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## PERVAPORATION PERFORMANCE OF ETHANOL-WATER USING CHITOSAN-CLAY COMPOSITE MEMBRANE

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**Abstract.** The pervaporation performance for the separation of ethanol-water azeotrope mixture was assessed by chitosan-clay composite membranes. Composite hydrophilic chitosan membrane was prepared from commercial available chitosan powder. The chitosan powder was dissolved using dilute acetic acid to produce chitosan solution. The chitosan solution was blended with small amount of clay and casted on a porous support which prepared from polysulfone to produce composite membrane. The performance of the membrane for the pervaporation separation of ethanol-water mixtures with various concentrations was explored. The effects of feed temperature on the permeation flux and separation factor were also investigated. The membrane was tested for ethanol-water mixtures separation with different ethanol concentrations (10 wt%, 30 wt%, 50 wt%, 70 wt% and 90 wt%) at room temperature. The effects of feed temperature was studied using a feed solution containing 90 wt% ethanol; the feed temperature was varied from 30 °C to 70 °C at permeate pressure below 0.07 bar. The results showed chitosan-clay composite membrane performed better with low water content carried out at low temperature and permeate pressure. There was a trade-off between the permeation flux and the separation factor where the flux decreased while the separation factor increased with the increasing of ethanol concentration in the ethanol-water mixtures.

**Keywords:** Pervaporation; chitosan; clay; hydrophilic; permeation flux; separation factor

**Abstrak.** Penyelidikan ini bertujuan untuk mengkaji proses pervaporasi dengan menggunakan komposit membran chitosan-tanah liat bagi pemisahan campuran larutan etanol-air. Membran komposit chitosan bersifat hidrofilik disediakan dari pada serbuk chitosan. Serbuk chitosan dilarutkan di dalam larutan asid asetik lemah untuk menghasilkan larutan chitosan. Larutan chitosan dicampur bersama tanah liat dan dituang ke atas sokongan poros yang disediakan daripada polisulfon untuk menghasilkan komposit membran. Keberkesanan membran bagi pemisahan pervaporasi campuran larutan etanol-air untuk perbagai kepekatan dikaji. Kesan suhu masukan terhadap fluk kebolehesapan dan faktor pemisahan juga dikaji. Membran diuji untuk pemisahan campuran larutan etanol-air bagi kepekatan etanol yang berbeza (10 wt%, 30 wt%, 50 wt%, 70 wt% dan 90 wt%) pada suhu bilik. Kesan suhu masukan dikaji dengan larutan masukan yang mengandungi 90 wt% etanol, suhu masukan berubah dari 30 °C kepada 70 °C pada tekanan di bawah 0.07 bar. Keputusan menunjukkan bahawa membran komposit chitosan-tanah liat mempunyai kesan yang lebih baik bagi kandungan air yang rendah pada suhu dan tekanan rendah. Fluk kebolehesapan menurun apabila faktor pemisahan meningkat dengan peningkatan kepekatan etanol dalam campuran larutan etanol-air.

**Kata kunci:** Proses pervaporasi; chitosan; tanah liat; hidrofilik; fluk kebolehesapan; faktor pemisahan

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## 1.0 INTRODUCTION

Pervaporation has been intensively studied recent years for the separation method involving the breaking of azeotropes, heat-sensitive products, dehydration of solvents, and organic-organic solutions by partial vaporization through a non-porous or porous membrane. The simple principle of pervaporation makes it as an alternative preferable technique for industrial usage. The challenge faced in the pervaporation is to fulfill the available membranes in good separating properties where to fight against the concentration polarization rather than to find the right material for specific applications. According to this, various types of membranes has been imposed. According to Nawawi and Hassan, the membrane materials, which contain hydrophilic groups in the polymer structure for the dehydration of alcohol mixtures, are preferred [1]. In fact, for many chemical processes such as solvent extraction, acetone production and manufacture of hydrogen peroxide, the purification of alcohol from its water solution are necessary. Hence, a chitosan composite membrane for the separation of ethanol–water solutions was chosen in this study.

