

Modification of Chitosan-Based Membranes Using Zeolite for Pervaporation Separation of Isopropanol-Water Mixtures

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Abstract

In this paper, the performances of zeolite-filled chitosan membranes were studied. The zeolite-filled chitosan membrane was prepared by adding a calculated amount of zeolite into the aqueous acetic acid solution and mixing thoroughly until the solution become homogeneous. A pre-weighed quantity of chitosan was added into the solution and was stirred overnight. Membrane was treated and dried in the similar way as for the homogeneous chitosan membrane. Scanning Electron Micrograph analysis shown that the membrane exhibit a dense structure. The dry membrane samples were weighed and subsequently immersed in a 90 wt% isopropanol-water mixture for 72 h at room temperature. The effective membrane area is 52.8 cm². The downstream pressure was maintained at 3-5 mm Hg by using a vacuum pump. The permeation rate was determined by measuring the weight of permeate collected in a given period of time. The membranes characteristics were determined through swelling test and the pervaporation dehydration of isopropanol-water mixtures. The results showed that, membrane filled with zeolite exhibited a higher permeation flux with some loses in the separation factor. The optimum value for zeolite content in the membrane is about 0.1 wt%. At higher zeolite content in the membrane, the separation factor decreased very significantly which is due to less selective 'leaks' formed around the zeolite crystals during preparation.

Keywords:

Pervaporation, chitosan membrane, zeolite-filled membrane, isopropanol/water mixtures.

Introduction

The pervaporation dehydration of alcohol-water mixtures through hydrophilic polymer membranes have been studied extensively by Huang and Jarvis[1]. But most of the studies were concentrated on the PVA membranes. Only recently, chitosan was found to be very attractive and very promising as the pervaporation membrane material. Chitosan is the partially-deacetylated form of chitin, which is the second

most abundant biopolymer found in nature. Chitosan have been studied as pervaporation membranes [2-5]. However, the pervaporation performance of pure chitosan membrane was not satisfactory due to the larger free volume formed between the molecular chains. Various techniques have been adopted to improve its performance by blending it with other polymers, such as PVA[6] and silk fibroin[7]. Alternatively, improvement can also be obtained by incorporation of zeolite in the membrane matrix. Besides the separation efficiency, the membrane stability in aqueous solution may also be improved.

Zeolite-filled membrane was first introduced by Hennepe et al[8]. Through their studies, it is found that the addition of hydrophobic zeolite to silicone rubber membranes had improved both permeation flux and separation factor of the membrane in the separation of dilute alcohol solution. Many efforts have been done to improve the membrane by blending the hydrophobic polymer with zeolites. But, very little attention have been paid towards using hydrophilic polymer-zeolite pairs blending. For hydrophilic polymer-zeolite pairs, the filler used should be hydrophilic in nature. The hydrophilic zeolite typically have a high alumina to silica content in order to have a high hydrophilicity properties. Zeolite-filled PVA membranes have been extensively studied by Gao and coworkers [9] for the separation of alcohol-water mixtures. These authors noted an increased flux through the membrane for hydrophilic zeolites such as zeolite NaX, CaX, NaA and KA. It was also seen that the fluxes increased with increasing zeolite pore size. Works by Chen et al.[10] also revealed that the separation factor of chitosan membranes can be successfully improved by blending it with zeolite HY.

In this work, chitosan membranes were modified by blending it with zeolite 13X at varying zeolite weight ratios to chitosan. In the preliminary stage, the optimum zeolite loading were determined. The zeolite-filled membranes were further investigated for the pervaporation dehydration of isopropanol-water system.

Experiments and Materials

Zeolite 13x were purchased from Sigma-Aldrich(M). Chitosan was prepared from chitin which was obtained from a domestic shrimp shells. Acetic acid, sodium hydroxide and hydrochloric acid were purchased from Merk. Isopropanol and ethanol were purchased from T.T. Baker(USA).

Membrane preparation

The chitosan membrane was prepared by casting a chitosan solution onto a petri dish and allowing the solvent to evaporate. The zeolite-filled chitosan membrane was prepared by adding a calculated amount of zeolite into the aqueous acetic acid solution and mixing thoroughly until the solution become homogen. Then a pre-weighed quantity of chitosan was added into the solution and was stirred overnight. Membrane was treated and dried in the similar way as for the homogeneous chitosan membrane.

Membrane characterization

Scanning electron microscopy(SEM) (Philips XL-40) was used to investigate the morphology of the membrane. 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. The dry membrane samples were weighed and subsequently immersed in a 90 wt% isopropanol-water mixture for 72 h at room temperature. The swollen samples were weighed immediately after careful blotting.

