CS-011

EFFECT OF TEMPERATURE AND COMPOSITION ZEOLITE ON THE PERFORMANCE MEMBRANE-ZEOLITE FOR SEPARATION OF ETHANOL-WATER BY PERVAPORATION

Ridwanto[1,*], **Rahmat Nauli**[2], **Ani Sutiani**[2], and **Anny Sartika Daulay**[1]

[1]*Department of Pharmacy, UMN Al-Washliyah Medan;*
[2]*Department of Chemistry, State University of Medan*
**Email: Rid. fillah66 @ gmail.com*

ABSTRACT

The aim of this study is to create a membrane chitosan derived from shrimp shell waste. Membranes were obtained by modifying the natural zeolites with various compositions to improve membrane performance. They will be determined the value of the flux and selectivity by varying the temperature and the operating pressure of the separation process in pervaporation of ethanol and water. Results of studies have shown that chitosan-making process begins with the isolation of chitin from shrimp shell waste through deprotonation with NaOH and demineralization with HCl. Transformation of chitin into chitosan was done through deacetylation using sodium hydroxide. From the results of characterization by using IR spectrophotometer earned the degree of acetylation of chitosan membranes of 83.92%. Data of Membrane performance test shows that the increased temperature caused the flux permiasi increased while selectivity decreases. While the addition of zeolite to the formation of chitosan-zeolite membranes causing membrane performance increased where permiasi flux and membrane selectivity increased in the separation of water ethanol mixtured by pervaporation. Laboratory-scale testing at a pressure of 200 mmHg was indicated that the highest flux values obtained at 55°C with a flux value (J) output reached 10.492 L / m 2 h, and the selectivity, α = 18.379 obtained on the composition of the addition of 20% zeolite. While the highest selectivity obtained at 35°C with a value of α = 39.251 and the value of the flux (J) = 4.431 L / m^2 hour were obtained in the addition of 20% zeolite.

***Keywords**: Chitosan, Natural Zeolites, Membrane, Flux, selectivity*

INTRODUCTION

Today research on membrane technology continues to evolve at a rapid pace, as this technology has the functionality associated with the process of separation, purification and concentration. In general, a semi-permeable membrane is a thin layer which serves to separate a mixture of several components based on the physical properties and chemical properties. Pass through the membrane separation process is due to the driving force such as pressure, temperature, electric potential and the chemical potential. A critical criterion in determining the performance of the membrane as a permeable separator is selectivity and permeability. The properties depend on the number and size of pores. Therefore, to obtain a specific membrane with a pore size specified, then the operational conditions such as concentration, temperature, pressure and duration of treatment either during manufacture of the membrane and in the process must be carefully monitored (Kesting, 1985)

Some other factors that must be considered is the membrane resistance to chemical and mechanical strength such as compressive strength and tensile strength during the separation process will determine the effectiveness of the performance of the membrane. Therefore the selection of either the manufacture of membrane polymer and non-polymer material affects the bait and the results to be obtained. Jijin et al (2000) reported that the presence of deformation of the membrane pore structure and widening during the treatment process in the membrane causes a decrease in the mechanical properties of the membrane. Besides, the composition of the printing solution greatly affects the performance of the membrane.

One of the important issues in the development of the membrane is making membranes of natural polymers, because the membrane is made of natural materials will allow the membrane is dissolved and reformed back when the material is not used anymore. Research that has been done related to the membrane is the manufacture of cellulose acetate membrane of the material. Marlina (1998) has conducted research meeting manufacture of cellulose acetate membranes for the separation of a mixture of methyl tertiary butyl ether (MTBE) with methanol in pervaporation. Research results indicate that maximum performance is obtained on the membrane flux value of 12.6 L / m^2 h and selectivity of 39.8%.

