitosan and the zeolite molecules were tight and the chitosan content in the membranes decreased, thus leaving less free volume segments than the unmodified chitosan. Therefore, the modified membranes were less swollen. The sorption selectivity started to diminish at zeolite content of 0.25 wt.%. At a low content of zeolite, the IPA molecule saturated with the IPA and the water molecules in the pores. With this, the sorption selectivity in the chitosan zeolite membranes was the same as in the unmodified membranes. The sorption selectivity decreased significantly at 0.5 wt.% concentration of zeolite. When the zeolite content increase, both water and IPA sorbed much more in the zeolite pores. The addition of zeolite made the membranes less hydrophilic and selective.

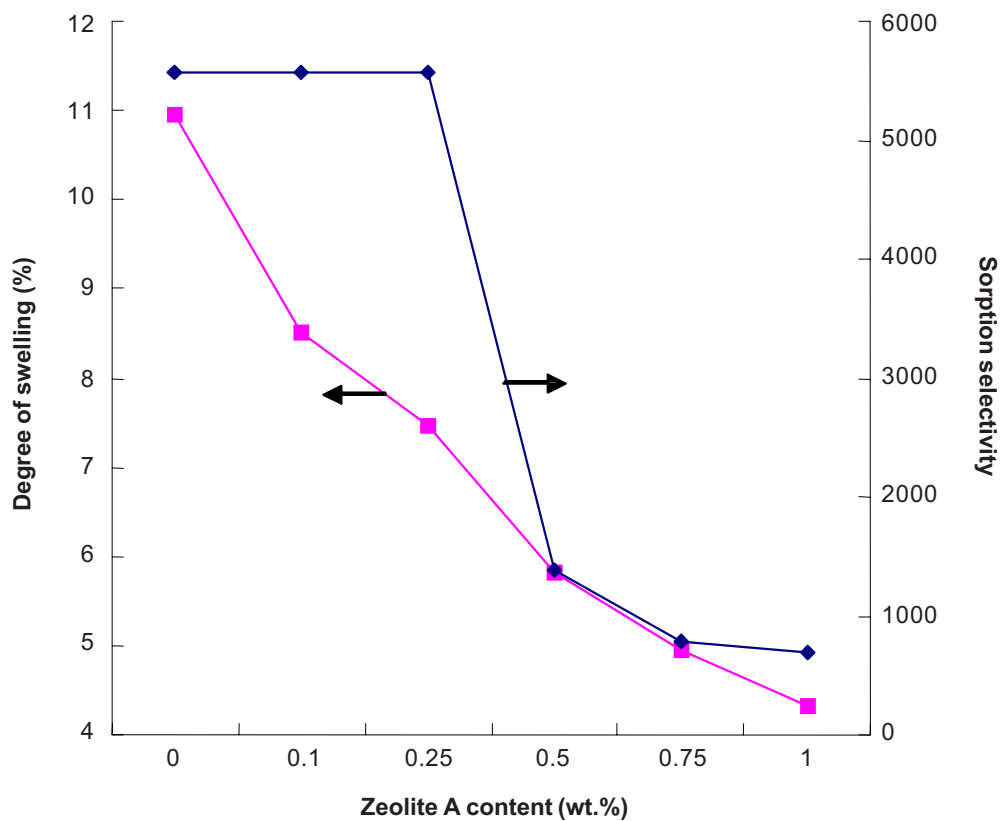


Figure 3 The degree of swelling and sorption selectivity

3.3 The Effect of Zeolite A Concentration

The PV separation of isopropanol-water was carried out at 90 wt.% IPA in the feed. The total permeation flux and separation factor are shown in Figure 4. The total flux increased slightly with the addition of zeolite concentration up to 0.5 wt.%. The diffusion through chitosan zeolite membranes took place in the polymer chain of chitosan and zeolite pores. The interactions between the chitosan and zeolite molecules prevented IPA molecules to pass through. Due to that, the separation factors at 0.1 and 0.25 wt.% zeolite were higher than the unmodified membrane. However, the zeolite pores also affected the permeate flux and the separation factor. Therefore, the permeate flux increased while the separation factor decreased with the increase of zeolite.