Chitosan, a polysaccharide found in the exoskeletons of crustaceans so called chitin. It has attracted with a great interest as a basic pervaporation membrane material due its high abundance, natural occurrence, hydrophilicity, chemical resistance, adequate mechanical strength, good membrane forming properties, functional groups that can be easily modified and ease of processing [2]. Chitosan's advantages are particularly apparent in non-toxic and biodegradable characteristics.

## 2.0 EXPERIMENTAL

### 2.1 Materials

Chitosan was added with clay to form the chitosan-clay composite membrane. The chemicals purchased from Labscan Asia Co. Ltd., included acetic acid ( $\text{CH}_3\text{COOH}$ ), sodium hydroxide ( $\text{NaOH}$ ), chitosan powder, clay powder-kaolin,  $\text{N,N}$ -dimethyl formide (DMF), and liquid nitrogen. Ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) was supplied by Rinting Scientific; polysulfone by Amoco; and methyl cellosolve (ethylene glycol monomethyl ether) by Krass. All these chemicals were reagent grade and used without further purification. Distilled water was used throughout the entire study.

### 2.2 Preparation of Chitosan-Clay Solution

2 wt% of chitosan was weighted and dissolved in a beaker contained 10 wt% of acetic acid solution. Then, 24 hours stirring process was run for the solution at room temperature to produce a clear homogeneous casting solution. Vacuum filter was used to filter the resulting casting solution to remove impurities and undissolved materials. The solution was then added with clay powder with appropriate ratio and

stirred magnetically by a stir plate without heating for another 24 hours. To prepare the composite membrane, the chitosan-clay solution was coated onto the polysulfone substrate membrane, where the casting procedures were stated latter.

### **2.3 Porous Polysulfone Support Layer Preparation**

Porous polysulfone membrane was prepared through the phase inversion process of the solution contained 12 wt% of polysulfone, 11 wt% of methyl cellosolve (ethylene glycol monomethyl ether), and 77 wt% of N,N-dimethyl formide (DMF). The casting solution was poured onto a drawing paper which held along with glass plates. The thickness of film formed was aided using the glass rod and it was immersed into a 50 wt% dimethyl formamide (DMF) in deionised water gel bath for 10 minutes. The resulted porous membrane was then again immersed in distilled water for 24 hours before being dried in air at ambient temperature.

### **2.4 Clay Filled Chitosan Composite Membrane Preparation**

The above homogeneous blend solution was hand-coated with the help of a dropper and a glass rod onto the pre-cut porous substrate and the coated membrane was dried at room temperature. Next, the membrane formed was immersed in a mixture with 3 wt% of NaOH, 47 wt% of ethanol and 50 wt% distilled water for 24 hours at room temperature. This step was to neutralize the acetic acid of homogeneous chitosan-clay composite membrane. To remove the remaining NaOH, the membrane formed was washed and rinsed repeatedly with distilled water. Lastly, the composite membrane was dried by keeping it between two filter papers and glass plates for 2 days.

### **2.5 Pervaporation**

The chitosan-clay composite membrane was mounted on the pervaporation apparatus and operated under various feed concentrations. A continuous pervaporation unit was used for evaluating the pervaporation performance of the membrane. Tests were carried out at room temperature (30 °C) and the permeate pressure was set to be maintained below 0.07 bar. The membrane area, placed in the permeation cell which consisted of two stainless steel parts assembly was approximate 0.0069 m<sup>2</sup>. The temperature was controlled by circulating water from a thermostatic bath to a water jacket that surrounded the feed compartment.

Prior to pervaporation, the feed reservoir was filled with 3 L of ethanol-water feed solution and the specimens were equilibrated for at least half an hour. Ethanol-water solution prepared with desired compositions was well mixed by a magnetic stirrer for the entire process. The vacuum pump at the downstream side of the membrane was to supply the required driving force, while the upper stream pressure was kept

at atmospheric pressure since hydrodynamic pressure can hardly affect pervaporation transport. After a steady state was attained, permeate was condensed in a cold trap. Study was concerned with steady state of pervaporation; when the permeation rate and permeate concentration became constant, the steady state equilibrium vapor phase concentration was assumed.

