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The effect of glutaraldehyde concentration and immersion duration on cellulose acetate/chitosan composite membrane crosslinking and its application for ethanol/water pervaporation

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Abstract

Pervaporation is an alternative process for mixture separation because its advantages in term of energy saving and more environmentally friendly. Cellulose acetate (CA)/ chitosan (CH) composite crosslinked with glutaraldehyde (GA) can be used for pervaporation membrane for separating ethanol and water mixture. Crab shell which is an abundance waste can be used as source of chitosan. The purpose of the present study was to determine the optimum concentration and immersion duration of GA for the pervaporation performance of CA 20% and CH 20% composite membrane. The result of the present study indicate that 0.3 % (w/w) GA compared to 0.1% (w/w) and 10 minutes immersion give the best membrane result with selectivity and flux 302.92 and 131.41 g/m^{2}h, respectively.

Keywords: pervaporation, membrane, cellulose acetate, chitosan, glutaraldehyde.

Full length article **Corresponding Author*, e-mail: *ernawati@unpad.ac.id*

1. Introduction

The pervaporation (PV) separation method is a more environmentally friendly method and uses lower costs [1,2]. In order to obtain separation with high purity, the separation must be carried out on a molecular scale for which PV can be the best method [2]. PV commonly used in the process of separating azeotropic mixtures and mixtures that have relatively the same chemical and physical properties [3]. This process uses a semi-permeable dense membrane. Molecular transport in PV occurs by a solution-diffusion mechanism consisting of three stages, namely sorption, diffusion, and desorption [4]. The advantages are that it can be operated under normal (not extreme) conditions, has high separation capability, and is energy [5,6]. The membrane chemical properties have to be relatively the same with the substance which wanted to be absorbed. Therefore, the separation of PV is strongly influenced by the composition of the membrane. For dehydration of ethanol, hydrophilic membrane is needed [7,8]. One of the most commonly used hydrophilic membranes is cellulose acetate (CA). CA is a derivative of cellulose and widely used in various fields such as adhesives, film materials commonly used in cameras, or in separation processes [9]. CA is commonly used as a membrane material, because it is easy to obtain, environment friendly, and hydrophilic. The hydrophilicity of the membrane can be increased by adding chitosan (CH). CH has good hydrophilic properties and can be obtained from deacetylation of chitin from shrimp and crab shells [10]. CH has been widely used as a PV membrane such as composited with poly(tetrafluoroethylene) (PTFE) to improve the membrane performance in isopropanol dehydration [11], also CH membrane was composited with polybenzoimidazole (PBI) also for isopropanol dehydration [12]. The addition of CH can increase the hydrophilicity and selectivity of the membrane. CA and CH swell easily because of their hydrophilic nature [13,14]. Swelled membrane selectivity will decrease and it is known that cross-linking can reduce swelling [13]. Crosslinking is one of many methods of membrane modification to improve membrane performance [15]. The research carried out in this project was to observe the effect of glutaraldehyde (GA) as a crosslinker between SA-KS membrane on ethanol/water pervaporation. GA is reactive because it has two carbonyl groups (C=O) [16]. The factors that influence the crosslinking reaction are the concentration and immersion time of the crosslinker.

2. Materials and methods

2.1. Materials

The materials used in this study were cellulose acetate (Sigma-Aldrich), crab shells (collected from Cirebon, West Java), acetone (Merck), ethanol (analytical grade) (Merck), liquid nitrogen, glutaraldehyde 25% (Merck), sulfuric acid (Merck), sodium hydroxide (Merck), glacial acetic acid (Merck) and hydrochloric acid 37% (Merck).

2.2. Preparation of Chitosan

2.2.1 Demineralization

The crab shell was boiled, washed with water, then dried in an oven at a temperature of 110-120°C for one hour. After drying, the crab shell was ground and sieved. Crab shell powder was soaked with 1.5 M HCl with a ratio of powder and solvent 1:15 (w/v). The mixture was heated at a temperature of 70-80°C for 4 hours while stirring, then filtered. The solids from the filter were washed with distilled water to pH 7. Furthermore, the solids were dried in an oven at 70°C for 24 hours [17].

2.2.2 Deproteination

The yellowish-brown dried crab skin powder resulting from demineralization was put into a beaker, then 3.5% (w/w) NaOH solution was added with a ratio of 1:10 (w/v). The mixture was heated at a temperature of 65-70°C for 4 hours while stirring. Subsequently, the solids were filtered and cooled to obtain a yellow precipitate, then washed with distilled water to pH 7 [18].

2.2.3 Deacetylation

A total of 5.58 g of the yellow precipitate that had been produced in the deproteination process was put into a 60% (w/w) NaOH solution in a ratio of 1:20 (w/v), while stirring at a temperature of 120°C for 4 hours. The result is a filtered slurry, the precipitate is washed with distilled water to pH 7. After that, the solid is dried at 70°C in an oven for 24 hours [17].

2.3. Preparation of Composite Membrane CA-GA-CH

As much as 4 g of cellulose acetate was added slowly to 16 g acetone while stirring. After that, 20% w/w CH solution was added to the CA solution slowly. The solution that has been made was stirred for 24 hours and then put in the refrigerator for another 24 hours. The solution was molded by a phase inversion technique, previously conditioned at room temperature. The CA-CH membrane that had been separated from the mold was immersed in a GA solution with concentration variation of 0.1; 0.2; 0.3; 0.4; and 0.5 w/w %, and with immersion time variation of 5, 10, 15, 20, and 30 minutes. The soaked membrane then rinsed with distilled water and dried in a desiccator.

