CHITOSAN–BENTONITE COMPOSITE MEMBRANES FROM VANAME SHRIMP (*LITOPENAEUS VANNAMEI*) SHELLS FOR DIRECT METHANOL FUEL CELL APPLICATIONS

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Abstract

Direct Methanol Fuel Cell (DMFC) is an environmentally friendly technology that serves as an alternative energy source in addressing energy crisis issues. DMFC operates on the principle of converting the chemical energy of methanol into electrical energy. Nafion membranes, as electrolyte membranes, have high proton conductivity but are susceptible to methanol permeation. This study aimed to investigate the characteristics of chitosan–bentonite composite membranes and evaluate their potential as a membrane for Direct Methanol Fuel Cell (DMFC) applications. The chitosan used in this study was derived from vaname shrimp (Litopenaeus vannamei) shells and was composite with bentonite using the sol-gel method. The degree of deacetylation of chitosan from whiteleg shrimp shells (Litopenaeus vannamei) obtained in this study was 75%. The characterization tests of the chitosan-bentonite composite membrane included thickness testing, tensile strength testing, water uptake, methanol uptake, and proton conductivity. The best results were obtained at a bentonite composition of 15%, with a membrane thickness of 0.06 mm, tensile strength of 0.018738 MPa, water uptake of 155%, methanol uptake of 0%, and proton conductivity of 3,42 x 10^{-7} S/cm. These results indicate that the 15% chitosan–bentonite composite membrane has potential as an environmentally friendly, economical, and efficient alternative electrolyte membrane material for DMFC applications.

Keywords: Chitosan, Bentonite, Composite Membrane, Fuel Cell, DMFC

I. INTRODUCTION

The energy crisis due to dwindling fossil fuel reserves is a major global problem. The increasing use of petroleum fuels has led to a higher energy demand, necessitating the need for environmentally friendly alternative energy sources. One technology that can be used is the fuel cell. A fuel cell is an electrochemical device that converts chemical energy into electrical energy through oxidation and reduction reactions, with water as a byproduct. In a fuel cell, one of the components that plays a crucial role in the energy production process is the membrane (Malis Eko et al., 2022). Chitosan is a biopolymer that is very abundant in nature through the deacetylation of chitin and is used as an environmentally friendly membrane (Mashuni et al., 2021). One type of industrial waste that can be used to produce chitosan is the shell of white shrimp (*Litopenaeus vannamei*). Shrimp shell waste can be utilized as a raw material for chitosan production, which can subsequently be developed into membrane material for various applications (Kusumawati and Tania., 2012).

White shrimp (*Litopenaeus vannamei*) is a marine culture that is very popular among people worldwide because of its very sweet meat and very high nutritional value. However, because of the large number of shrimp lovers, its processing produces waste in the form of shells and heads (Majekodunmi et al., 2017). Research conducted by (Astuti et al., 2022) white shrimp (*Litopenaeus vannamei*) contributes 35%–50% of the total shrimp weight in the form of shells. The main components in shrimp shells are 25%–44% protein and 20–50% chitin. Chitosan from shrimp shells is very good as an adsorbent, coagulant, or environmentally friendly (Mustafiah et al., 2018).

Research conducted by (Lola, 2022) stated that the synthesis of chitosan from white shrimp shells (*Litopenaeus vannamei*) was carried out in 4 stages, namely deproteination, decalcification, decolorization, and deacetylation with a deacetylation value of 92.74%. Further research was conducted by (Malis Eko et al., 2022) Utilization of chitosan/montmorillonite-glutaraldehyde, varying the concentration of methanol 2,3,4,5, and 6 M. The best absorption capacity was at 6

M methanol with an absorption percentage of 49.0654%. Furthermore, composite chitosan-valine/bentonite for DMFC membranes with the addition of 6% bentonite with the highest proto-conductivity value of 0.108 S/cm and the lowest methanol permeability value of 7.03 x 10-5 cm^2/s (Purwanto et al., 2023). Therefore, research was conducted using chitosan-bentonite as a membrane in a Direct Methanol Fuel Cell (DMFC).