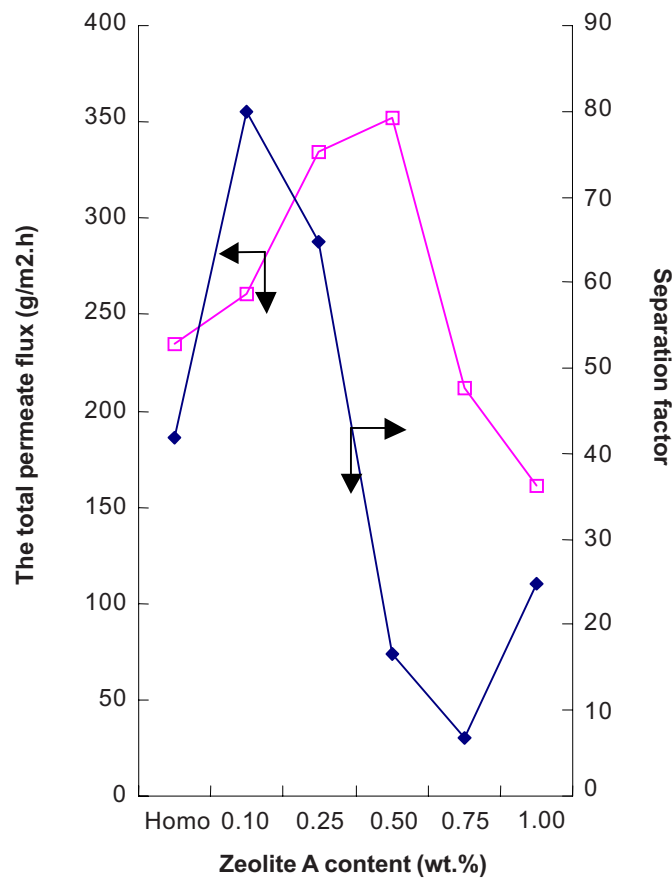


Figure 4 The total permeation flux and separation factor versus zeolite concentration of all types of membranes

When the zeolite content was higher than 0.5 wt.%, the permeate flux diminished significantly, while the separation factor only increased at 1 wt.% zeolite. For the tensile strength, chitosan zeolite membranes showed the significant increase starting from 0.5 wt.% zeolite. The links between chitosan and zeolite molecules were stronger and tighter. This prevents water and IPA from passing through the membrane. Therefore, the permeate flux reduced and the separation increased at 1 wt.% of zeolite-A.

The Overall performance was determined by Pervaporation Separation Index (PSI), which combined the total permeation flux and the selectivity. Figure 5 shows the PSI versus the zeolite concentration. PSI of modified chitosan membranes improved only at low zeolite content.