2.4. Characterization CA-GA-CH Membrane

2.4.1 Swelling Degree

The membrane was cut to a size of 2 × 2 cm^2 then weighed. After that, the membrane was soaked for 24 hours

$$DS = \frac{Ww - Wd}{Wd} \times 100\% \ldots \text{(Eq. 1)}$$

Where DS is the degree of swelling (%), Ww is the mass of the wet membrane (g), and Wd is the mass of the dry membrane (g).

2.4.2 SEM and FTIR Characterization of Composite Membrane CA-GA-CH

SEM characterization was carried out to determine the morphological structure of the CA-GA-CH membrane. SEM analysis was carried out on a cross-section of the CA-GA-CH membrane with concentrations of 0.1 and 0.3%. FTIR characterization was carried out to determine is the crosslinking reaction formed by analyzing the functional groups present in the CA-GA-CH membrane.

2.5. Pervaporation

The membrane was placed on a horizontal support in the design of the pervaporator. 100 g of 96% ethanol was put into a flask and heated to 40°C. The pervaporation process was carried out at 0.5 mbar. The permeate was taken four times every hour. The concentration of the permeate was determined to calculate the selectivity by equation (2) and its mass was weighed to calculate the flux by equation (3). Where α is the separation selectivity, *Yw* is the concentration of water in the permeate, *Ya* is the concentration of ethanol in the permeate (%), *Xw* is the concentration of water in the feed (%), and *Xa* is the concentration of ethanol in the feed (%). J is the total flux value (g/m^2h), A is the area of the membrane (m^2), and dm/dt is the slope of the graph between permeate mass against time.

$$\alpha = \frac{(Yw/Ya)}{Xw/Xa} \ldots \text{(Eq. 2)}$$

$$J = \frac{1}{A}\frac{dm}{dt} \ldots \text{(Eq. 3)}$$

3. Results and Discussions

3.1. Chitosan Prepared from Crab Shell

The CH yield of chitin deacetylation was 82.82%. CH was obtained by processing the crab skin in 3 stages, namely demineralization, deproteination, and deacetylation. Demineralization was carried out by soaking the crab shell powder in 1.5 M HCl. $CaCO_3$ reacts with HCl to form $CaCl_2$ which is soluble in water. After that, the protein contained in the crab shell was removed by adding 3.5% (w/w) NaOH which can be seen in Figure 1. The protein in the crab shell binds with Na^+ ions from NaOH to form sodium proteinate so the crab shell left with chitin [20]. The chitin deacetylation process, with the addition of NaOH, breaks the bond between the acetyl group ($-CH_3CO$) and the nitrogen atom, becomes an amine group ($-NH_2$) and forms CH which can be seen in Figure 2 and Table 1 [21].

CH functional groups were analyzed using FTIR which can be seen in Figure 3. The FTIR spectrum (a) shows the main spectral characteristics of standard CH, namely at wavelengths 3379 (O-H stretching), 2880 (C-H stretching), 1658 (N-H bending), 1378 (-O- stretching), and 1076 cm^{-1} (C-O stretching). Meanwhile in CH from the crab shell showed peaks at wavelengths of 3379, 2926, 1627, 1381, and 1078 cm-1. The functional groups on the CH of crab shells correspond to the standard spectrum.

Table 1: FTIR wave number of CH standard dan from crab shell

Functional groups	Wave number (cm^{-1})	Standard CH wave number [22] (cm^{-1})	Crab shell CH wave number (cm^{-1})
O-H/ N-H	3500 – 3100	3379	3392
C-H	3000 – 2800	2880	2926
N-H Bending	1650 – 1580	1658	1627
O-H Bending	1420 – 1330	1322	1323
C-N	1250 – 1020	1154	1155
C-O	1083 - 1050	1076	1076

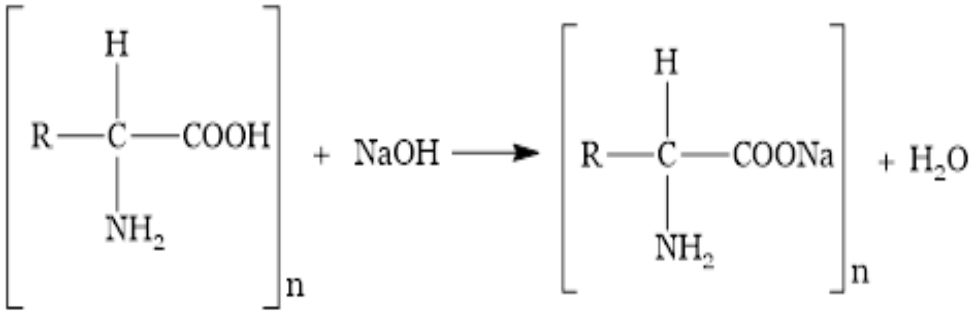

Figure 1: Deproteination reaction [20]