II. METHODS

Materials and Tools

The materials used in this study were distilled water (H_2O), hydrochloric acid (HCl) 1N p.a, acetic acid (CH_3COOH) 2% p.a, bentonite ($Al_2O_34SiO_2H_2O$), white shrimp shells (*Litopenaeus vannamei*), sodium hydroxide (NaOH) p.a and polyethylene glycol (PEG) catalog 6000.

The tools used in this study were Thermo Fisher Scientific 98-II-B Forier Transform Infra Red (FTIR), Fujitsu analytical balance, Kirin oven, Trytis Technologies magnetite hotplate stirrier, digital caliper, Universal Testing Machine (UTM), LCR-meter, blender, glassware, anumbra petri dish, 150 ˚C thermometer, mortar and pestle, 100 mesh sieve.

Chitosan Synthesis from White Shrimp Shell (Litopeaus vannamei)

Deproteination

300 grams of finely ground shrimp shells were weighed and placed in a beaker filled with 3.5% (w/v) sodium hydroxide (NaOH) at a ratio of 1:10. The mixture was then heated and stirred using a magnetic stirrer for 2 hours at 60–70°C at 400 rpm. The mixture was then separated and neutralized using distilled water. The residue was then dried in an oven at 45°C. It was then analyzed qualitatively using ninhydrin reagent (Ayyubi et al., 2021).

Decalcification

The deproteinized chitin was placed in a beaker filled with 1N (w/v) hydrochloric acid (HCl) in a 1:10 ratio. It was homogenized with a magnetite stirrer at 60–70°C for 2 hours. It was then allowed to stand until bubbles formed and neutralized with distilled water. The residue was dried at 45°C and then further analyzed using FTIR (Lola, 2022).

Deacetylation

The decalcified chitin was placed in a beaker filled with 50% (w/v) sodium hydroxide (NaOH) at a ratio of 1:15, heated and stirred using a magnetic stirrer for 4 hours at 100°C. The mixture was then separated and neutralized using distilled water. The residue was then dried in an oven at 45°C until dry. Further analysis was carried out using FTIR (Purwanti et al., 2021).

Preparation of Chitosan–Bentonite Composite Membranes

Chitosan–bentonite membranes were prepared by varying the concentration of bentonite: 3%, 6%, 9%, 12%, 15%, and 18%. A total of 0.3 grams of chitosan was weighed, dissolved in 10 mL of 2% acetic acid, and stirred for 4 hours using a stirrer. Next, 0.2 grams of polyethylene glycol (PEG) catalog no. 6000 was weighed and the bentonite was added. The mixture was then allowed to stand for 1 hour, then poured into a petri dish to dry and form a thin layer. The membrane was then dried at room temperature and analyzed using FTIR (Rusadi et al., 2018).

Characterization of Chitosan–Bentonite Composite Membrane

Chitosan Membrane Thickness Test

The membrane thickness was tested using a digital caliper. The chitosan-bentonite membrane was cut into 2x1 cm pieces and its thickness was measured using a digital caliper.

Membrane Tensile Strength Test

The chitosan–bentonite membrane was cut into 5x2 cm pieces and then tested using a Universal Testing Machine (UTM).

Water Uptake Test

Water uptake analysis was performed to evaluate the membrane's ability to absorb and retain water within its polymer matrix. The initial weight (Wd) of the chitosan–bentonite membrane was weighed. The membrane was then soaked in distilled water for 24 hours. The soaked membrane was then weighed to

calculate the water uptake value (Fath et al., 2024).

Methanol Uptake Test

The absorption test was conducted to determine the membrane's ability to absorb methanol. The initial weight (Wd) of the chitosan–bentonite membrane was weighed. The membrane was then soaked in methanol for 24 hours. The soaked membrane was then weighed to calculate the water uptake value (Fath et al., 2024).

