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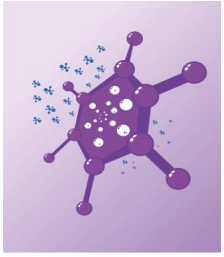

The Effect of Montmorillonite Concentration on Methanol Permeability and Methanol Uptake of Chitosan/Polivinil Alcohol-Montmorillonite Blend Membranes for Direct Methanol Fuel Cell Application

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Abstract. The synthesis of the chitosan / polyvinyl alcohol-montmorillonite (Cs / PVA-MMT) composite membrane was carried out using the phase inversion method. The effect of concentration MMT on the absorption and permeability of the membrane was investigated. The FTIR results showed that the CS / PVA-MMT composite membrane was successfully synthesized. Modification of chitosan with polyvinyl alcohol (3: 1) (w / w) improved the properties and performance of composites. Montmorillonite with a concentration of 2% shows the best results, with the percentage value of methanol absorption of 29.76%, water absorption of 46.93%, and permeability of methanol of 1.433 x 10^{-7} cm^2 s^{-1}.
Keywords: Chitosan; Composite Membrane; Direct Methanol Fuel Cell; Montmorillonite; Polyvinyl Alcohol

1. Introduction

Polymer Electrolyte Membrane is an important component in DMFC, which functions as a proton conductor and separator of methanol between the cathode and the anode. Currently, such perfluorosulfonic acid membranes Nafion® is the primary membrane which is often used in the DMFC. Even though Nafion® has high conductivity proton, Nafion does not meet the requirements for low methanol permeability, especially at low temperatures (<100 °C). Hence the methanol permeation reduces the open-circuit voltage in its electrochemical cell system and contaminates the electrocatalytic process at the cathode (Cui et al., 2009).
Hydrophilic membranes such as chitosan (Cs) are widely used in membrane-based applications due to their high hydrophilic properties, good chemical properties, and thermal resistance properties. Because it has hydroxyl and amino groups, chitosan can chemically modify into various forms and can react in various chemical reactions that produce salt formation. Hydrophilic groups play a role important in water diffusion through the chitosan membrane. Chitosan is generally mixed with hydrophilic polymers to overcome the reduced mechanical

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strength in wet conditions. For example, polyvinyl alcohol (PVA) is a strong hydrophilic polymer and will quite well spread in the chitosan matrix when processed into it (Smitha et al., 2006). The blending of chitosan with PVA in the study previously can improve mechanical stability, methanol permeability, and proton conductivity (Yang & Chiu, 2012)

Montmorillonite (MMT), a type of clay smectite naturally available in abundance and free poison properties, is a promising ingredient in the mixture of various industries of food, medicine, cosmetics, and health. With the addition of MMT, thermal stability and the mechanical properties of bionanocomposites can be improved. However, when the clay content is high, it presents a strong tendency to clot. Therefore many experiments such as ultrasonic and organic irradiation have been was performed to disperse MMT (Guo et al., 2013).

In this study, chitosan will be modified using PVA with a concentration ratio of 3: 1, further doped with Montmorilont filler with various concentrations of 2, 4, 6, and 8% of the weight of chitosan. The purpose of this filler weight percent variation is to strengthen the interactions that occur between chitosan and montmorillonite. Hydrophobic properties owned by this montmorillonite, when used as a filler in the Cs / PVA composite membrane, will create new characteristics in these membranes' properties. Hence, this research carried out the manufacture of a composite membrane derived from chitosan, which acts as a polymer matrix organic and montmorillonite as inorganic fillers. This composite membrane was tested for methanol and water absorption, functional analysis groups, and methanol permeability as the inner membrane of the DMFC to determine its effectiveness as a polyelectrolyte membrane at various concentrations of montmorillonite.

2. Experimental Methods

2.1. Materials

Aquades (SAP Chemicals), shrimp shells (Penaeus monodon), montmorillonite K-10 (Sigma-Aldrich), polyvinyl alcohol (Merck), NaOH pellets (Merck), sulfuric acid solutions (SAP chemicals Indonesia), and acetic acid solutions (SAP Chemicals Indonesia).

2.2. Methods

2.2.1. Extraction of Chitosan

First of all, prepare dry shrimp shell powder. The shrimp skin is separated from the meat and cleaned to remove any stuck dirt. The clean skin is then dried. After that, the dry skin is collected and ground to form a powder. Furthermore, the results of grinding shrimp shells are sieved with a 40 mesh sieve.