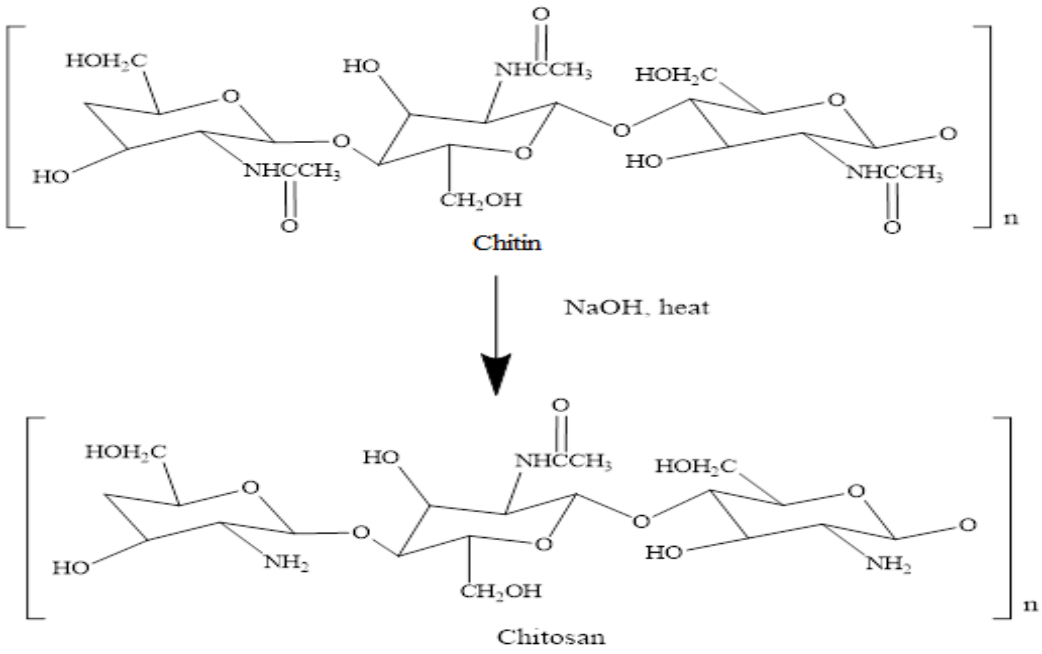

Figure 2: Deacetylation of chitin [13]

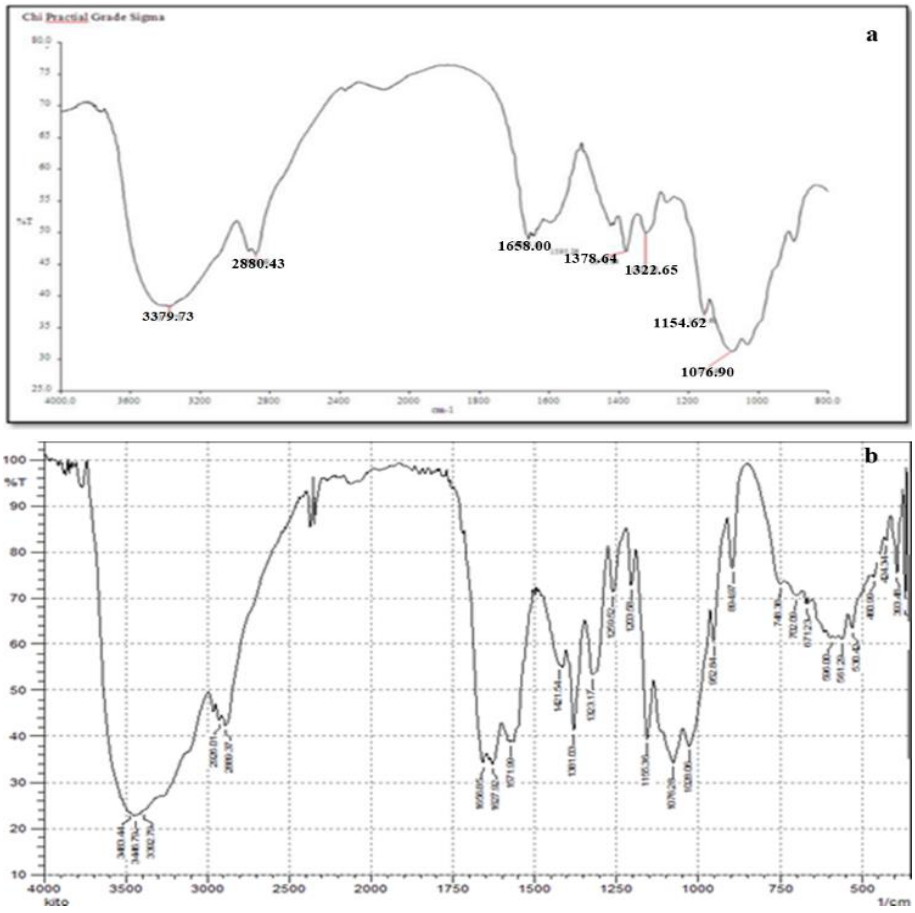

Figure 3: FTIR spectrum of KS (a) standard [22] and (b) from crab shell prepared in the present study

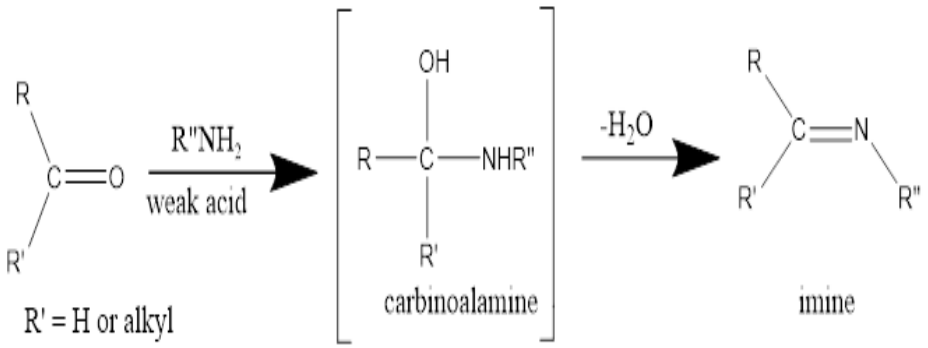

Figure 4: Schiff Base reaction [25]