In further analysis, the membrane performance was characterized in terms of permeation flux,  $J$  and separation factor,  $\alpha$ . The flux,  $J$ , which are defined as follows:

$$J = W/A.\Delta t \quad (2.1)$$

where  $W$  is the mass of the permeate (g);  $A$  is area of the membrane ( $m^2$ ); and  $t$  is the collection time (h) [3]. Whilst, the separation factor ( $\alpha_{\text{water/organic compound}}$ ) was calculated from the concentration ratio of permeate solution over feeding solution.

$$\alpha_{\text{water/organic compound}} = \frac{(Y_{\text{water}}/Y_{\text{organic compound}})}{(X_{\text{water}}/X_{\text{organic compound}})}$$

or, 
$$\alpha = (Y_w / Y_e)/(X_w / X_e) \quad (2.2)$$

where  $Y$  and  $X$  are mass fractions of the permeate and the feed, respectively; the subscripts  $e$  and  $w$  denote ethanol and water, respectively [4]. Both of these quantities were obtainable directly from pervaporation experiments. The results were also analyzed by refractive index measurement later.

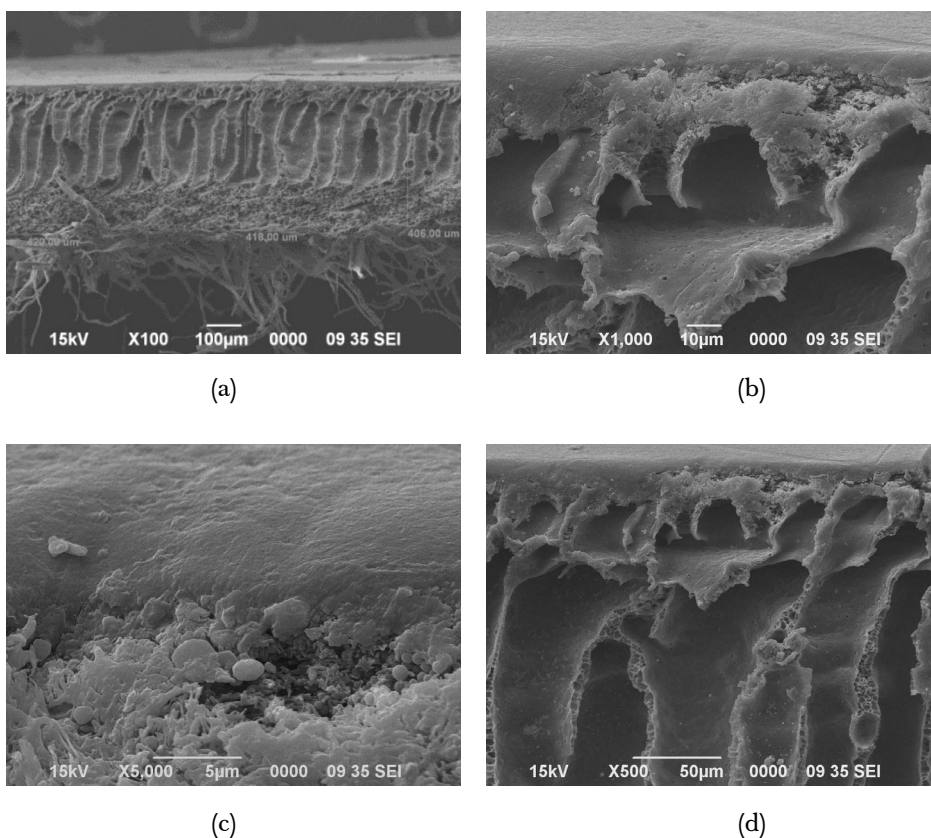
## 2.6 Scanning Electron Microscopy (SEM)

Membrane morphology was examined under high resolution using the scanning electron microscope (SEM). The membrane sample was immersed in liquid nitrogen to break it. Then, the broken out sample was mounted on top of a metal aluminum stub and the magnification up to  $\times 5000$  was observed. The cross sectional view of chitosan-clay composite membrane obtained was analyzed later.