Deproteination, the results of the 40 mesh sieve of 200 grams were dissolved in 3.5% NaOH with a ratio of 1: 10 (w / v) of powder to 3.5% NaOH. The dissolved powder was stirred using a magnetic stirrer for 2 hours at a temperature of 65 °C. The results of this stirring will form sediment and filtrate. The filtrate is separated from the sediment by the decantation method. The precipitate is washed using aqua DM to neutral pH, then filtered with a cotton cloth and dried in an oven for 4 hours at 105 °C. The result of heating in an oven in the form of the dry precipitate is then tested using ninhydrin to ensure protein is not present. The deproteination percentage is calculated using equation (1) below.

$$\%\ \text{Deproteination} = 100\% - \left[\frac{\text{Final weight}}{\text{Initial weight}}\right] x100\% \qquad (1)$$

Demineralization, the result of deproteination in the form of dry precipitate mixed with 1 N HCl solution in a ratio of 1: 15 (w / v). The result of mixing the precipitate with 1N HCl solution was stirred using a magnetic stirrer at 800 rpm for 30 minutes. The effect of stirring in the form of a mixture is allowed to settle, and the precipitate is separated from the filtrate by the decantation method. The precipitate was washed with aqua DM to neutral pH, then filtered with

a cotton cloth and dried in an oven for 4 hours at 105 °C. The resulting dry precipitate was analyzed using FTIR spectroscopy to confirm that the IR wave peaks belonged to chitin. The demineralization percentage is calculated using equation 2 as follows.

$$\%\,\text{Demineralization} = 100\% - \left[\frac{\text{Final weight}}{\text{Initial weight}}\right] x100\% \quad (2)$$

Deacetylation, the result of demineralization in chitin, is mixed with 50% NaOH solution with a ratio of 1: 10 (w / v) while heated for 4 hours at 120 °C. The mixture residue in the form of a mixture is separated from the filtrate using a Buechner funnel. Then, the precipitate obtained from the filter was washed with aqua DM to neutral pH and dried in an oven at 100 °C for 4 hours. The result of drying the chitosan precipitate was analyzed by FTIR spectroscopy to determine the degree of deacetylation and the suitability of the IR wave of chitosan with the standard. The percentage of deacetylation is calculated using equation 3 as follows. The final result of chitosan powder is shown in figure 1.

$$\%\,\text{Deacetylation} = 100\% - \left[\frac{\text{Final weight}}{\text{Initial weight}}\right] x100\% \quad (3)$$

Figure 1 Chitosan results of the chitin deacetylation process

2.2.2. Preparation of pure chitosan membrane

A total of 2 g of chitosan was mixed into 75 mL of 2% acetic acid then stirred and heated at 80 °C for 2 hours until homogeneous. The chitosan solution was put into the ultrasonic cleaner for 30 minutes. The solution is poured into an acrylic dish that has been rinsed with acetic acid and allowed to dry below room temperature to form a membrane sheet. The dried membrane was soaked with 1 N NaOH solution and washed with aqua DM to neutral pH. The membrane is allowed to dry below room temperature.

2.2.3. Preparation of Cs/PVA membrane

A total of 0.5 g of PVA was mixed into 12.5 mL aqua DM. Then stirred and heated to 70 °C for 2 hours until homogeneous, covered with plastic wrap. A total of 1.5 g of chitosan was mixed into 37.5 mL of 2% acetic acid solution. Then stirred and heated to 70 °C for 2 hours until homogeneous. The chitosan solution was put into the ultrasonic cleaner for 30 minutes. The two PVA solutions and chitosan solutions were mixed while stirring for 3 hours at room temperature until homogeneous. Then the solution was poured into an acrylic dish that had been rinsed with acetic acid and allowed to dry below room temperature to form a membrane sheet. The dried membrane was soaked with 2M H_2SO_4 solution and washed with aqua DM until a neutral pH. The membrane is allowed to dry below room temperature.