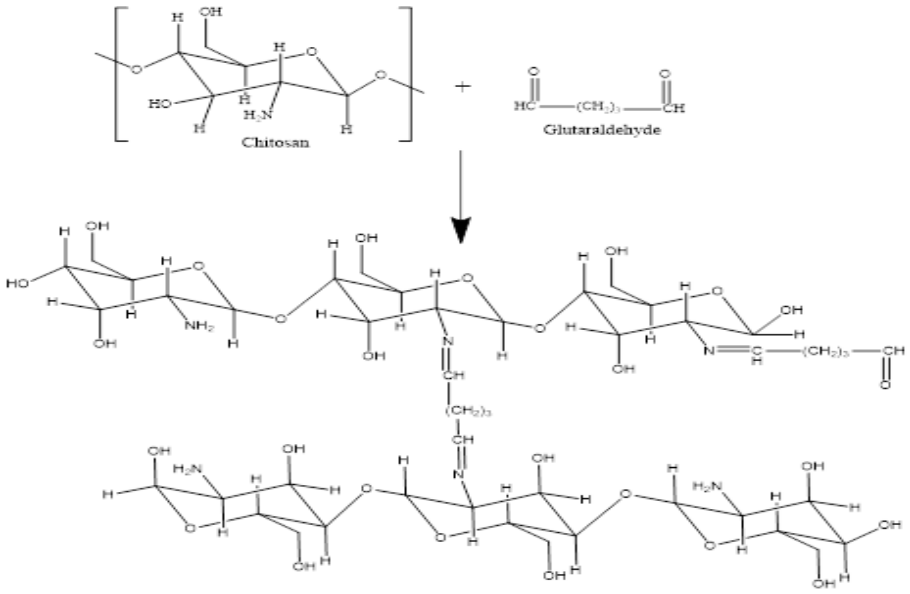

Figure 5: Reaction between glutaraldehyde and chitosan [26]

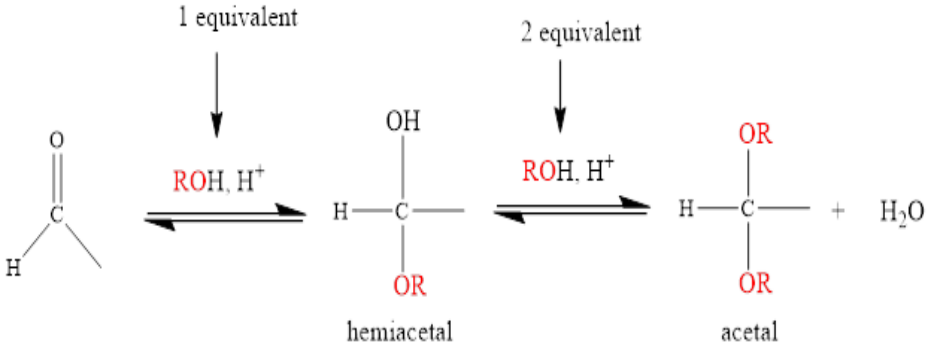

Figure 6: Hemiacetal and acetal formation reaction [25]

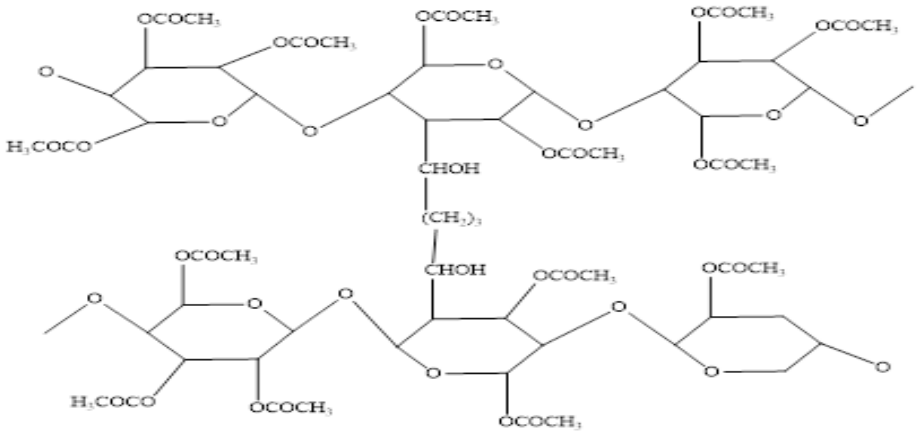

Figure 7: Structure of cellulose acetate crosslinked with glutaraldehyde [25]