## 3.0 RESULTS AND DISCUSSION

### 3.1 Characterization of Membrane

Casting chitosan solution on the modified polysulfone film surface with addition of clay become practicable. The cross-sectional SEM microphotographs with four different magnification of chitosan-clay composite membrane, which made from casting a chitosan solution containing small amount of clay (the chitosan solution concentration 2 wt%) was shown by Figure 5.1. Besides, the membrane thickness could be estimated from the microphotographs. It was observed that the chitosan-



**Figure 5.1** SEM microphotographs of cross-section of the chitosan-clay membrane; (a)  $\times 100$ , (b)  $\times 500$ , (c)  $\times 1000$ , (d)  $\times 5000$  magnification

clay composite membranes demonstrate the formation of some strong interactions between the membrane interfaces due to its peel strength. The polysulfone surface was completely covered with chitosan-clay and the resulting surface was smooth.

There was a two-layer structure with a top layer and a support layer; where the lower part was exhibited the porous structure of polysulfone film. This verified the existence of a two-layer structure in the composite membrane. The similar hydrophilicity or chemical affinity between the top layer and the support membrane of a prepared composite membrane had several advantages, such as the improvement of structural stability and reduction of top layer thickness. Chitosan-clay layer thickness play an important role on pervaporation separation performance, where it resulting the easy spreading of the top layer solution.

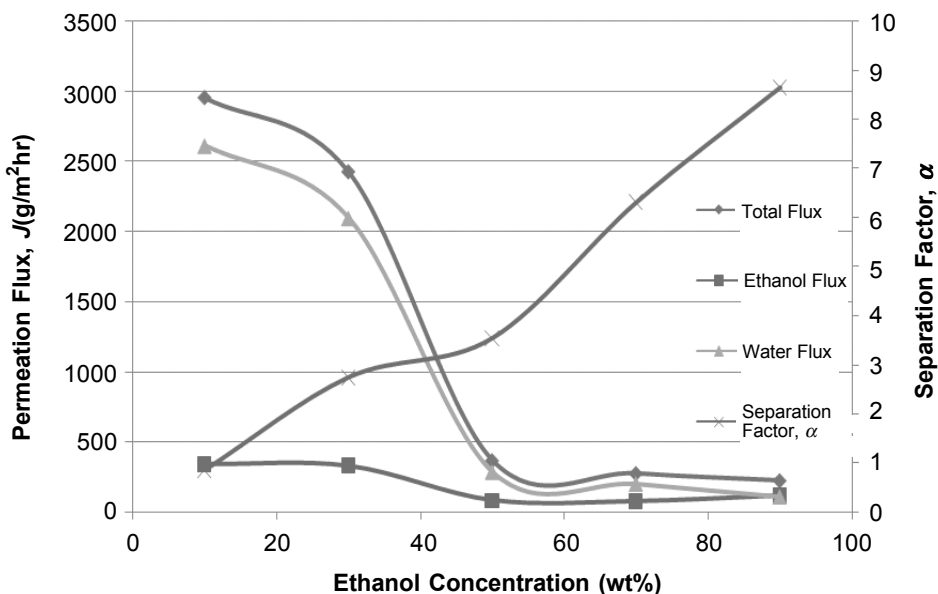
### 3.2 Effects of Feed Concentration on Pervaporation

Basically, the efficacy of membrane in pervaporation was assessed based on the permeation of individual components. In each test a different membrane had been

used and none of them had been used twice. Membrane separation ability could be expressed in terms of permeation flux and separation factor which usually take place in contra-way. Both of them were important parameters in the separation process, which given the opposite relationship that, separation factor increase accompanied by a decrease in permeation flux. Therefore, the extent of permeation of individual components could be determined by plotting the total flux of ethanol-water compositions in the membrane. In this study, the effect of different temperature and feed concentrations of ethanol aqueous solution on the pervaporation performance was obtained.

Many aspects contribute to the separation characteristics of a specific membrane such as the interaction between the permeants, the interaction between the permeant and membrane, and molecular sizes of the feed components [5]. The results for various feed compositions in the pervaporation test were shown below.