Proton Conductivity Test

Proton conductivity tests were conducted using an LCR meter. The chitosan-bentonite composite membrane was first cut into 2 cm x 1 cm pieces and then soaked in distilled water for 24 hours. The resistance value of the soaked membrane was then measured ((Purwanto et al., 2023).

III. RESULT AND DISCUSSION

This study investigated the physicochemical properties of chitosan–bentonite composite membranes through several characterization analyses. Chitosan samples were derived from vaname shrimp shells composited with bentonite. Several stages were carried out in this study, namely sample preparation, deproteination process, decalcification, deacetylation, synthesis of chitosan-bentonite composite membranes and the final stage, namely the characterization stage of the composite membrane using test parameters of thickness, tensile strength, water absorption, methanol absorption and proton conductivity.

The chitosan process from white shrimp shells (*Litopenaeus vannamei*) is carried out through 3 stages, namely deproteination, decalcification and deacetylation. The deproteinization stage is carried out to break the chitin bond with the protein contained in the white shrimp shell. Amanda's research (2022) stated that the NaOH solvent used in the deproteinization process in an alkaline environment will be more effective because the protein can dissolve better in the use of alkaline solvents than acid. During the hydrolysis process, the mixture has a very thick texture because the protein content in the shrimp shell is released from the chitin group and binds with Na^+ ions in the solution. The positive ions in NaOH will bind with the negative ions contained in the protein so that the protein will be extracted and exist in the form of Na-proteinate. The next stage is decalcification which aims to remove the mineral content contained in the shrimp shell. (Dompeipen et al., 2016), said that the main mineral content found in shrimp shells is calcium carbonate ($CaCO_3$) and calcium phosphate ($Ca_3(PO_4)_2$ which are physically bound.

Deacetylation is the final stage in transforming chitin into chitosan. The deacetylation process is carried out under hydrolysis conditions using high concentrations of NaOH. Deacetylation of chitin and chitosan is carried out for 4 hours at a temperature of 100 ˚C with an alkaline solution (Citrowati et al., 2017). During the deacetylation process, the bonds between chitin and carbon and nitrogen with amines will be broken. This reaction is known as amide hydrolysis using a strong base solution in the reaction, chitin will act as an amide and NaOH acts as a strong wet solution. In this study, a yield value of 58% was obtained with a chitosan weight of 28 grams. The mechanism of transformation of chitin into chitosan can be seen in Figure 1.

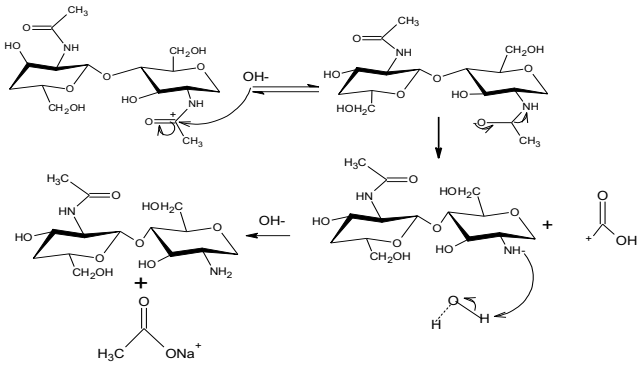


Figure 1 Mechanism of Chitin to Chitosan Transformation (Source: Amanda, 2022)

Synthesis of Chitosan–Bentonite Composite Membrane

Composite membrane synthesis was carried out using the sol–gel method. (Berghuis et al., 2020) stated that the sol–gel method is the best method for producing composite membranes for application in fuel cells such as the Direct Methanol Fuel Cell (DMFC). One of the main advantages of producing composite membranes using the sol–gel method is that it allows the synthesis of hybrid organic–inorganic materials through two condensation and hydrolysis reactions. This combination of inorganic and organic materials facilitates the design of new engineering materials (Bokov et al., 2021).

Membrane synthesis in this study used a chitosan-bentonite composite. Bentonite is known to be environmentally friendly and has very high water absorption, reduces permeability, and can increase proton conductivity. The manufacture of chitosan bentonite composite membranes was carried out by varying the bentonite concentration of 3%, 6%, 9%, 12%, 15%, and 18%. The synthetic composite membrane can be seen in Figure 2.