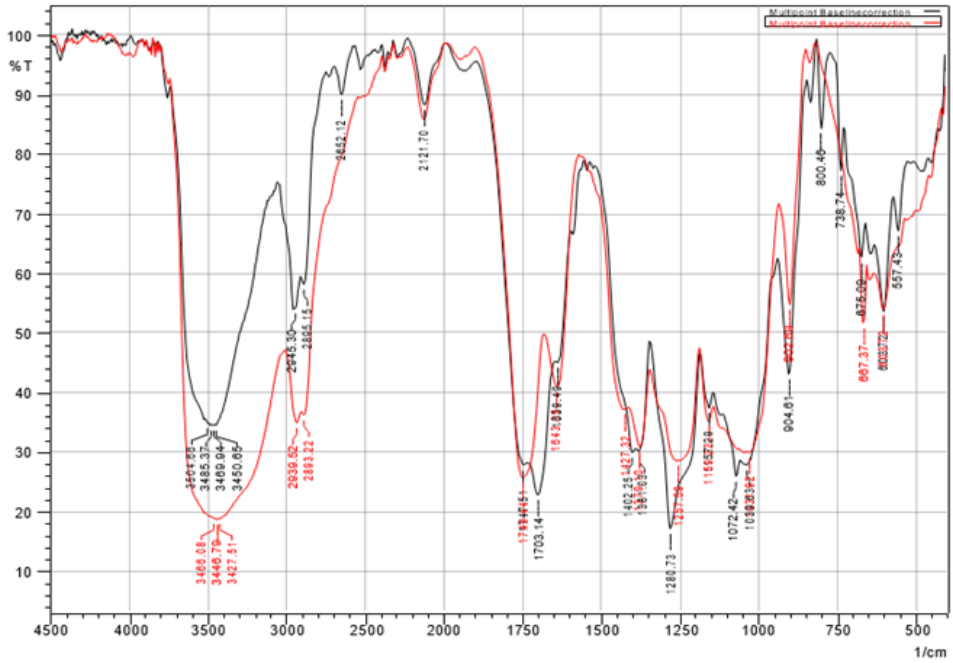

Figure 8: FTIR spectrum of CA/CH membrane before (black) and after (red) addition of GA