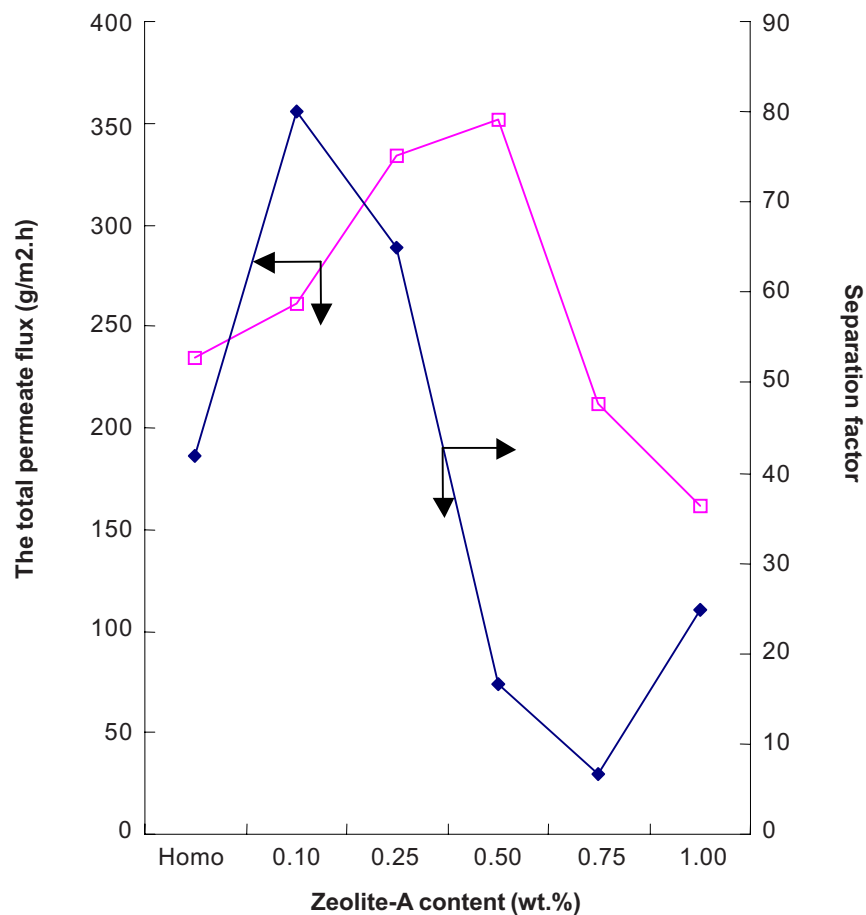


Figure 5 Pervaporation separation index

3.4 The Effect of Feed Temperature

The effect of feed temperature was carried out from room temperature to 70°C. The feed concentration was 90 wt.% IPA. The effect of feed temperature of membranes with 0.25 wt.% zeolite was chosen to study. The total permeation flux of unmodified membrane at room temperature was assumed to be 1. The normalized flux, which is the ratio of the permeate flux to the unmodified membrane at room temperature, and the separation factor are shown in Figure 6. When the feed temperature increased, the permeation flux of modified membrane increased much higher than that of unmodified membrane. All the separation factors decreased with the increase of the feed temperature but the chitosan zeolite membranes declined faster than the homogeneous ones. Only at low temperature, both types of the membranes gave a higher selectivity. Both the increase of the permeate flux and the decrease of the separation factor at high temperature was probably caused by the thermal motion of the feed components and the polymer chains in the membranes. As the temperature rose, the thermal agitation increased and created more free volume in the polymer matrix. Therefore, the permeation flux increased very fast and more molecules of alcohol and water can diffuse through the membranes. However, both the permeation flux and the separation

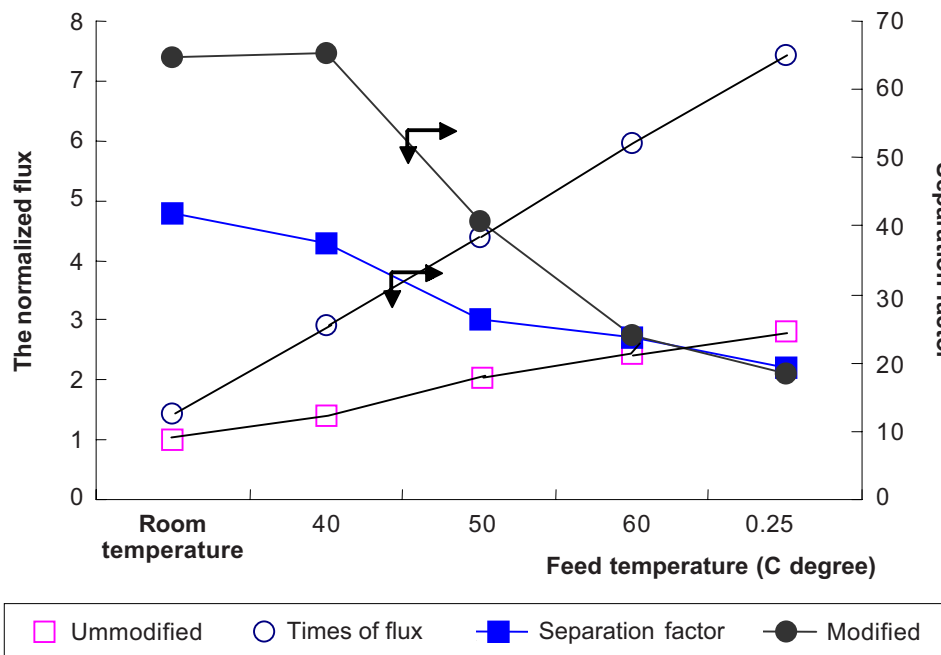


Figure 6 The times of permeation flux compared with the unmodified at room temperature and separation factor of both unmodified and modified membranes versus feed temperature

factor of chitosan zeolite membranes were higher than homogeneous membranes, except at 70°C. The pervaporation activation energy of homogeneous chitosan membranes was 4.47 kcal/mol for water and 8.43 kcal/mol for IPA, while that of the modified membranes was 6.95 kcal/mol for water and 13.88 kcal/mol for IPA.

4.0 CONCLUSION

The conclusions that can be drawn from this study are as follows:

- (i) As the zeolite content increases, the tensile strength as well as Young's modulus also increase but the elongation decreases. The modified membranes become stronger but more brittle than the unmodified membranes.
- (ii) The chitosan zeolite membranes with 0.25 wt.% in the chitosan solution gives the best performance. The membranes improve both the permeation flux and the selectivity at low zeolite concentration. The overall PSI of chitosan zeolite membranes is always higher than the homogeneous membranes and gives a better performance at low feed temperature.

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