Pervaporation Experiment

Pervaporation experiments were carried out in a continuous pervaporation apparatus as illustrated in Figure 1. The effective membrane area is 52.8 cm². The downstream pressure was maintained at 3-5 mm Hg by using a vacuum pump. The permeation rate was determined by measuring the weight of permeate collected in a given period of time. The permeate compositions were analyzed according to Kalfisher method [11]. The separation factor was calculated from:

$$\alpha_{H_2O/Isopropanol} = \left(\frac{Y_{H_2O} / Y_{Isopropanol}}{X_{H_2O} / X_{Isopropanol}} \right) \quad (2)$$

where Y_{H_2O} , $Y_{Isopropanol}$ and X_{H_2O} , $X_{Isopropanol}$ are the weight fractions of water and isopropanol in the permeate and feed, respectively. Pervaporation separation indexes (PSI) were determined from equation:

$$PSI = J(\alpha - 1) \quad (3)$$

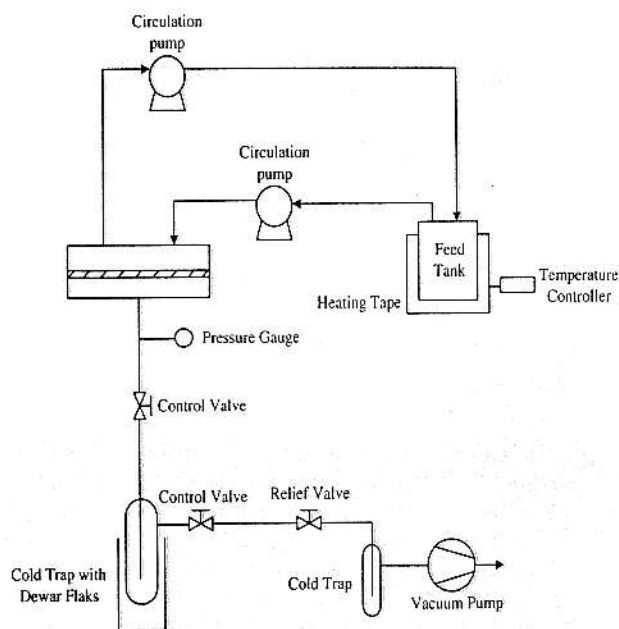


Figure 1- A schematic Diagram of Pervaporation Apparatus

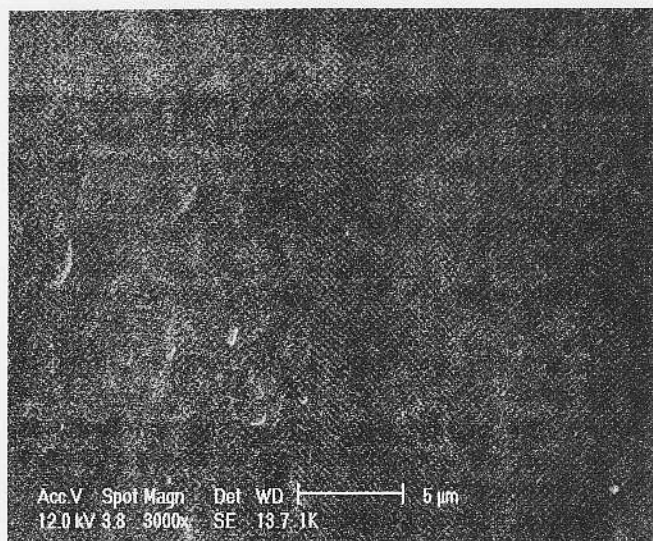
Results and Discussion

Structure morphology of zeolite-filled chitosan membrane

SEM was employed to study the morphology of the zeolite-filled chitosan membranes. Figure 2 shows the picture of cross-section of the membrane prepared from 0.1 wt % zeolite. The picture shows that, the pore is not visible at high magnification. The zeolite-filled membrane shows a dense structure. However, the presence of zeolites in the membrane cannot be seen for the fact the zeolite content is at very low weight percent.

Swelling characteristic of zeolite-filled chitosan membranes

Figure 3 shows the swelling degree versus the zeolite content in the chitosan membrane. The swelling degree of the membranes is decreased with zeolite content except at 0.1 wt% zeolite content. The swelling degree shows a maximum value at zeolite content 0.1 wt%. At this point, it is believed that the increase in swelling is due the coupling sorption. At zeolite content of more than 0.1 wt% in the membrane, the hydrophilicity of the membrane is reduced resulting in the decrease of swelling degree.



(a)



(b)

Figure 2- SEM of (a) Surface View (b) Cross Section Membrane Prepared with 0.1 % Zeolite

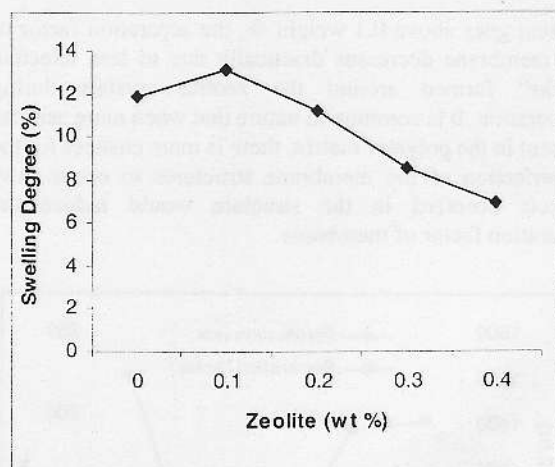


Figure 3-The Swelling Degree of Zeolite-Filled Membrane as a Function of Zeolite ratio at 90 wt% Isopropanol in feed