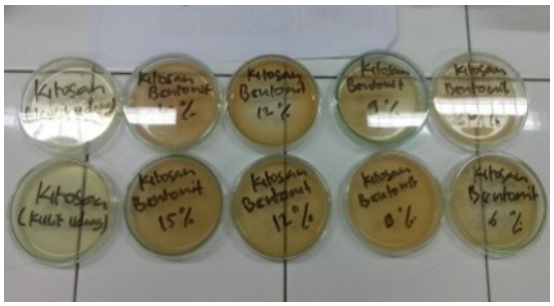


Figure 2 Chitosan-Bentonite Composite Membrane

Characterization of Chitosan–Bentonite Composite Membrane

Fourier Transform Infrared Spectroscopy analysis

The FTIR spectra indicate differences in functional groups among chitin, chitosan, and the chitosan–bentonite composite membrane, indicating significant changes due to the synthesis process. The results of the characterization can be seen in Figure 3.

Chitin exhibits strong spectral bands at wavenumbers 3452.43 cm^{-1} and 3270.75 cm^{-1}, originating from O–H and N–H stretching, respectively, indicating the presence of strong intermolecular hydrogen bonds. Meanwhile, chitosan exhibits broad spectral bands at 3432.07 cm^{-1} and 2911.50 cm^{-1}, indicating an increase in the intensity of the O–H and N–H groups due to the formation of primary amine groups ($–NH_2$). Furthermore, the spectral bands at 1654.14 cm^{-1} and 1558.51 cm^{-1} are characteristic of C=O stretching and N–H bending vibrations, respectively. Meanwhile, in chitosan, there was a decrease in intensity in the spectral bands in the 1650.53 cm^{-1} and 1596.60 cm^{-1} regions, indicating a reduction in amide groups, which indicates that the deacetylation process was successful.

A significant difference between the FTIR results of chitin, chitosan, and chitosan–bentonite composite membranes is the appearance of a band at 559.58 cm^{-1}, which is absent in pure chitin or chitosan. The absorption at this wavelength was identified as Al–O–Si from the bentonite structure, proving that bentonite was successfully composited into the chitosan matrix. In addition, the spectral bands at 1053.14 cm^{-1} and 1025.25 cm^{-1} indicate Si–O–Si strain. The shift in these bands indicates the formation of physical interactions and hydrogen bonds between the functional groups of chitosan and the silicate structure of bentonite. The shift in this band to a higher frequency indicates the interaction between the hydroxyl groups of chitosan and the silanol groups (Si–OH) of bentonite, thus forming intermolecular hydrogen bonds as an early sign of composite formation (Jia Junjie and Yanjun Liu, 2021)

