The Current-Voltage Properties of Ch/AgNP Composite Membranes: A Study on the Effect of AgNP Content

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Abstract. In this study, we report the properties of current-voltage (I-V) of Ch/AgNP (chitosan/silver nanoparticles) composite membranes with emphasis on the effect of the content of AgNP. Composite membranes were made by a casting method using chitosan as matrix, 1% acetic acid as solvent and AgNP as filler. The content of AgNP added was 10, 100, 250, 500, 750, and 1000 μg. The I-V measurements were conducted using a two-compartment cell, which contains two working electrodes and two Ag/AgCl reference electrodes. The electrolyte solutions used were KCl and CaCl2 with a concentration of 0.025 M. All measurements were done at room temperature of ± 28 °C. Also, it has been conducted FTIR analysis. The results showed that the absorbance peak of the -OH group in composite membranes are sharper compared with Ch membrane and also it has been observed peaks of Ag-O metal oxide at around 671 and 507 cm⁻¹. The I-V curve of the composite membranes in the range 0.66-0.98 mA is ohmic. The conductance of the composite membranes is smaller than that of Ch membranes, it decreased as increased the content of AgNP added, and it is greater in the KCl solution than in CaCl2 solution.

Keywords: chitosan; AgNP; composite membranes; I-V characteristics; conductance

1. Introduction

Recently, invention and development activity in the application of chitosan (Ch) has been drastically increasing due to its advantages such as biodegradability, non-toxicity, biocompatibility, and renewability [1-3]. Chitosan is a copolymer of glucosamine and N-acetyl glucosamine units which linked by 1-4 glycosidic bonds [1,2]. Chitosan is produced by N-de-acetylation process on chitin. Chitin is a natural polymer that composed by poly(β-(1→4)-N-acetyl-D-glucosamine) which naturally as the structural component of cell walls of fungi, exoskeletons of insects and shells of crustaceous [4].

In nature, chitosan is the second largest biopolymer after cellulose. It has a low cost and has a membrane-forming ability. Also, it has a significant affinity for proteins, water solubility and ease of modification and processing [2]. Accordingly, Chitosan is suitable to be used in many pharmaceutical and medical fields [5-7]. It can be sterilized by some method [8] such as antifungal, antibacterial, and painkilling properties [3,9-12]. Chitosan is known as a versatile biomaterial which presents in many useful forms which commercially available such as microcrystalline powders, fiber, film, membrane, gels, and solutions [13-15]. To improve the features of Ch, it can be done by modifying its structure...
Chemically [9]. Even though, Ch still shows some limitations such as weak mechanical properties, high water content and lack of proper biological response [14]. To solve these, Ch composites with polymers or with other filling materials have been produced [9].

The combination of polymers with nanoparticles (NP), called nanocomposites, produces a family of new materials that are expected to provide better performance [16]. Basically, the combination of inorganic materials into the Ch polymer is intended to improve mechanical properties and sometimes to provide bioactivity to inert materials [17]. Some inorganic materials such as ZnO₂, Cu or Ag have been studied as alternatives to antibiotics for preventing and controlling bacterial infection [18]. The addition of different inorganic fillers to the membranes has affected the microstructural interactions on the surface state. It is varying according to the type of the fillers added. The variations also observed in their conductivity that has been correlated to the interactions take place between the lithium ions and/or polymer on the surface of the oxides [19,20]. A mixture of different materials in a composite can lead to a combination of benefits from a single material. This has been applied in various fields included from the motorized manufacturing to aerospace technology and medical equipment [19].

Based on the background above, the effect of the number of fillers, in this case, the silver nanoparticles (AgNP) on the current-voltage characteristics of the chitosan composite membrane has been investigated.

2. Methods

2.1. Materials

Materials used were chitosan powder with a deacetylation degree (DD) of 87.4%, the average molecular weight of 900 kDa and the solubility in acetic acid is 99.4%. Acetic acid and sodium hydroxide were analytical grades, and the solutions were prepared using demineralized water. Silver nanoparticles used were synthesized by biological methods using Sambiloto (Andrographis paniculata) leaf extract. Its characteristics are particles sizes of 10-30 nm, Surface Plasmon Resonance (SPR) wavelength of 423 nm and crystal structure of face center cubic (FCC) with lattice parameter (a) of 4.03 Å.

2.2. Membranes preparation

Membranes were made by a casting method with a matrix of chitosan, a solvent of 1% acetic acid and a filler of AgNP. The composites membranes prepared were based on chitosan membrane 2% by adding various amounts of AgNP. The amount of AgNP used was 10, 100, 250, 500, 750 and 1000 μg. Those membranes named as Ch/AgNP10, Ch/AgNP100, Ch/AgNP250, Ch/AgNP500, Ch/AgNP750, and Ch/AgNP1000 respectively. Chitosan membrane 2% named Ch has been prepared as a comparative membrane. The preparation included of mix 2% wt chitosan powder with AgNP until homogeneous then add with 1% (v/v) acetic acid and stirred for 4 hours at ambient temperature of 30 °C. The casting solution was poured on a glass plate (size of 18.5 cm x 24.0 cm) then allowed to dry at ambient temperature (for 12 days). The dried membrane was dipped in 1 M NaOH for 12 minutes, continued to be washed using distilled water three times and then dried again. Lastly, it got a dry composite chitosan membrane that is ready to be characterized or used. The casting method was as described in [21,22].