One natural polymers that are reasonably priced and widely available is a chitosan compound, which has a structure similar to that of cellulose acetate polymer compound carbohydrate group. Research relating to the manufacture of chitosan showed that chitosan can be made from materials containing chitin by deacetylation process. Development of chitosan into a membrane that has a specific selectivity and permeability will be able to increase the value of a higher and wider application of chitosan compounds. The research that has been conducted by Glasser et al (1999) showed that the greater the concentration of chitin membrane selectivity of the membrane rises, while the permeability decreases in the manufacturing process as osmosis membrane behind. Chitosan which is a derivative of chitin potential to be used as a dialysis membrane (Krajang et al, 2000). Membrane composition of chitosan-silica (Ridwan, I and Rispiandi, 2011) and chitosan membrane-type zeolite-A (Saim, N & Hashim H, 2008) was used to separate the isopropanol-water pervaporation.

Zeolites are alumino silicate compound that is composed of the main elements of silicate (SiO_2) and alumina (Al_2O_3).Zeolites are also commonly referred to as 'molecular sieve' / 'molecular mesh' (molecular sieves)because the zeolite has a pore size of m o lekuler so capable of separating or filtering molecules of a certain size.When zeolite is added to the chitosan, the zeolite will be dispersed into the chitosan so that the structure of chitosan be changed.Zeolites are polar so it tends to absorb polar compounds.Results of research conducted Nasrun (2005) shows b ahwa modified cellulose acetate membranes by addition of zeolite NaY + can increase the selectivity of 1182 into 1634. While the research conducted Jewel (2008) suggests the addition of natural zeolite Malang on cellulose acetate membrane can increase the flux of 1.35 to 1.4 times and selectivity of 3.5 to 8.2 times compared to pure cellulose acetate.

Ethanol is one of the chemicals that are very important because it has a very broad benefits, among others, as a solvent, liquid fuel, disinfecting materials, raw materials in various industries, and so on. In use, ethanol is often required with high purity, which can be obtained by the distillation process. However, the process of distillation of ethanol from water is only able to produce ethanol with a maximum of 95.6% purity. At these concentrations will form an azeotrope so if distilled further will not result in higher ethanol concentrations (Nasrun, 2005). Different boiling point azeotrope with a boiling point of each pure substance component azeotrope. At 1 atm pressure, the boiling point of water is 100°C and a boiling point of ethanol was 78.3°C, while the azeotropic boiling point is 78.174°C.

Widodo et al (2004) states that one of the techniques that can be done to produce ethanol with a purity of 100% can be *exstractive distillation* process (distillation-extraction). This process requires the addition of benzene in ethanol-water azeotrope system in order to obtain a benzene-water azeotrope which is then distilled to obtain ethanol as a distillate. But ethanol containing a little benzene, which would be very dangerous if ethanol is used in medicine and cosmetics industry. Therefore we need another technique to separate ethanol-water in order to obtain absolute ethanol.

In this research has been done taking chitin from shrimp shell waste will be converted into chitosan.Furthermore, chitosan will be processed into a specific chitosan membrane through the process of dissolution, evaporation, and solidification. Membranes obtained will be added to the natural zeolite to improve the performance of the membrane. The membrane obtained will be determined value of flux and selectivity of the separation process pervaporation of ethanol and water.

METHODS

This was purely an experimental study in the laboratory. The study design for manufacturing chitosan membrane through pervaporation process using chitosan from shrimp shell waste that was modified by the addition of natural zeolite planned in this study consists of six stages, namely: (a) the isolation or separation of chitin from shrimp shell and head (waste shrimp), which includes the removal of the protein (deproteinization), and removal of minerals (demineralization), and p roses transformation into chitosan by deacetylation using strong alkaline solution of high concentration. (b) Preparation of zeolite including the activation of natural zeolite (c) Preparation of pure chitosan membrane. (D) Preparation of membranes modified with natural zeolite (e) Characterization of the membranes covering the determination of flux and selectivity. (F) trials or applications resulting membranes for the separation process a mixture of ethanol and water by pervaporation.

Plans for natural zeolite-chitosan membrane with the basic ingredients of shrimp shell waste basically make membranes in pervaporation. Pervaporation process is one method of separation with membranes (permeation) followed by evaporation. Membrane material used is a combination of organic and inorganic compounds, so it is often said to be a hybrid membrane/composite.