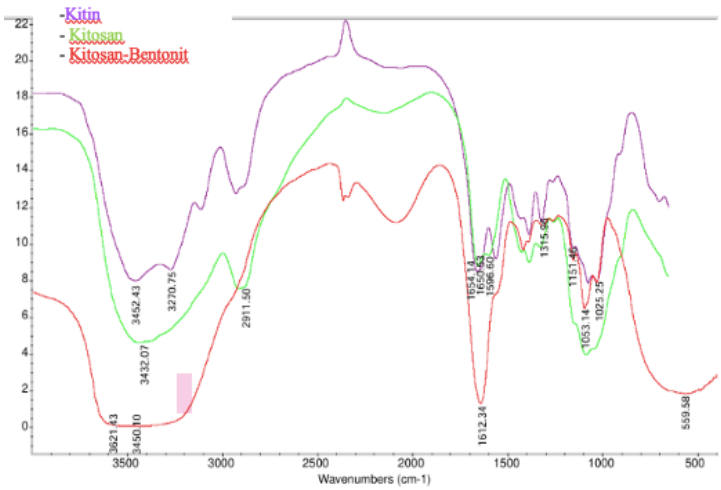


Figure 3 FTIR Spectrum of Chitin, Chitosan and Chitosan–Bentonite Membrane

Chitosan–Bentonite Composite Membrane Thickness Test

The composite membrane thickness test in this study used a digital micrometer screw gauge with an accuracy of 0.01 mm, resulting in precise measurements. In this study, the composite membrane was cut to a size of 2 cm x 1 cm. The results of the chitosan-bentonite composite membrane thickness test can be seen in Table 1. Membrane thickness directly influences physical properties such as permeability and mechanical strength (Savitri, 2017). The thicker the membrane, the lower its porosity value. In this study, it was shown that the addition of bentonite can reduce the membrane thickness.

Table 1. Results of Chitosan–bentonite Composite Membrane Thickness Test

Sample	Thickness (mm)
Chitosan	0.08
Chitosan-bentonite 3%	0.06
Chitosan-bentonite 6%	0.13
Chitosan-bentonite 9%	0.06
Chitosan-bentonite 12%	0.06
Chitosan-bentonite 15%	0.06
Chitosan-bentonite 18%	0.05

Tensile Strength Test of Chitosan–Bentonite Composite Membrane

The membrane tensile strength test in this study used a *Universal Testing Machine* (UTM). The membrane tensile strength test was conducted to determine the strength and elasticity of the membrane. The denser the membrane structure, the closer the molecules are spaced, resulting in greater tensile strength.

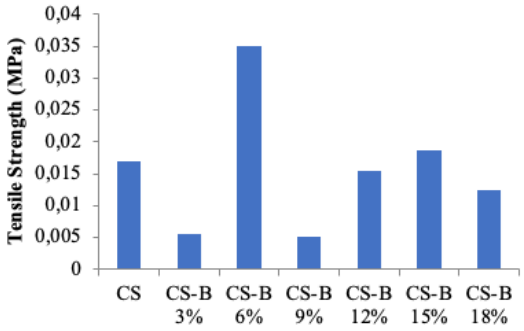


Figure 4 Tensile Strength Test Graph of Chitosan–bentonite Composite Membrane

The tensile strength test in this study was carried out in a dry state or non-hydrated chitosan bentonite composite membrane. Figure 4 shows the results of the tensile strength test of the chitosan-bentonite composite membrane for each variation, namely chitosan-bentonite 3% 0.005492 MPa; chitosan-bentonite 6% 0.035031 MPa, chitosan-bentonite 9% 0.005142 MPa, chitosan-bentonite 12% 0.015521 MPa, chitosan-bentonite 15% 0.018738 MPa and chitosan-bentonite 18% 0.012488 MPa. These results indicate that chitosan with the addition of 6% bentonite has the highest tensile strength, this is because 6% chitosan—bentonite has a greater membrane thickness compared to other chitosan—bentonite.

Water uptake and methanol uptake test of chitosan bentonite composite membrane

This test is conducted to determine how strong the membrane is in absorbing a solution. According to (Ayyubi at al., 2021), water and methanol absorption tests are conducted to determine how effective the membrane is in diffusing water or methanol. This test can be used as a parameter for further tests such as proton conductivity and methanol permeability. Research conducted by (Kharisma Tria et al., 2020) membranes that have a high water uptake value are very suitable for use in Direct Methanol Fuel Cell (DMFC) systems and should not exceed 300%.