Figure 5.2 was demonstrating the permeate flux increased with increasing water content in the feed solution while the selectivity towards water decreased. It is clearly noticed that the total flux and the flux of water were almost close to each other; whereas, the flux of ethanol was negligibly small throughout the investigated range of ethanol composition, indicating that the membrane developed in the present study was hydrophilic nature. Bartels, *et al.* reported that the characteristics of the sorption depended on the difference between the affinity of the components towards the polymer, the mutual interactions of the component, and the way the interactions



**Figure 5.2** Variation of permeation flux,  $J$  and separation factor,  $\alpha$  with different mass fraction of ethanol in feed solution

with the polymer of each component affects the interactions of the other penetrates with the polymer [6].

From the plot, the overall selectivity of the membrane was increased gradually with further increasing the ethanol concentration in the feed. This might be due to the formation of a strong interaction between the membrane and water molecules. Decrease in permeation rate of the organic component, with an increase in the concentration of organic component in the feed solution, might be attributed to the dominant highly water selective of chitosan-clay membrane. As the organic component concentration in the feed was increased, this hydrophilic nature might lead to an increase in the solubility of organic component in the membrane.

Membrane separation factor ( $\alpha$ ) is the ratio of water and ethanol permeabilities, while the permeation flux ( $J$ ) complies with the water content in feed. For hydrophilic membrane, water has the better affinity compare to ethanol. In addition to the strong interaction, the smaller water molecules than ethanol molecules make the diffusion of water easier than ethanol. It is known that when the concentration of the component to be removed is relatively low, pervaporation is especially attractive. Under the condition of high ethanol concentration solution (>50 wt%) the molecular structure of the blend membrane of chitosan and clay was packed much more tightly and restricted the diffusion of permeant, thereby reducing the ethanol permeability as the ethanol concentration increased.

### 3.3 Effect of Temperature

For most of the polymeric pervaporation membranes, the increase of feed temperature results in linear increase of the permeation flux. It is well accepted that increased feed temperature enhances the thermal mobility of the polymeric chain, thus the diffusion rate of the permeating molecules is significantly increased. In other words, considering the driving force of the pervaporation process, the increase of the chemical potential difference in terms of the temperature difference leads to the flux increase [5].

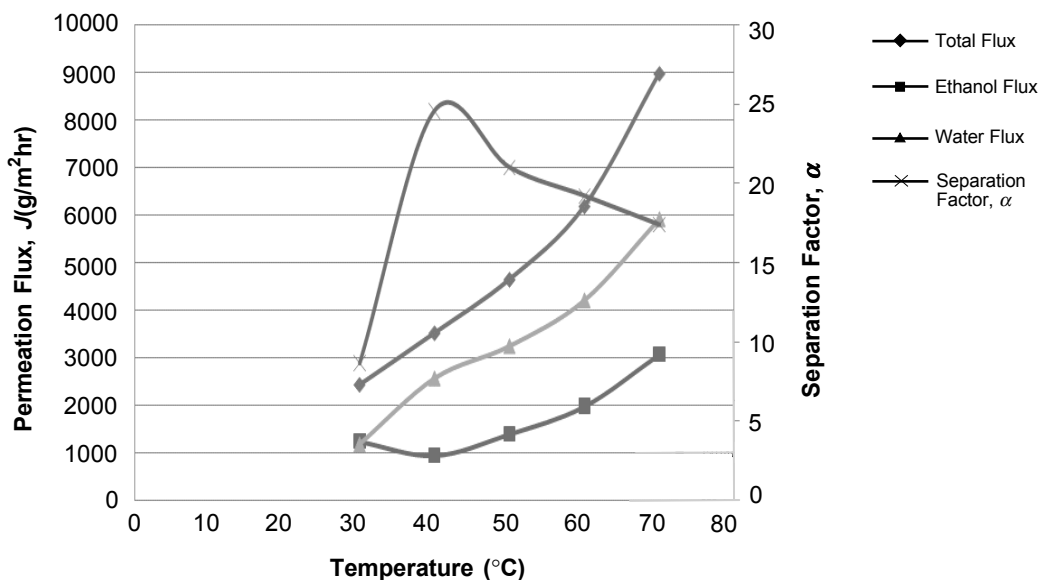
Li, *et al.* stated that the higher  $\alpha$  is obtained using a high ethanol concentration (*i.e.*, 95 wt%) [7]. These experimental results are in agreement with other researchers [8 – 10], as well as the permeation flux increase with an increase of the feed solution temperature. Therefore, the 90 wt% concentration of ethanol was chosen to determine the effects of different temperature towards the pervaporation process.