2.2.4. Preparation of Cs/PVA/MMT membrane

A total of 0.5 g of PVA was mixed into 12.5 mL aqua DM then stirred and heated to 70 °C for 2 hours until homogeneous in a closed state with plastic wrap. A total of 1.5 g of chitosan was mixed into 37.5 mL of 2% acetic acid solution, then stirred and heated to 70 °C for 2 hours until homogeneous. The chitosan solution was then put into the ultrasonic cleaner for 30 minutes. A total of 0.04 g; 0.08 g; 0.12 g; 0.16 g montmorillonite each dissolved in 25 mL of 2% acetic acid

until homogeneous. This solution is called the MMT solution. Furthermore, both PVA solutions and chitosan solutions were mixed while stirring for 3 hours at room temperature until homogeneous. This solution is called the Cs / PVA solution. The Cs / PVA solution is mixed with MMT solution while stirring and heated to 80 °C for 30 minutes, then put into an ultrasonic container for 30 minutes. The solution is then poured into an acrylic dish that has been rinsed with acetic acid and allowed to dry below room temperature to form a membrane sheet. The dried membrane was soaked with 2 M H_2SO_4 solution and washed with aqua DM until a neutral pH. The membrane is allowed to dry below room temperature. All the final results of the membrane that have been synthesized are shown in figure 2.

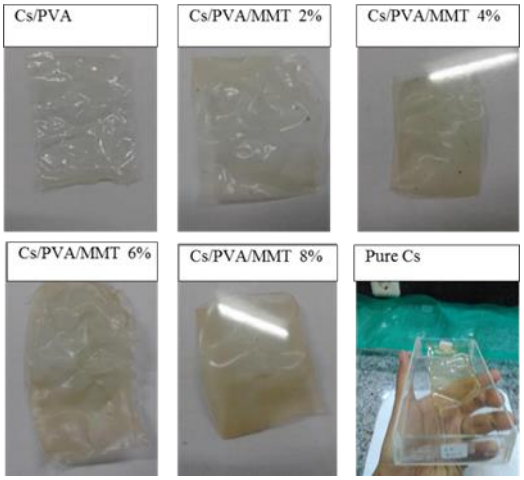

Figure 2 All membrane composites prepared by casting

2.2.5. FTIR analysis

The membrane to be analyzed for functional groups is taken with a thickness of 10 - 15 µm, then an analysis of measurements is carried out at a wavelength between 4000 - 400 cm^{-1} (Lavorgna et al., 2010).

2.2.6. Water uptake and methanol uptake measurements

The water uptake and methanol uptake tests were carried out by measuring the difference in membrane weight before and after immersion in water or methanol. Wet weight (W_{wet}) is measured from membranes immersed in 5 M water or methanol, while dry weight (W_{dry}) is measured from dried membranes for 24 hours at room temperature. For the calculation of water uptake and methanol uptake, the following equation is used.

$$\%\,\mathrm{WU} = \frac{W_{wet} - W_{dry}}{W_{dry}} \qquad (1)$$

2.2.7. Methanol permeability test

Compartments A and B are filled with methanol and distilled water, respectively, as shown in Figure 3, then a circular sample is placed between them (Wu et al., 2007). In the next testing process, each compartment containing methanol and distilled water was stirred. To test the permeability of methanol, a 5 M methanol solution will be used. Every 20, 40, 60, 80, 100 minutes, the compartment containing distilled water is taken as much as the pycnometer volume to determine the methanol concentration through a technique using a pycnometer. The permeability value of methanol is obtained using the equation (Yang & Chiu, 2012):

$$\%\,\mathrm{Permeability} = \frac{SV_B L}{AC_{A0}} xC_{A0} \qquad (1)$$

S is the slope of the chart; V_B (mL) is the volume of compartment B (distilled water); C_{A0} (mol

/ L) is the initial concentration of methanol in compartment A (methanol), L (cm) is the thickness of the membrane, and A (cm^2) is the area of the membrane.

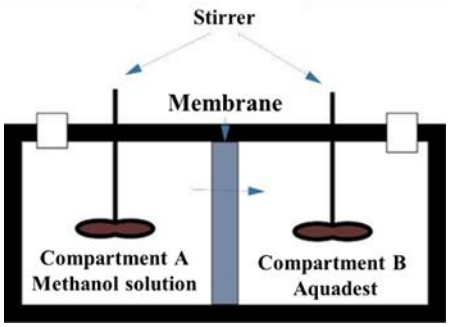

Figure 3 Illustration of methanol permeability test scheme (Neburchilov et al., 2007)

3. Results and Discussion

3.1. Fourier transformation infrared (FT-IR) spectra

To ensure the purity of chitosan, several qualitative and quantitative test parameters are necessary. The qualitative test can be seen from the absorption of functional groups from the FTIR spectra of chitosan; this distinguishes the shift in wavenumbers between chitin and chitosan. Meanwhile, the quantitative test is determined by calculating the degree of deacetylation (DD) of the transformation of chitin and chitosan. Figure 4 shows the results of FTIR characterization between chitin and chitosan. Generally, the absorption of infrared functional groups on chitosan can be seen in Table 1.