2.3. Characterization methods

The current-voltage (I-V) characterization was done using a cell which contained two compartments. The area of the membrane used was 9.616 cm² and the electrodes used were platinum. The voltage was measured by Ag/AgCl electrodes. All experiments were done at room temperature of 28.7 °C. Also, to study of any structural changes occurred, the infrared spectra have been recorded using a Fourier Transform Infrared (FTIR) spectrophotometer, IR Prestige-21, Shimadzu over a region of 400 to 4000 cm⁻¹ with a resolution of 4 cm⁻¹.
3. Results and Discussion

3.1. IR spectrum analysis
The infra-red (IR) spectrum of all membranes are presented in Figure 1 and its functional group’s analysis are presented in Table 1.

![IR spectrum of membranes](image)

**Figure 1.** The IR spectrum of membranes: Ch, Ch/AgNP10, Ch/AgNP100, Ch/AgNP250, Ch/AgNP500, Ch/AgNP750 and Ch/AgNP1000.

The FTIR spectrum of Ch membrane shows that broadband at around 3468 cm$^{-1}$ corresponds to the stretching vibrations of -OH and N-H groups. The absorption band at around 2864 and 1656 cm$^{-1}$ represent vibrations of the C-H groups and C = O carbonyl groups, respectively. The peaks at around 1170 and 2933 cm$^{-1}$ are related to vibration of -CN and -CH$_2$ groups [21-23]. The peaks at around 3400 and 1606 cm$^{-1}$ were the characteristics of stretching and bending vibrations of the -NH$_2$ amine groups. The peaks at around 1417 and 1386 cm$^{-1}$ correspond to the vibration of the -OH and -CH groups on the pyranose ring. The peak at around 1053 cm$^{-1}$ is associated with anti-symmetric C-O-C glycoside stretching.

The FTIR spectrum of the Ch-AgNP10 composite membrane shows that all bands observed on the Ch membrane were also observed in the Ch-AgNP10 composite membrane. Also in the fingerprint region, it has been observed peaks at around 671 and 507 cm$^{-1}$ represent vibration of Ag-O metal oxides [22-24]. The absorption characteristic of metal oxide was influenced by the type of metal and the composition of organic compounds in it [23]. The same peaks also were observed in those composite membranes: Ch/AgNP100, Ch/AgNP250, Ch/AgNP500, Ch/AgNP750, and Ch/AgNP1000. In general, the change from Ch membrane to Ch/AgNP composite membranes could be identified through changes in the –OH absorption bands. The -OH absorption band in the Ch membrane was broader compared within the Ch/AgNP composite membranes. This could be due to the reduced hydrogen bond in chitosan with the present of AgNP fillers.
Data on Table 1 shows that the peaks appear to have undergone several changes, including the shifting of the peak. The absorption peak of OH stretching in the composite membranes were shifted to the greater wavenumber compared with that of membrane Ch. The same thing also occurred to the stretching vibration of the C-H group. Meanwhile, C=O amide groups are almost constant or not shifted. The -CH₂ group in the composite membranes have shifted to the smaller region, except for the Ch-AgNP10 composite membrane, the peak does not shift. The shifting phenomenon of each functional group on each membrane is shown in Table 1. Similarly, there was a change in the intensity of transmittance. The transmittance intensity of composite membranes increased with an increasing mass of fillers from 10 µg to 750 µg, whereas at the addition of mass to 1000 µg the intensity of transmittance reduced. In this case, the transmittance intensity was smaller than the addition of 750 µg. These indications signified changes in the chemical structure of the composite membranes occurred.