Research has been done a dalah isolation of chitin and chitosan manufacture of shrimp shell waste, natural zeolite preparation until the activation phase zeolite membrane production test, pervaporation membrane applications, as well as the characterization of the resulting membrane. The isolation or separation of chitin from shrimp shell and head (shrimp waste) performed by deproteinization process using NaOH 1M for 3 h at 80 ˚ C with continuous stirring, followed by filtration and washing until neutral residue. Then follows the demineralization using 1M HCl and allowed to stand for 12 hours at room temperature. The mixture was then filtered and the residue washed and washed until neutral. Transformation of chitin into chitosan done through deacetylation with 60% NaOH while stirring for 4 hours at a temperature of 80 ^{o} C. The mixture was then filtered, washed with distilled water and dried in an oven to a temperature of 80 ˚ C for 4 hours. (Ridwanto, 2007). Phase whitening performed by the addition of 100 mL of H_2O_2 3% allowed to stand for 24 hours. The mixture was filtered and then washed with distilled water and dried in an oven at 80 ˚ C for 4 hours and the results are characterized by IR.

Zeolite preparation is done by destroying the zeolite using a ball mill and then do the sifting with a size of 150 mesh. The resulting zeolite activated by heating at a temperature of 200°C to 900°C at a pressure of 1 atm. Zeolite activity performed with the aim to increase the surface area and adsorption capability.

Making the pervaporation membrane made by mixing chitosan polymer and solvent aetat acids with additional natural zeolite to produce chitosan membrane-Natural zeolites. Natural zeolite used is varied between 5% -20%. Pervaporation process is done by varying the temperature and pressure. Thin layer obtained by casting process is molding above the glass plate with a thickness of the membrane according to the thickness selotif used. The mold material left for some time to evaporate the solvent, thus forming a thin layer of the membrane. Flowchart of the study are presented in Figure 1.

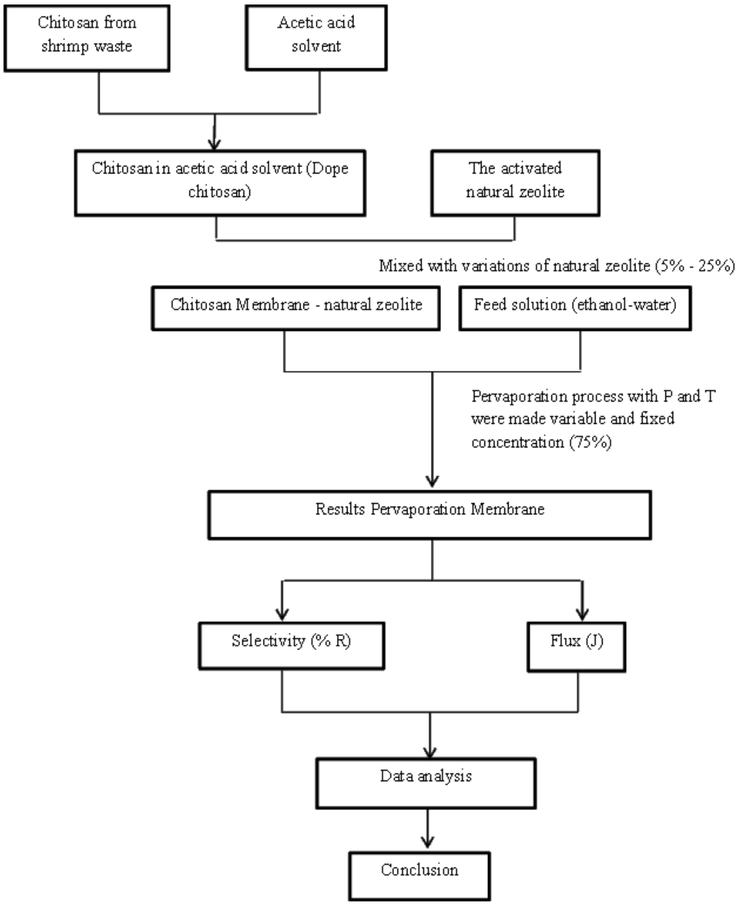

Figure 1. Flowchart of Research

RESULTS AND DISCUSSION

Research has been done to date is the manufacture of chitosan by doing isolation of chitin from shrimp shell waste and the process of transformation of chitin into chitosan through the deacetylation process. After it is done making of chitosan-natural zeolite membrane to modify the content of zeolite is used. Membrane characterization performed in this study is the determination of membrane flux and selectivity determination, so as to obtain the effect of adding zeolite concentration on the performance of the resulting membrane for separation of ethanol-water. It also made changes in temperature and pressure in membrane applications, so it can be studied the effect of changes in temperature and pressure on the performance of the resulting membrane.