Effect of zeolite content on the pervaporation performance

The pervaporation performance of zeolite-filled chitosan membranes at 90 wt% isopropanol in the feed solution was investigated in terms of their permeation flux and separation factor. The results were shown in Figure 4. For the entire range of zeolite content, the total permeation flux is increased with the increase of zeolite content in the membrane. The increase in the total permeation flux become more drastic after zeolite content in membrane is above 0.3 wt%. The increase in the permeation flux is due to the facilitation of transport of penetrant molecules through the membrane filled with zeolites. For the filled membrane, the penetrant can have two different channel for the transport to occur. That is transport through polymer matrix and through the zeolite pores. The pore size of zeolites 13 X is believed to be large enough for both water and isopropanol to diffuse through the zeolite channel. As the zeolites content increases, the permeation flux also increases.

However, the separation factor is decreased with the increase of zeolite content for the whole range zeolite content studied. The largest separation factor for the filled-membrane is achieved at 0.1 wt% zeolite in membrane. It can be said that both water and isopropanol transport are possible through the zeolite pores. At zeolite content of 0.1 wt%, the reduction in the separation factor is not very pronounced since most of the water and isopropanol transport through the non porous chitosan matrix. The presence of zeolite in membrane results in the decrease of chitosan concentration. At zeolite content 0.1 wt%, the transport of permeating component through zeolite pores will eventually become saturated and as a result, the permeating molecules for both components only have to depend on chitosan channel. This is why, the separation factor is slightly decreased from 0 wt % zeolite to 0.1 wt% zeolites in the membranes. As the zeolite

content goes above 0.1 weight %, the separation factor of the membrane decreases drastically due to less selective "leaks" formed around the zeolite crystals during preparation. It is common in nature that when more zeolites present in the polymer matrix, there is more chances for the imperfection of the membrane structures to occur. Any defects occurred in the structure would reduce the separation factor of membrane.

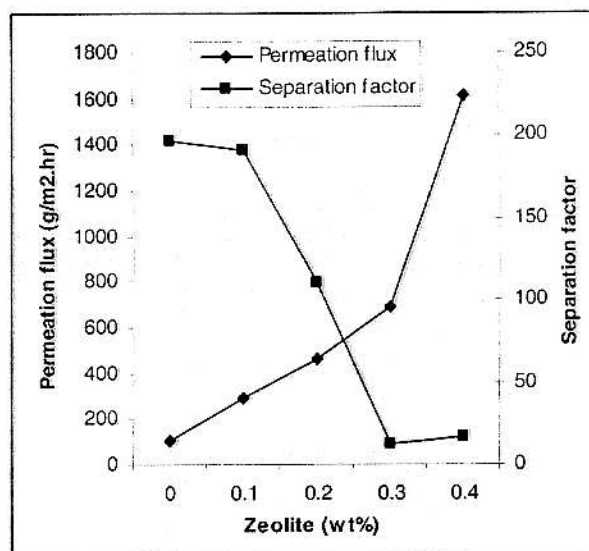


Figure 4 - The Total Permeation Flux and Separation Factor at Different Zeolite Weight Percent

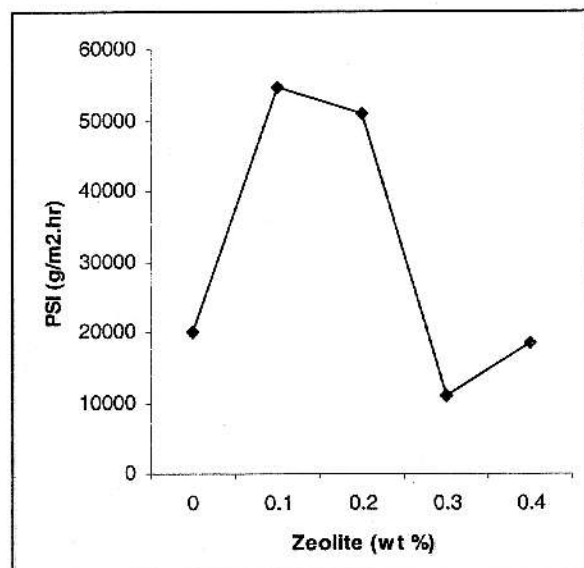


Figure 5- Pervaporation Separation Index at Different Zeolite Content

Figure 5 shows the pervaporation separation index (PSI) at different zeolite weight percent. From the graph, membranes filled with zeolite show a higher value of PSI for 0.1 and 0.2 wt% of zeolites. The maximum value at 0.1 wt% zeolite indicating that the zeolite blending technique has a good potential in improving the membrane pervaporation properties.

Conclusions

The following conclusions can be withdrawn from the present study:

1. The total permeation flux of the membrane was improved after introducing suitable zeolites into polymer matrix.
2. Membranes filled with zeolite exhibited a lower separation factor. The decrease in separation factor is more pronounced at zeolite content over 0.1 wt%.
3. Membrane with 0.1 wt% zeolite content give the highest value of PSI. It shows that membrane blended at 0.1 wt % of zeolite is more effective for the pervaporation separation of isopropanol-water mixtures.

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