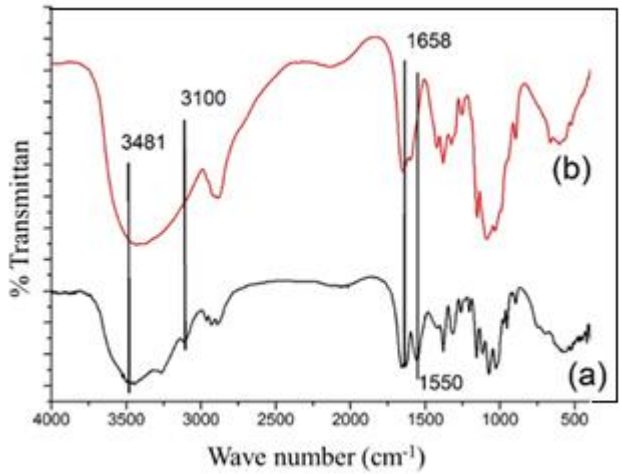

Figure 4 Comparison between FTIR between Chitin (a) and Chitosan (b)

Table 1 Types of functional group vibrations in chitosan

Wavenumber (cm^{-1})	Types of vibration	Vibration of functional group
3000 - 3500	Stretch	O-H and N-H
2926	Stretch	CH, CH3
1621	Stretch	C=O amide
1403	Buckling	C-H
1159	Stretch	C-O-C

Khan et al. (2012)

The success of the formation of this amine group (chitosan) can be determined quantitatively. Quantitative determination is done by calculating the deacetylation degree of chitosan. According

to (Khan et al., 2002), the degree of deacetylation of chitosan produced affects the quality and application of chitosan in various fields. Then the final result was chitosan with a deacetylation degree of 74.45%.

The FTIR test aims to see and confirm the formation of the Cs / PVA-MMT composite membrane that has been synthesized based on changes in functional groups. Figure 5 below presents the FTIR spectra of chitosan (CS) and CS/PVA / MMT membranes with montmorillonite concentrations of 2 and 8%.

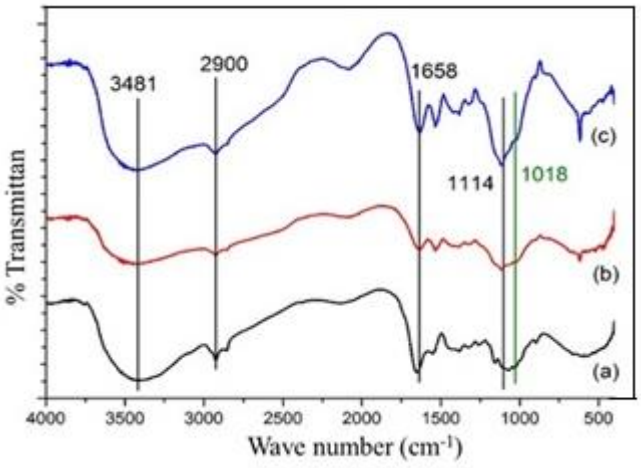

Figure 5 FTIR absorption results for Pure Cs (a), Cs/ PVA/MMT 2% (b), and Cs / PVA-MMT 8% (c) membranes

From the data obtained above, it shows that the CS / PVA / MMT composite membrane has been successfully synthesized, seen from the absorption of the functional groups formed, which is a combination of the spectrum of the constituent elements of the membrane, namely chitosan, polyvinyl alcohol, and montmorillonite. From Figure 5, it can also be estimated the effect of montmorillonite concentration on the CS / PVA / MMT membrane can be proven by the FTIR absorption, which is getting sharper along with the increasing concentration of montmorillonite in the 1108 cm^{-1} wavelength region, namely vibration of functional groups -Si- O and 618 cm^{-1} Al-O-Si vibration.

3.2. Water Uptake dan Methanol Uptake

To determine the membrane's ability to absorb water or methanol, a water uptake and methanol uptake test was carried out. This is done because the storage of water or methanol will determine the proton conductivity and membrane performance. The higher the water uptake value, the better the proton conductivity in the membrane; conversely, the higher the methanol uptake value, the worse the membrane performance is because too much methanol is absorbed, causing cross-over in the fuel cell, resulting in a decrease in voltage on the fuel cell. Figure 6 shows the water uptake and methanol uptake values of the composite membrane.