Making Chitosan. The process of Making chitosan begins with the isolation of chitin from shrimp shell waste that has been washed, dried and powdered by means ground and sieved to 150 mesh size. Then the process deproteinasi with NaOH and demineralization with HCl. Transformation of chitin into chitosan through deacetylation using NaOH.

Deproteinasi is a process of separation or release of the bond between the protein and chitin. With this process, the protein will be separated and form Na-proteinat that can dissolve and disappear during the process of washing and filtering. This is done with the color of the solution changes from clear to brown. The filtrate brown solution and precipitate obtained was pure white. The next process is depigmentation using hydrogen peroxide oxidizer. Depigmentation is a color separation process and the obtained results are white membrane. The next process is demineralized by using HCl to remove minerals mainly $CaCO_3$ and $Ca_3(PO_4)_2$. While deacetylation stage is the process of eliminating or reducing the acetyl group (-$COCH_3$) and replaced by hydrogen atoms so that the amide groups (-$NHCOCH_3$)turns into an amine group (-NH_2)

From the results of characterization by IR spectrophotometer obtained degrees aseti Outcome chitosan membrane by 83,92%. This value is obtained from the IR spectrum by comparing absorbance (absorbance) carbonyl at 1655 cm $^{-1}$ wave number of the acetyl group and the uptake of NH at 3444 cm $^{-1}$ wave number of amine groups, as shown in Figure 2.

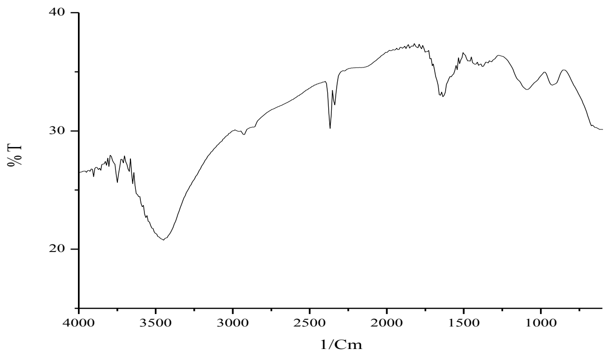

Figure 2. IR spectra of Chitosan Membrane

Synthesis Chitosan-Natural zeolite membrane. Manufacture of membranes made by phase inversion method through solvent evaporation technique. The membrane is made of chitosan and chitosan with the addition of natural zeolite. Used to dissolve chitosan acetic acid. Making chitosan *dope* done by mixing chitosan piecemeal in order to obtain a mixture of 15% -b chitosan. The mixture is then stirred using a magnetic stirrer for 24 hours until dissolved perfectly and form a homogeneous solution. Results stirring form a clear solution. Then the *dope* into chitosan added gradually natural zeolite with a variation of 0, 5, 10, 15, and 20% of the weight of chitosan, stirring constantly so that all of the zeolite dispersed perfectly into *dope.* The mixture is then stirred for 24 hours to form a homogeneous mixture, and stored in the refrigerator to eliminate bubbles. Then left in the open air until it reaches room temperature. The formation of a thin layer of the membrane is done by pouring the solution over the glass plate.

Layer formed is left at room temperature to evaporate the solvent, and then placed in a desiccator for 3 days before the membrane is used. The results show that the pen gamatan chitosan membrane-produced natural zeolite white.

Effect of Temperature on Performance Membrane Feed. To study the effect of feed temperature, experiments were performed by varying the temperature of the feed at a temperature of 35° C - 55°C at a pressure of 200 mmHg.

