Pervaporation dehydration of isopropanol-water mixtures using chitosan zeolite-a membranes

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Abstract

Pervaporation (PV) dehydration of isopropanol (IPA) using modified chitosan membranes was studied. The membranes were prepared from chitosan and were 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 glass plate and dried at room temperature. The dried membranes were treated with alkaline solution and were thoroughly washed in deionized water. The hydrophilicity of the membranes was studied through 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 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, 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

1. 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 biocompatable and biodegradable. Besides cellulose and its derivatives, the next most common natural polymer is chitin and chitosan. Chitosan have been used not only in pharmaceutics, ophthalmology, cosmeites, agriculture, 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, NaX. With KA zeolites, the flux rised with increasing zeolite content and the separation factor is maintained upon 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 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 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. 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, 4Å with the average particle size \sim 5 µm and the pore diameter approximately 4Å, 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 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 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. The membranes were treated with the alkaline solution. Then membranes were washed with deionized distilled water to remove 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 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 (%) =
$$\frac{The \ weight \ of \ swollen \ membrane}{The \ weight \ of \ dry \ membrane} = \frac{W_s - W_d}{W_d} \times 100$$
 (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 μ m. The permeate pressure was kept at 720 mmHg under vacuum. The membrane effective area was 52.81 cm². 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:

$$J = \frac{Q}{A} \tag{2}$$

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

$$\alpha = \frac{Y_W/Y_{IPA}}{X_W/X_{IPA}}$$
(3)

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

And the pervaporation separation index PSI was calculated from: $PSI = J.(\alpha-1)$ (4)

3. 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. As the increase of zeolite A, the tensile strength and Young's modulus also increase but the percentage of elongation declines. It is suggested that the interaction between chitosan and zeolite molecules is stronger than the interaction among the chitosan molecules. Therefore the higher the zeolite added in the membrane, the stronger the modified membranes 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 break their interactions among the chitosan molecules, which reduced the plasticity. So the increase of zeolite content made the chitosan membranes more brittle. In general, the more the zeolite content in the chitosan membranes, the stronger but more brittle the membranes.



Figure 2: The Tensile Strength, Elongation and Young's Modulus

3.2. The hydrophilicity of membranes

The degree of swelling and the sorption selectivity was shown in Figure 3. The degree of swelling decreases with the increase of the zeolite. When the zeolite concentration increases, the chitosan content will decrease. The chitosan membranes have the free volume segments while zeolite adsorbed through its pore size. As suggested above, the interactions between the the chitosan and zeolite molecules are tight and the chitosan content in the membranes decreases, thus leaving less free volume segments than the unmodified chitosan. Therefore the modified membranes are less swollen. The sorption selectivity started to diminish at zeolite content 0.25 wt.%. At the low content of zeolite, the IPA molecule saturated with the IPA and water molecules in the pores. So the sorption selectivity in the chitosan zeolite membranes is the same as in the unmodified membranes. The sorption selectivity decreases significantly at 0.5 wt.% concentration of zeolite. When the zeolite content increased, 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 were shown in Figure 4. The total flux increases slightly with the addition of zeolite concentration up to 0.5 wt.%. Actually the diffusion through chitosan zeolite membranes took placed in the polymer chain of chitosan and the zeolite pores. The interactions between the chitosan and zeolite molecules prevent IPA molecules to pass through. So the separation factors at 0.1 and 0.25 wt.% zeolite are higher than the unmodified membrane. However the zeolite pores also affected the permeate flux and separation factor. Therefore the permeate flux increases while the separation factor decreases with the increase of zeolite.

When the zeolite content is higher than 0.5 wt.%, the permeate flux diminishes significantly while the separation factor only increases at 1 wt.% zeolite. For the tensile strength, chitosan zeolite membranes showed the significant increase started at 0.5 wt.% zeolite. The links between chitosan and zeolite molecules are stronger and tighter. This prevents water and IPA to pass through the membrane. So the permeate flux reduces and the separation increases at 1 wt.% of zeolite A.

Overall performance is determined by Pervaporation Separation Index (PSI), which combines 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 4: The Total Permeation Flux and Separation Factor versus Zeolite Concentration of all types of membranes



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 separation factor were shown in Figure 6. When the feed temperature increases, the permeation flux of modified membrane increases much higher than that of unmodified membrane. All the separation factors decrease with the increase of the feed temperature but the chitosan zeolite membranes decline faster than homogeneous ones. Only at low temperature both 2 types of the membranes give the higher selectivity. Both the increase of the permeate flux and the decrease of the separation factor at high temperature is probably caused by the thermal motion of the feed components and the polymer chains in the membranes. As the temperature raises, the thermal agitation increases and create more free volume in the polymer matrix. Therefore the permeation flux increases very

fast and more molecules of alcohol and water can diffuse through the membranes. However both the permeation flux and the separation factor of chitosan zeolite membranes are higher than homogeneous membranes except at 70°C. The pervaporation activation energy of homogeneous chitosan membranes is 4.47 kcal/mol for water and 8.43 kcal/mol for IPA while that of modified membranes is 6.95 kcal/mol for water and 13.88 kcal/mol for IPA.



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

4. Conclusion

The conclusions that can be withdrawn from this study:

1. 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.

2. 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 the better performance at low feed temperature.

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