| Functional groups          | Reference*       | Ch       | Ch/AgNP10 | Ch/AgNP100 | Ch/AgNP250 | Ch/AgNP500 | Ch/AgNP750 | Ch/AgNP1000 |
|----------------------------|------------------|----------|-----------|------------|------------|------------|------------|-------------|
| OH and NH stretching       | 3700-3000        | 3400     | 3431      | 3423       | 3477       | 3448       | 3483       | 3410        |
| C-H stretching             | 3000-2800        | 2864     | 2937      | 2935       | 2920       | 2920       | 2941       | 2956        |
| C=O amide                  | 1700-1500        | 1656     | 1662      | 1653       | 1653       | 1656       | 1656       | 1664        |
| CN                         | 1350-1000        | 1170     | 1170      | 1170       | 1172       | 1168       | 1172       | 1174        |
| CH₂                        | 3000-2850        | 2933     | 2947      | 2850**     | 2858       | 2877       | 2883       | 2881        |
| NH₂ stretching and amine   | 3500-3400        | 3400     | 3431      | 3423       | 3477       | 3448       | 3483       | 3410        |
| bending                    | 1640-1560        | 1606     | 1566      | 1593       | 1612       | 1597       | 1597       | 1598        |
| OH and CH pyranose         | 1500-1200        | 1417     | 1425      | 1411       | 1425       | 1411       | 1411       | 1400        |
|                            | 1500-1300        | 1386     | 1390      | 1394       | 1392       | 1381       | 1381       | 1381        |
| C-O-C anti-symmetric      | 1200-1050        | 1053     | 1124      | 1124       | 1124       | 1122       | 1126       | 1130        |
| glycoside                  |                  |          |           |            |            |            |            |              |
| Ag-O (metal Oxide)         | 400-600          | -        | 513       | 513        | 513        | 511        | 507        | 513         |

* Silverstein (1981)[22]
** The peak is weak.

3.2. I-V characteristics.
Figure 2 and Figure 3 shows the I-V curve of Ch/AgNP composite membranes observed in ion transport in KCl and CaCl₂ electrolyte solutions with a concentration of 0.025 M. The curves show the ohmic characteristic where the current increase linearly with increased the potential. The conductance (1/R or G) of the membranes in each solution was obtained from the slope of I-V curves as shown in Table 2.
Figure 2. The I-V curves of Ch/AgNP composite membranes in KCl solution with a concentration of 0.025 M.

Figure 3. The I-V curves of Ch/AgNP composite membranes in CaCl₂ solution with a concentration of 0.025 M.
Table 2. The conductance (G) of Ch/AgNP composite membranes in KCl and CaCl$\textsubscript{2}$ solutions with a concentration of 0.025 M.

| Membranes   | Conductance (mA/V) | KCl  | CaCl$\textsubscript{2}$ |
|-------------|--------------------|------|------------------------|
| Ch          | 0.711              | 0.662|
| Ch/AgNP10   | 0.650              | 0.650|
| Ch/AgNP100  | 0.659              | 0.611|
| Ch/AgNP250  | 0.620              | 0.633|
| Ch/AgNP500  | 0.589              | 0.633|
| Ch/AgNP750  | 0.548              | 0.532|
| Ch/AgNP1000 | 0.520              | 0.516|

Data in Table 2 shows that the membrane conductance in KCl solution is greater than in CaCl$\textsubscript{2}$ solution except in Ch-AgNP250 and Ch-AgNP500 composite membranes, their membrane conductance in CaCl$\textsubscript{2}$ solution is greater than in KCl solution. The greater conductance indicates that the ability of a membrane to carry ions is greater than that of a membrane with smaller conductance. The results are in accordance with what has been reported by Jae-Hwan Choi, et al. [25] and Rupiasih [26]. The difference in the conductance occurred is due to both electrolyte solutions have different of molar conductivity and radius of Stoke. The conductance of the membrane is greater in a solution that has a smaller molar conductivity and radius of Stoke. The molar conductivity and Stoke radius for KCl solution were 73.55 x 10$^4$ S.m$^2$.mol$^{-1}$ and 0.125 nm; whereas CaCl$\textsubscript{2}$ solution is 119.0 S.m$^2$.mol$^{-1}$ and 0.308 nm [25,26].

The effect of the addition of AgNP as a filler on the Ch/AgNP composite membranes is that the conductivity of the Ch/AgNP composite membranes is smaller than that of the Ch membrane. The conductivity of the Ch/AgNP composite membranes is decreased with increasing the mass of AgNP added. This was observed in both types of electrolyte solutions used, KCl and CaCl$\textsubscript{2}$. So it can be said that the addition of AgNP as filler will reduce the membrane conductance of Ch membrane and the greater the mass of AgNP added, the smaller the conductivity of the Ch-AgNP composite membranes. This behavior is associated with the changes in the chemical structure occurs in the composite membranes due to the presence of AgNP [19,22,23]. These results are confirmed by the results of the analysis of the FTIR spectrophotometer, namely the change in transmittance intensity and the shift of wavenumbers of peaks, especially in the -OH functional group [23].

4. Conclusion

The study reported the properties of current-voltage (I-V) of Ch/AgNP composite membranes with a stressing on the effect of the content of AgNP as filler. The results showed that the absorbance peak of the -OH group in composite membranes were sharper compared with Ch membrane and also it has observed the peaks of Ag-O metal oxide at around 671 and 507 cm$^{-1}$. The I-V curve of the Ch/AgNP composite membranes in the range 0.66-0.98 mA is ohmic. The conductance of the composite membranes was smaller than that of Ch membranes, it decreased as increased the content of AgNP added, and it was greater in CaCl$\textsubscript{2}$ solution.

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