Based on the results obtained, overall, the Cs/PVA/MMT membrane that has been synthesized has a large water absorption capacity, which is around (40% -55%) and has a low methanol absorption, which is about (25% -35%) as shown in Figure 6. This is due to the nature of PVA, which is very hydrophilic and soluble in warm water but insoluble in alcohol solvents (Palani et al., 2014).

The graph also shows that the Cs / PVA membrane has a greater methanol absorption than the pure Cs membrane but has lower water absorption than pure Cs membranes. This is because the percentage of Cs is more dominant than PVA, which is 3: 1 w/w so that the membrane is semipolar and tends to absorb semipolar methanol more easily. On the other hand, the Cs / PVA membrane will decrease its ability to absorb water, which is more polar than methanol.

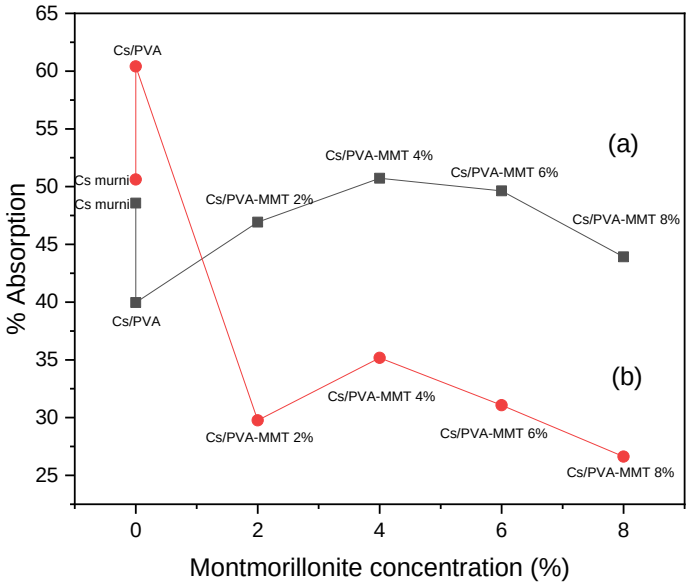

Figure 6 Results of the methanol uptake test (a) and water uptake (b)

Based on the graph, the addition of montmorillonite inorganic filler concentration tends to reduce the absorption of water and methanol (Umar et al., 2016). This phenomenon due to the nature of MMT's crystallinity and insoluble in chitosan solution. In this study, the membrane with the composition of Cs / PVA-MMT 2% had the best physical properties of all the synthesized membranes. Based on the graph, the addition of 2% MMT has a fairly large water absorption capacity and a small absorption capacity of methanol, which is proportional to the absorption capacity of water and methanol at the addition of 8% MMT.

3.3. Methanol permeability

To determine the membrane's performance for Direct Methanol Fuel Cell (DMFC) applications, a methanol permeability test was carried out. When the number of methanol molecules passing through the membrane is very large, it can cause a voltage drop, thus impairing the fuel cell's performance (Miyake et al., 2001).

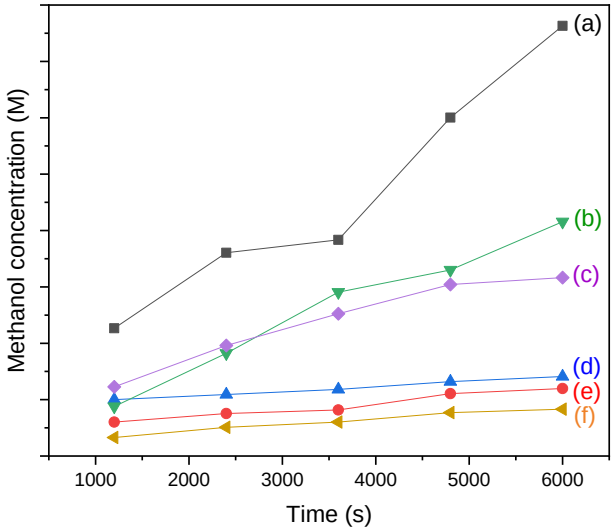

Figure 7 Graph of methanol concentration vs time (a) Pure Chitosan, (b) Cs / PVA-MMT 4%, (c) Cs / PVA MMT 6% (d) Cs / PVA-MMT 2% (e) Cs / PVA (f) Cs / PVA-MMT 8%

Based on figure 7, the permeability was determined by the slope of the relationship between time and concentration of methanol. After obtaining a membrane concentration curve for 5x20 minutes, the slope of the curve is used to calculate the permeability of methanol using the equation (5). Table 2 showed the results of the permeability of pure Cs, Cs / PVA, and Cs / PVA-MMT membrane methanol as follows.