In general, the feed temperature rise will increase the flux and lower selectivity to the feed solution. With increasing temperature on pervaporation process, diffusion of molecules into the membrane permeation rate is increased so that the total becomes higher and lower separation factor. While the addition of zeolite will cause an increase in the flux and selectivity of the membrane. Effect of feed temperature on the experimental results can be seen in Table 1.

The data in Table 1 shows that the increase in temperature will cause the value of the flux increased while the selectivity decreases. This phenomenon is due to the double effect of the temperature on the driving force of mass transfer and membrane permeability.

Table 1. The flux and selectivity of membranes at various temperatures

No.	Membrane Code	Flux (J) Membrane At Various Temperatures			Selectivity (α) Membrane At Various Temperatures		
		35°C	45°C	55°C	35°C	45°C	55°C
1	KZA-00	0.441	2.083	3.301	30.347	18.379	9.640
2	KZA-05	1.254	3.753	4.213	35.913	20.347	10.484
3	KZA-10	1.768	5.207	7.285	37.191	21.651	12.309
4	KZA-15	2.967	7.093	8.469	38.492	22.913	16.532
5	KZA-20	4.431	8.253	10.492	39.251	27.214	18.379

The increase in temperature causes an increase in thrust force mass transfer (partial pressure and chemical potential) and increase the thermal motion in the polymer chain at random, thus increasing the empty space in the polymer. While the increase in vapor pressure and membrane permeability due to the influence of temperature causes an increase in the flux and selectivity decrease significantly. The decrease of the selectivity seen from the water concentration in the permeate decreased along with the increase in temperature.

From the data in Table 1 also can be argued that the addition of zeolite to the formation of chitosan-zeolite membranes causing increased membrane performance where flux membrane permeation and selectivity increased in the separation of a mixture of ethanol water pervaporation. Hydrophilic properties of chitosan and polarity zeolite membrane leads to a tendency to absorb water molecules than ethanol so as to increase the concentration of ethanol. The increase in membrane performance in line with the increase in the amount of zeolite is used, however, can not be determined optimum conditions the addition of zeolite to the performance of the resulting membrane. Testing laboratory scale at a pressure of 200 mm Hg indicates that the highest flux values obtained at 55°C, with a value of flux *(J*) output reached 10.492 L/m^2.jam;and selectivity, α = 18.379, which was obtained on the composition of the zeolite addition of as much as 20%.While the highest selectivity was obtained at a temperature of 35°C, with a value of α = 39.251 and the value of the flux (J) = 4.431 L/m^2.jam, obtained on addition of 20% zeolite. In the graph, the data of temperature and composition of the zeolite membrane performance is presented in Figure 3 and 4.

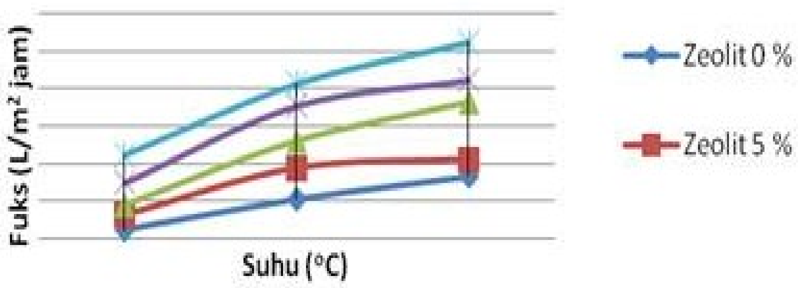

Figure 3. Effect of Temperature Feedback and composition of zeolite against Chitosan Membrane Flux