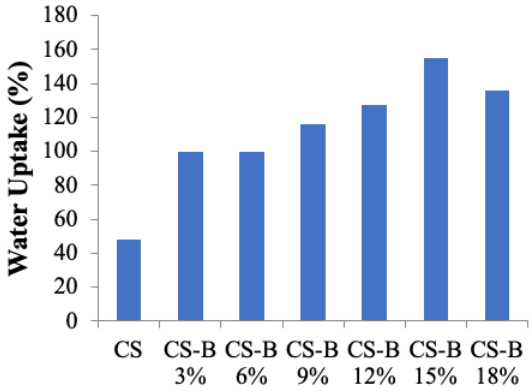


Figure 5 Water uptake test results of chitosan

Water uptake test is needed to test the water absorption capacity of the membrane, as a parameter of how strongly water can be absorbed by the membrane. Water absorbed in the fuel cell membrane can act as a medium for transporting H^+ protons at a certain level, which is related to proton conductivity, so it can be used to improve membrane performance, when the membrane changes from its initial condition. The results of the water uptake test for pure chitosan showed a value of 48.27%. Chitosan is a polysaccharide obtained from the deacetylation of chitin, which has hydrophilic properties due to the presence of amino and hydroxyl groups in its structure. This property allows chitosan to interact with water, although the absorption value obtained is relatively low compared to the chitosan-bentonite composite. It can be seen that the addition of 15% and 18% bentonite resulted in higher absorption values, namely 155% and 136%. This indicates that the addition of bentonite increases the ability of chitosan to absorb water. When chitosan is mixed with bentonite, physical and chemical interactions occur that can increase the water absorption capacity. Bentonite has a layered structure that allows water to be trapped between the layers, while chitosan can function as a water-binding matrix ((Jia Junjie and Yanjun Liu, 2021).

Based on the graph in Figure 5, it can be seen that in the 18% chitosan-bentonite composite, the absorption value of 136% decreased due to the increased density of the mixture, which inhibited the ability of water to enter the structure. According to Savitri (Savitri, 2017) in certain circumstances bentonite particles can bind to each other and form aggregates, which reduces the surface area available for interaction with water so that absorption can decrease in some circumstances. Research conducted by (Kharisma Tria et al., 2020) has carried out the characteristics of clay-modified chitosan/ PVA-based composite membranes. The best water uptake test results were in chitosan/PVA with the addition of 0.3 and 0.6 g of clay with an absorption percentage of 69.08% to 93.03% and decreased when adding 0.9 g of clay with an absorption capacity of 56.69%.

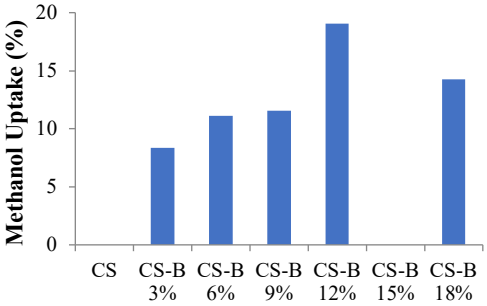


Figure 6 Methanol uptake test results of chitosan-bentonite composite membrane

concentration affect the absorption rate. At bentonite concentrations of 3%, 6%, 9%, 12%, 15% and 18% the absorption values obtained were 8.3%, 11.11%, 11.53%, 19.04%, 0% and 14.28% respectively. Methanol uptake decreased with increasing bentonite concentration, suggesting that bentonite reduced methanol diffusion through the membrane matrix. According to (Pieróg et al., 2009) the absorption mechanism in this composite membrane is influenced by the interaction between functional groups on

chitosan and the bentonite surface. When the membrane is immersed in methanol, methanol molecules will interact with amino and hydroxyl groups on chitosan, causing changes in the dimensions and mass of the membrane. However, at higher bentonite concentrations, the barrier effect of bentonite particles can reduce methanol penetration, thereby reducing absorption.

From the results obtained there is an increase in the membrane's ability to absorb methanol, the absorption value obtained is still relatively low this is due to the interaction that occurs between Si–O–Si in bentonite which causes methanol to be absorbed by the membrane. According to research conducted by (Hartanto et al., 2007) stated that SiO_2 modified chitosan membranes can absorb methanol due to the polarity of methanol which is similar to water but has a larger surface area in SiO_2. At a bentonite concentration of 15%, the absorption value becomes 0%, which indicates that the addition of bentonite at this level has effectively blocked methanol penetration. According to research conducted by (Kharisma Tria et al., 2020) a good composite membrane is applied in Direct Methanol Fuel Cell (DMFC) when the methanol uptake value and methanol permeability value are low.