Table 2 Methanol permeability of composite membranes

Membrane	Methanol permeability ($\times 10^{-7}$ cm^2 s^{-1})
Cs	31.84
Cs/PVA	3.98
Cs/PVA/MMT 2%	1.43
Cs/PVA/MMT 4%	22.29
Cs/PVA/MMT 6%	12.73
Cs/PVA/MMT 8%	2.38

Whereas Figure 8 shows the graph methanol permeability of composite membranes. Figure 8 shows that the addition of the MMT concentration on the membrane tends to decrease the permeability value of membrane methanol. The addition of MMT concentration increases the membrane's crystallinity by dispersing MMT in the pore and matrix channels, thereby increasing the tortuosity and narrowing the methanol pathway through the membrane. The Si-O-Al bond on the stiff presses the polymer chains' space volume between the chitosan (García-Cruz et al., 2016). Besides that, the insoluble nature of PVA in alcoholic solutions makes methanol more difficult to pass through the membrane. This can be seen from the sharp decrease in the permeability of Cs when mixed with PVA. Based on Figure 8, the addition of 2% MMT became the lowest permeability value of methanol 1.43 x 10^{-7} cm^2 s^{-1}.

Furthermore, there was a sharp increase in the permeability of methanol on the membrane with a concentration of 4% MMT and continued to decrease until a concentration of 8% MMT. This is because the composition of MMT 2% is the composition of MMT, which is most suitable with the number of cross-links between chitosan so that MMT is well dispersed. The increase in methanol permeability at a concentration of 4% was caused by too many MMT particles trying to enter the cross-linking pores between chitosan. The pore cavities were not filled with MMT completely. The decrease in methanol permeability at 6% MMT and 8% MMT was further due to the increased crystallinity from the addition of montmorillonite concentrations.

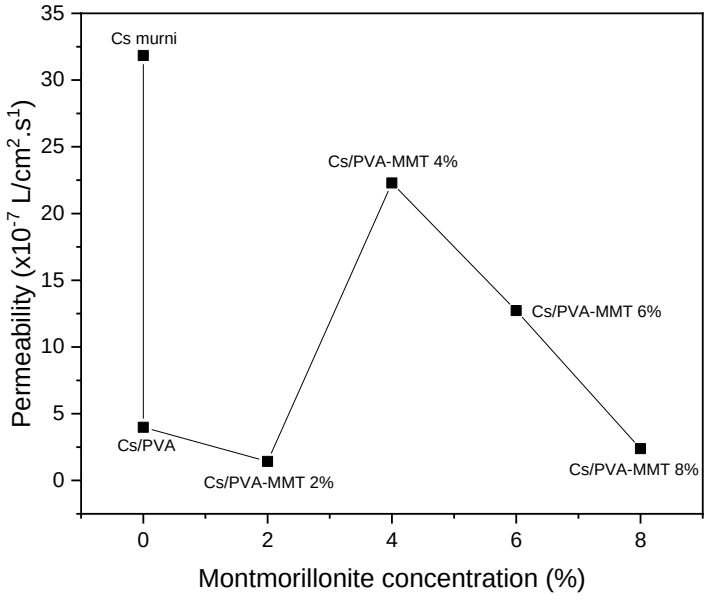

Figure 8 Graph of methanol permeability composite membranes

4. Conclusions

Research on the effect of montmorillonite (MMT) concentration on chitosan (Cs) composite membranes mixed with polyvinyl alcohol (PVA) with a ratio of Cs and PVA of 3: 1 w / w has been successfully carried out. The result is a membrane with a light brown physical appearance with a tougher texture than a pure Cs membrane. The addition of MMT concentrations tended to reduce water and methanol absorption. FTIR testing showed differences in absorption groups between pure Cs, Cs / PVA, and Cs / PVA-MMT membranes. In the methanol permeability test, it was found that the addition of the concentration in MMT tended to decrease the permeability of methanol, and the optimal concentration of MMT with the lowest methanol permeability was obtained, namely, at 2% MMT concentration, which had a methanol permeability value of 1.43×10^{-7} cm^2 s^{-1}.

In the analysis of water uptake and methanol uptake in general, the addition of montmorillonite concentration can increase the percentage of water uptake and reduce methanol uptake. The best water uptake value was obtained at a 4% MMT concentration, while the lowest methanol uptake value was obtained at 8% MMT concentration.

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