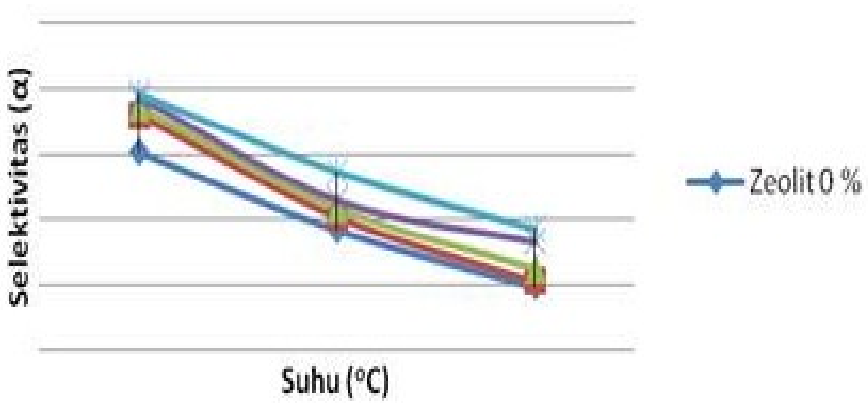

Figure 4. Effect of temperature and composition of the zeolite Feed for Chitosan Membrane Selectivity

CONCLUSION

Making chitosan process begins with the isolation chitin from shrimp shell waste through a process deproteination with NaOH and demineralization with HCl. Transformation of chitin into chitosan done through deacetylation using NaOH is a strong base. From the characterization by IR spectrophotometer obtained the acetylationdegree of chitosan membrane was 61.09%.

The increasedof temperature caused permiasi flux increased while the selectivity decreases. While the addition of zeolite in the formation of chitosan-zeolite membrane caused the membrane performance increased where permiasi flux and selectivity increased in the separation membrane water pervaporation of ethanol mixture. Beside laboratory scale testing at a pressure of 200 mm Hg indicated that the highest flux values obtained at 55°C with a value of flux (J) output reached 10.492 L / m^2h, and selectivity, α = 18.379 obtained on the composition of the zeolite addition of 20%. While selektifi highest bags obtained at 35°C with a value of α = 39.251 and the value of the flux (J) = 4.431 L/m^2h were obtained on addition of 20% zeolite.

REFERENCES

Glasser, Wolfgang, G., Samaranayake.,Gamini., Toffey., and Ackah., (1999), *Chitin-base Coating,* United States Patent, 5, 900,479.

Jijin, G., Cui, Y., Yan,Y., and W. Jiang, (2000) The Effect of Structure on Pervaporation of Chitosan Membrane, *.Journal. of Membrane Science,*165, page 75-81.

Kesting, R.E., (1993), *Synthetic Polymeric Membranes,* John Wiley & Sons, EdisiKedua, New York.

Krajang, S.J., Anil Kumar Anal, Willem F. Stevens., (2000), *Separation of Biomolecules Through Chitosan membranes in Continous Dialyzing Chamber,* Abstact.

Marlina., (1998), *Pembuatan Membran Rapat Selulosa Asetat untuk Pemisahan MTBE-Eter dengan Pervaporasi,* Tesis Magister, Program PascaSarjana, ITB, Bandung.

Nasrun., (2005), Studi Pemakaian Zeolit untuk Meningkatkan Perfomansi Membran, *Prosiding National Conference On Chemical Engineering Science and Applications 9ChESA),* Universitas Syiah Kuala, 83-92.

Permata, A.A., (2009), *Aplikasi Membran CA/Zeolit untuk Pemisahan Campuran Alkohol-Air,* Tesis Magister, Institut Teknologi Bandung, Bandung.

Ridwanto., (2007), Pembuatan Membran Kitosan UntukPemisahan Ion Cd(II) dalam Air*, Laporan Penelitian,* Dinas Pendidikan Sumatera Utara Subdis Pendidikan Tinggi, Medan.

Ridwan, I dan Rispiandi., (2011), Pembuatan Membran Komposit Kitin-Sekam Padi untuk Proses Pervaporasi, *Journal Fluida,* VIII (1), page 12-17.

Saim, N and Hashim Hassan., (2008), Preparation of Pervaporation MembraneUsing A-Type Zeolite Filled Chitosan Membrane for The Separation of Isopropanol / Water Mixtures, *Jurnal Teknologi,* 49(F), 197-205.

Widodo, S., I.N Widiasa., dan I.G. Wenten., (1995), Pengembangan Teknologi Pervaporasi Untuk Produksi Etanol Absolut, ITB, Bandung.