Since both the permeation flux ( $J$ ) and separation factor ( $\alpha$ ) were influenced by the change in temperature, the pervaporation process was known to be temperature dependence. The results showed the flux increased with temperature, while the separation factor increased from 30 °C to 40 °C and then decreased (Figure 5.3). Generally, the overall selectivity of a membrane is explained on the basis of interaction between the membrane and permeating molecules, molecular size of the permeating species and pore diameter of the membrane.

It was observed that the separation factor increased from 30 °C to 40 °C and then it dropped slowly after 40 °C, this might be because the membrane needed time to enlarge its “holes” which increase the diffusion of water and ethanol but more strongly for water as the smaller molecule than ethanol. At high temperature, the decreasing of the separation factor was probably caused by thermal motion of polymer chains in the membrane.

Figure 5.3 displayed that the total permeation flux was increased throughout the temperature change. According to the classical Eyring theory of diffusion, penetrate-scale transient gaps generated by the thermal motion of polymer chain in the polymer matrix, through which the permeating molecules can diffuse. As the temperature increases, the thermal motion intensified and the transient diffusive gap become larger. Consequently, the transport bulkier ethanol molecules, along with water, were enhanced, leading to an increase in permeate flux and less significant decrease in permeation separation factor.

The permeation flux of ethanol was lower than the permeation flux of water which could be explained by the total free volume theory. The total free volume of chitosan-clay molecules increased when the operating temperature increased, which means that the diffusion of permeating molecules were increasing due to thermal expansion of the polymer chains. Besides, the increasing of total permeation flux might also be caused by the plasticizing effects of water molecules in the membrane. In contrast, at low temperature, only the smaller size of molecules (water) could move through the polymer chains.



**Figure 5.3** Variation of permeation flux,  $J$  and separation factor,  $\alpha$  with different feed temperature



Ethanol transported through the hydrophobic amorphous network of the membrane, thus, the flux depends strongly on the polymer chain segment mobility. Because an increase in temperature could increase polymer mobility, permeation flux of ethanol strongly increased with feed temperature and is more strongly dependent on temperature than water [10]. As the operating temperature increased, the flux also increased but the separation factor should be gradually decreased. This phenomena reflected the change in the permeate concentration. These behaviors could be explained back with the diffusion of components; where in increase of feed temperature made the polymer chain mobile.

#### **4.0 CONCLUSION**

In this study, a hydrophilic clay-incorporated chitosan membrane using a solution technique was prepared. The membranes were used to separate the ethanol-water mixture through pervaporation process. The effects of ethanol concentrations in the feed solutions and the feed solution temperatures on pervaporation performance of the chitosan-clay composite membrane were discussed. Both of the parameters affected the transport of components in the liquid feed and in the membrane. Further, the micro-porous structure of the clay filled chitosan membrane had been observed through SEM. From the microphotographs, the membrane was believed to have a three dimensional, lacy pores structure. Owing to the strong interaction between the chitosan and clay, the unique structure of the membrane was maintained.

Results showed that chitosan-clay composite membrane was attainable to undergo separation of organic solution. The membrane developed was giving positive attributes to the pure polymeric and ceramic membrane combined with asymmetric composite that was both chemically and physically stable.

With an increase of ethanol concentration in the feed solutions, the permeation flux of the membrane decreased and the separation factor increased. This showed that hydrophilic membranes have a better affinity with water than ethanol. Ethanol is normally difficult to diffuse because of its bigger molecules therefore resulted in larger increased of water flux than ethanol flux. Under higher operating temperature, the results showed that the membrane exhibited a higher permeation flux and a lower selectivity. This might due to the reason of the polymer chains; they were more flexible at higher temperatures and caused larger available free volume of polymer matrix for diffusion. Concisely, an increase of feed temperature and water concentration in feed solution enhanced the permeation flux but reduced separation factor.

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