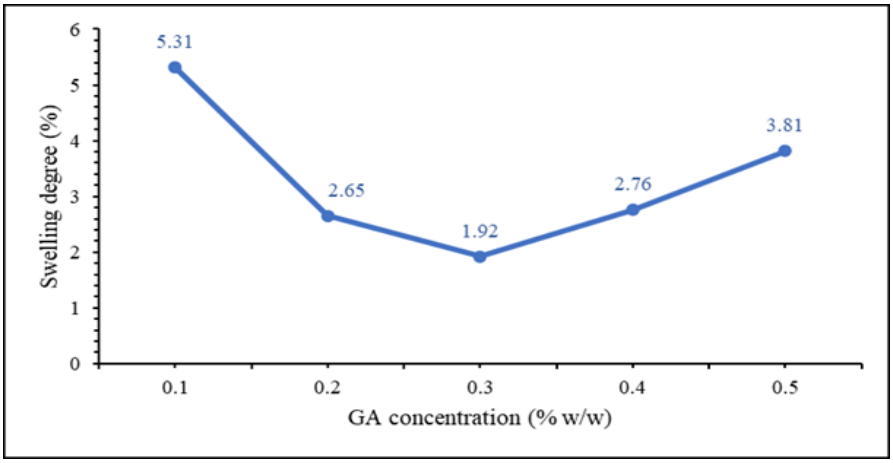

Figure 9: Effect of glutaraldehyde concentration on swelling degree

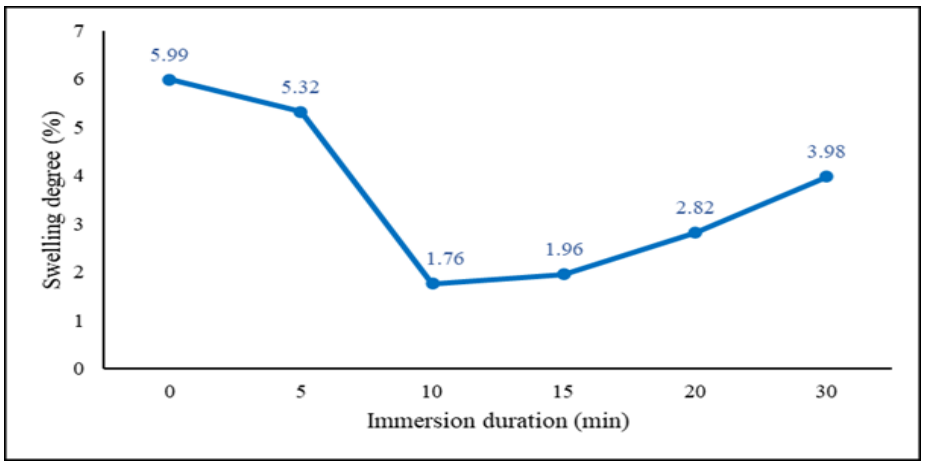

Figure 10: Immersion duration effect on swelling degree

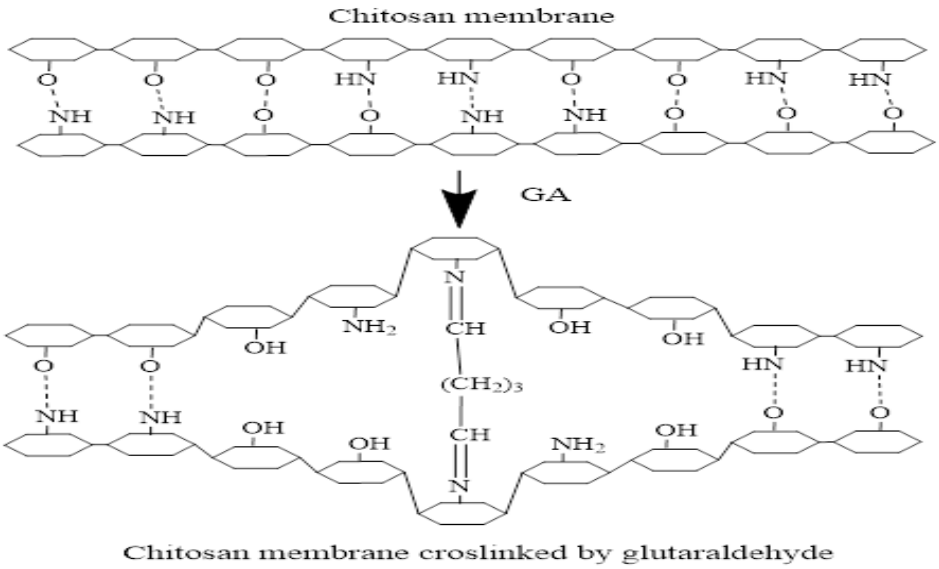

Figure 11: Structure model of CH crosslinked with GA [26]

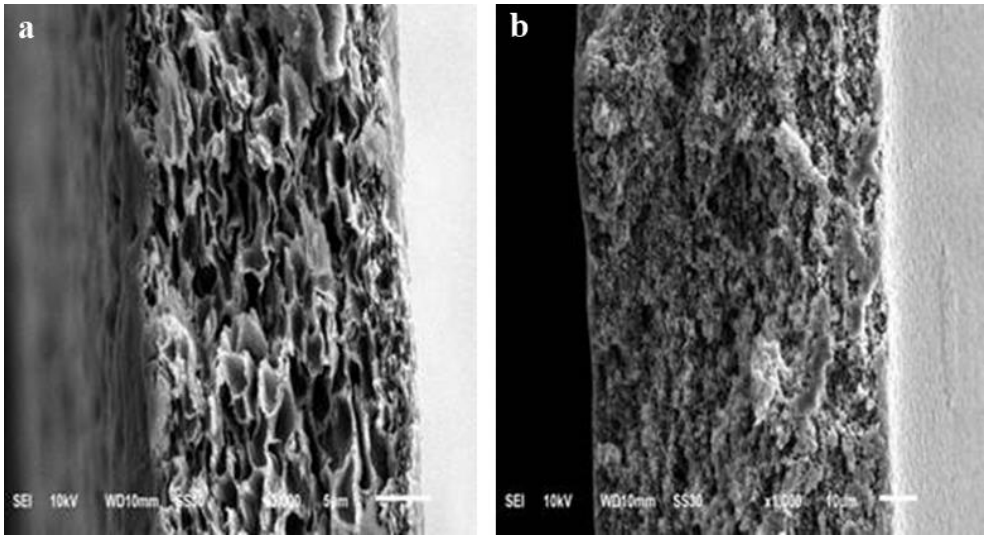

Figure 12: SEM image of CA/CH composite membrane with (a) 0.1% glutaraldehyde and (b) 0.3% glutaraldehyde