Conductivity Test of Chitosan–Bentonite Composite Membrane

Proton conductivity testing was performed to evaluate the ability of the membrane to transport protons, which is a critical parameter for DMFC performance. Membranes with high conductivity typically exhibit good ion transport capabilities (Selyanchyn Olena, 2020). The test results, based on resistance values, are shown in Table 2.

In the proton conductivity test of the membrane, an LCR-meter was used to determine the resistance value so that it can be converted into conductivity units, namely S/cm. This study aims to determine the effect of variations in bentonite concentration on the resistance and conductivity values of the chitosan-bentonite composite membrane. The highest resistance value was shown by the pure chitosan membrane, which was 100.2×10^{-8} Ω, which was inversely proportional to its lowest conductivity value, which was 3.992×10^{-13} S/cm. This indicates that pure chitosan has very low electrical conductivity due to its polymer structure which does not support ion mobility. (Ivana, 2017) stated that pure chitosan has a low proton conductivity value due to its monomer structure having three hydrogen atoms that are strongly bonded so that it is unable to carry electrical energy. With the addition of 3% bentonite, the resistance value decreased to 5.22×10^{7} Ω, and the conductivity increased to 5.747×10^{-11} S/cm. This decrease in resistance is due to the increased number of charged groups in the hydrophilic bentonite, which facilitates ion movement. The addition of inorganic fillers can increase or decrease the proton conductivity of the resulting membrane (Wardani, 2015).

Table 2. Proton Conductivity Test Results of Chitosan–bentonite Composite Membranes

Sampel	Resistance (Ω)	Conductivity (S/cm)
Kitosan	100,2 x 10^{8}	3,992 x 10^{-13}
Kitosan–bentonit 3%	5,22 x 10^{7}	5,747 x 10^{-11}
Kitosan–bentonit 6%	17,47 x 10^{7}	1,488 x 10^{-11}
Kitosan–bentonit 9%	5,51 x 10^{7}	6,612 x 10^{-10}
Kitosan–bentonit 12%	7,9 x 10^{6}	3,747 x 10^{-9}
Kitosan–bentonit 15%	7,87 x 10^{4}	3,42 x 10^{-7}
Kitosan–bentonit 18%	12,35 x 10^{5}	1,99 x 10^{-9}

The resistance value becomes 17.47×10^{7} Ω, with the conductivity decreasing to 1.488×10^{-11} S/cm in the 6% chitosan-bentonite composite membrane. The decrease in conductivity value is caused by the excessive tensile strength value and the membrane being too thick, thus reducing its conductivity value. According to (Luo et al., 2021), there are two factors that affect the proton conductivity value in the membrane, namely thickness and degree of absorption. Membranes that are too thick will reduce the proton conductivity value. Based on the results of the research conducted, these results are in line with the membrane thickness test carried out on 6% bentonite which has the highest thickness of 0.13 mm.

At bentonite concentrations of 9%, 12%, 15% and 18%, the conductivity values were 6.612×10^{-10} S/cm; 3.747×10^{-9} S/cm; 3.42×10^{-7} S/cm and 1.99×10^{-9} S/cm, respectively. These results show that at a bentonite concentration of 15%, the proton conductivity value is the

best and optimum. This is because the 15% chitosan-bentonite membrane is perfectly hydrated, resulting in a good proton conductivity value. This can be seen based on the resulting absorption value where the water uptake in 15% chitosan-bentonite is 155%. These results are parameters for the conductivity value of 15% chitosan-bentonite. The results obtained have poor conductivity values caused by several factors, namely the surface area is too small so that the proton transport process does not run perfectly. The proton conductivity value that is suitable for DMFC applications is >0.05 S/cm ((Junoh et al., 2020).

IV. Conclusion

Based on the research results, it can be concluded that the best characteristics of chitosan-bentonite composite membrane are obtained by adding 15% bentonite with a thickness test value of 0.06 mm; tensile strength test of 0.018738 MPa; water absorption and methanol absorption of 155% and 0% with a proton conductivity value of 3.42×10^{-7} S/cm.

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