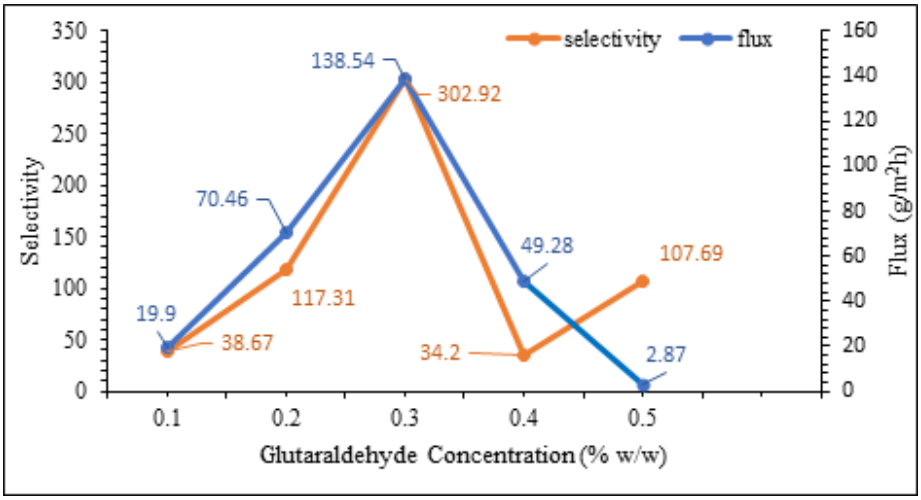

Figure 13: Glutaraldehyde effect on selectivity and flux

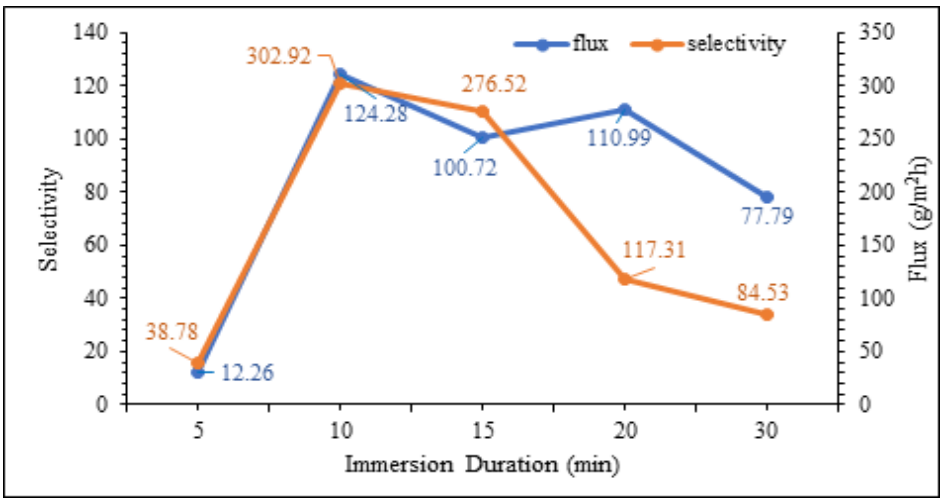

Figure 14: Immersion duration effect on selectivity and flux

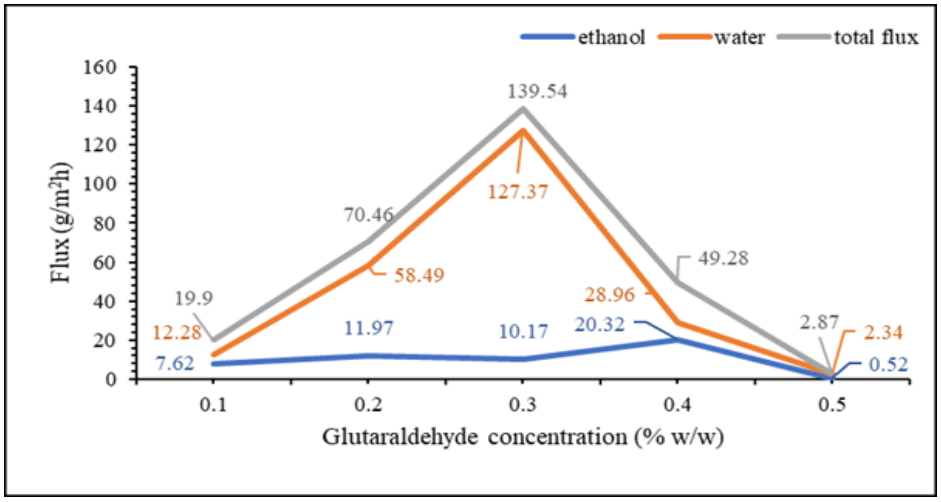

Figure 15: Glutaraldehyde concentration effect on ethanol and water partial flux

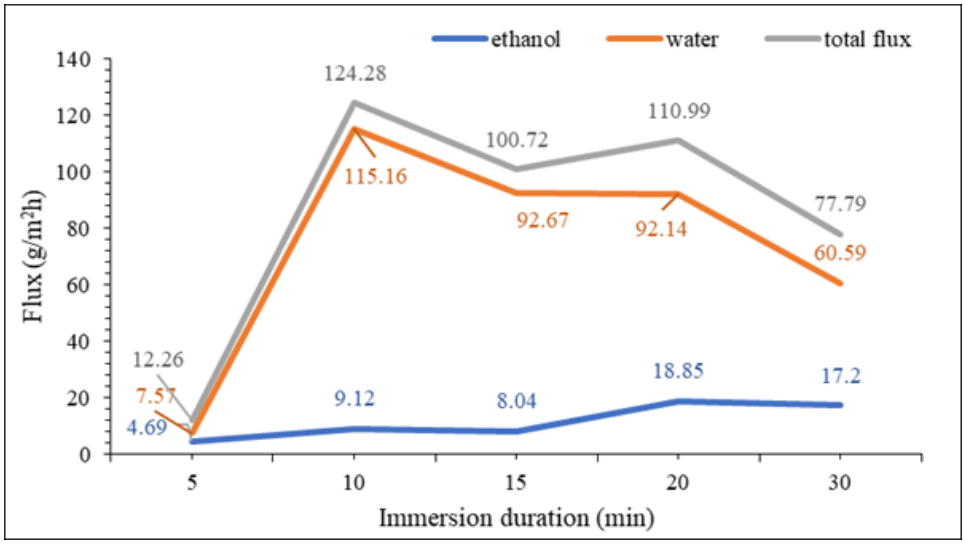

Figure 16: Immersion duration effect on ethanol and water partial flux

Table 2: FTIR wave number of CA/CH before and after addition of GA

Functional groups	Wave number (cm^{-1})	Wave number before GA addition (cm^{-1})	Wave number after GA addition (cm^{-1})
N–H / O–H	3500 – 3100	3466	3469
C–H	3000 – 2800	2939	2945
C=N	1640 – 1690	1639	1643
C–O	1250 – 1000	1157	1159

3.2. CA-GA-CH Membrane Fabrication

CA was used with a concentration of 20% (w/w) because, if < 20% (w/w), the membrane formed was very brittle and easily torn. CH used as an additive, so that if the concentration of CH is greater than CA, the membrane will not form. CH that added beyond the concentration of CA would not be homogeneous because CH was not dissolved in solution but interacted directly with CA, because CA was the matrix that retained CH [23]. The concentration of the CH solution used was 20% (w/w). CA which had been added with CH was then cross-linked using GA. The GA crosslinker was prepared in a concentration of 0.1; 0.2; 0.3; 0.4; and 0.5% (w/w).

3.3. Crosslinking Reaction and FTIR Analysis of CA-GA-CH Membrane

The reaction mechanism between CH and GA is a nucleophilic attack reaction which is also known as Schiff base as shown in Figure 4 (24). The C=O group of GA reacts with the N-H group on CH to form C=NR. Figure 5 shows the structure of CH when crosslinked by GA. The crosslinking of GA with CA is a hemiacetal or acetal formation reaction with a nucleophilic addition reaction as shown in Figure 6 [25]. The structure of CA cross-linked by GA can be seen in Figure 7. CA/CH membranes before and after adding GA were analyzed using FTIR. In the FTIR spectrum (Figure 8 and Table 2) the peak wave number is 3466 cm^{-1} which indicates the presence of N-H/O-H groups from CA, CH, and possibly from acetals. It can be seen that the wave number of 1643 cm-1 is the absorption of the C=N group. This is because it is thought that imine bonds are formed from the reaction between GA and CH. At the peak of the wave number 1159 cm^{-1} is the absorption of the C-O group which appear due to the formation of hemiacetal or acetal groups from the reaction between GA and SA. The peak can also arise from the C-O group in CA and CH so it is not very specific. It is estimated that from this FTIR result, GA reacts with CA and CH.

3.4. Swelling Degree

The degree of swelling (Figure 9) decreased from 5.31 – 1.92% with increasing GA concentration from 0.1 to 0.3% (w/w). It is because with the increasing concentration of GA, the cross-linking that occurs is increasing. Crosslinking causes the membrane to become denser, its density increases, and the mobility of the polymer chains decreases which causes the swelling degree decrease [13]. At a concentration of 0.4 – 0.5% (w/w), the swelling degree increases. This is due to the presence of an unreacted aldehyde group in GA. The free aldehyde groups in GA which were not crosslinked could absorb water [27]. Therefore, it can be concluded that the optimal GA concentration with the smallest degree of swelling is 0.3% (w/w). The swelling degree with respect to the immersion time of the membrane (Figure 10) decreased as the GA immersion time increased from 5-10 min. The longer the immersion time, the more cross-linking reaction occur. The degree of swelling rose again at the immersion time of 10 – 30 minutes. This is because, when GA reacts with CH, the hydrogen bonds between the NH_2 and OH groups present in CH and CA are broken so that they interact with water as shown in Figure 11 [28]. Therefore, it can be concluded that the optimal GA immersion time with the smallest degree of swelling is 10 minutes.

3.5. SEM Analysis of CA-GA-CH Membrane

Figure 12 shows SEM analysis of 0.1% and 0.3 % membrane. It is clear that higher the concentration of GA, the pore of the membrane gets denser. This indicate that more glutaraldehyde added to the membrane increase the number of crosslinks

3.6. Pervaporation Performance

Pervaporation membrane performance is seen based on its selectivity and flux. In Figure 13, the selectivity of the membrane increased from a concentration of 0.1% to 0.3% (w/w) because the membrane surface was getting tighter, making it more selective for water. The flux also increases because as the GA crosslink increase, the hydrophilic groups that can adsorb water also increase as shown in Figure 11. Furthermore, the selectivity at GA concentration > 0.3% (w/w) decreased because the reduced hydrophilic groups made the membrane less selective for water. The flux also decreases because the more the concentration of GA, the more cross-linking reactions occur, making the membrane tighter. In Figure 14, the selectivity of the membrane increased from the immersion time of GA 5 to 10 minutes because the membrane surface was getting tighter, making it more selective for water. The flux also increases because as the GA crosslinks increase, the hydrophilic groups that can adsorb water also increase as shown in Figure 11. Furthermore, the selectivity at immersion duration > 10 minutes decreased because the longer the crosslinker was immersed, the more crosslinking reaction occurred so that the hydrophilic groups also decreased, making the membrane less selective for water. The flux did not decrease significantly, or it could also be said to be relatively constant, so it can be said that the immersion time > 10 minutes did not have much effect on the flux.

3.7. Partial Flux of Ethanol and Water

Figure 15, shows the flux of water and ethanol to the concentration of GA. It can be seen that the water flux increased from 0.1 – 0.3% (w/w) GA concentration, while the ethanol flux remained low. This is consistent with the increase in the selectivity of the membrane to a concentration of 0.3% (w/w) that the membrane is more selective for water than ethanol. This is because as the concentration of GA increases, the crosslinking occurs also increases. The membrane becomes denser which makes it more selective to water so that the water flux increased [29]. At GA concentration > 0.3% (w/w) both water flux and selectivity decreased. In this condition the membrane becomes more hydrophobic so it is less selective to water. Figure 16 shows the flux of water and ethanol to the immersion time. At the 5-10 minutes, there was a significant increase in water flux. This is consistent with the increased selectivity of the membrane until the GA immersion time of 10 minutes which indicates that the membrane is more selective towards water than ethanol. At the GA immersion time > 10 minutes, the water flux and selectivity decreased, which means that with increasing GA concentration, the membrane became more hydrophobic so that the membrane was less selective for water.

4. Conclusions

As the crosslinker concentration increases, the membrane density also increases. The optimal GA concentration obtained was 0,3 % (b/b) and immersion duration obtained was 10 minutes, with selectivity and flux 302.92 and 131,41 g/m^{2}h respectively.

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