Electrical Characterization of Chitosan Film for Mercury Ion Detection by using Four-Point Probe Method

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ABSTRACT— ***This paper reports the results of electrical characterization of chitosan film for mercury ion detection. The electrical resistivity of the film with different concentration, temperature and contact time with mercury solution was studied. This parameters have been measured with four-point probe method by the measurement of current (nA) and voltage (mV). The experimental results show that the variation of the concentration, mercury solution temperature and contact time between chitosan film and the mercury solution affected the resistivity of the chitosan film. This study has shown the capability of chitosan to bind mercury ions by chelation as one of its main properties and the present study will be a good base for further development of lab-on-chip sensor for heavy metal detection.***

Keywords—- Chitosan, Mercury, Resistivity, Four-Point Probe

1. INTRODUCTION

Chitin is one of the most abundant polysaccharide occurring in nature (Rinaudo, 2006). The process of removing acetyl groups from the chitin backbone and replace with amine groups will produce chitosan (Nemtsev, Gamzazade, Rogozhin, Bykova, & Bykov, 2002):(Murray & Dutcher, 2006). Chitosan is a linear cationic polysaccharide, non-toxic, biodegradable and commonly found in the cuticles of many invertebrates such as crab and shrimp shells and occurs naturally in the cell walls of most fungi and some alga (W. Fen & Yunus, 2011) (Wan, Creber, Peppley, & Bui, 2003):Rhazi et al., 2002): (Moksin, Talib, & Yusof, 2011) (Wan Ngah, Endud, & Mayanar, 2002)(Rinaudo, 2006)(Mcilwee, 2008) (Adikary & Lanka, 2001). Chitosan was found to have outstanding absorbents capability compared to chitin in absorbing heavy metal ion due to the presence of a large number of amino groups in chitosan chain (Tikhonov, Radigina, & Yamskov, 1996) (Rhazi et al., 2002)(Yang & Zall, 1984)(Muzzarelli & Terbojevich, 2000).
Cases of heavy metal pollution have been increasingly reported in recent years. Based on survey by the Department of Environment Malaysia in 2009, 4.9 % of the 1705308.14 metric tons of schedule waste generated contain heavy metal sludge where it proved that heavy metal pollution has grown to a dangerous level(Y. W. Fen, Mahmood, Yunus, & Yusof, 2011). These include cases of heavy metal ions including mercury, being detected in water source, soil and in food products such as in shellfish. These contaminations originated from industrial pollution, improper disposal of electrical goods and also from agricultural activities. The exposure to mercury causes loss of myelinated nerve fibers, abnormal central nervous system cell division and autonomic dysfunction (Ozuah, 2000) . Autism and neurodevelopmental syndrome are also linked to the mercury poisoning. Several symptoms which are associated with autism such as immune, sensory, neurological motor and behavioral dysfunctions are found in mercury poisoning cases (Bernard, Enayati, Roger, & Binstock, 2002). Various methods can be used for detection of mercury ions. This ranges from spectroscopy methods, titration methods to electrochemical methods (Forzani, Foley, Westerhoff, & Tao, 2007;

Magee & Rahhan, 1965). Four-point probe is the well-established and expedient tool for the measurement of resistivity especially for semiconductor materials. Four-point probe have been extensively studied for years. It offers several advantages such as it permits measurement of resistivity in samples having a wide variety of shapes, including the resistivity of small volumes (Valdes, 1954). Four-point probe is an alternative method and capable to yield accurate results for in-situ measurement. The combination of four-point probe and chitosan film for detection mercury ion is described in this paper. To the best of our knowledge, four-point probe is yet to be used for mercury ion detection.

2. THEORY

Four-point probe is a technique used to measure electrical resistivity by superficial contact. It is mainly used in semiconductor industry, manufacturing and research field (Panta & Subedi, 2012). Four-point probe contains four thin collinearly placed tungsten wire probes which are made to contact with the sample under test. Four sharp probes are placed on the flat surface of the sample under test, while current is made to flow between the outer probes, and voltage is measured between the two inner probes, ideally without drawing any current. In this project, the resistivity measurement was carried out using four-point probe with equal spacing between the probes. Due to the current and voltage leads are separate, the errors due to electrical contacts are absent. Resistivity measurement on a large sample is given in Equation 1 (Valdes, 1954).

$$\rho = (V/I) \times 2\pi s \qquad [1]$$

Where V is the voltage in mV, I is the current in nA and s is the spacing between two point electrode. In this project, s = 1mm. For the case where the spacing between all probes are equal, the sheet resistivity obtained by formula as expressed in Equation 2 (Smits, 1958).

$$\rho = (\pi/\ln 2)\ (V/I) \qquad [2]$$

3. METHODOLOGY

All reagents were analytical grade and deionized water was used. Acetic acid glacial Grade AR, M= 60.05 g/Mol, standard solution of mercury with concentration 1000 ppm was purchased from MERCK (Merk, Darmstadt, Germany) and chitosan (medium molecular weight) was purchased from Sigma-Aldrich, USA with 75-85 % deacetylated. For the glass mould, a solid glass with thickness of 0.6 cm was used and a circular cut-out with diameter of 13 cm was made at the centre.

B. Preparation of mercury ion solution

Mercury ion standard solution (1000 ppm) was diluted by using dilution formula ($M_1V_1 = M_2V_2$) to produce mercury ion solution with concentrations of 0.5, 1, 2 and 2.5 ppm.

C. Preparation of chitosan solution

To prepare chitosan solution, 1.0 g of chitosan flakes is dissolved in 100 ml of 1% (v/v) acetic acid. The chitosan solution was stirred for 24 hours to obtain a homogenous solution.

D. Preparation of films

5 µm thin plastic sheet was placed underneath the glass mould and fix in place with silicon sealant. The prepared mould was left to dry for 24 hours to allow for the sealant to cure before the next process. The homogenous chitosan solution was poured into prepared mould. The solution was left on a flat surface for 2 weeks to dry at room temperature to produce smooth and even membrane. The surface has matte finish when the membrane is completely dry. The plastic sheet from the mould was then peeled away from the glass mould and dried membrane will adheres to the plastic sheet and form the film. The film was then cut to the required size, soaked in the deionized water for 1 hour and again dry for one day (Yusof & Ahmad, 2002). In the work presented here, the film was cut into squares with an area of 0.64 cm^2. The total thickness of the chitosan film was measured using micrometer screw gauge and the thickness is 0.024 cm.

E. Resistivity Measurement

Resistivity measurement of the chitosan film was carried out using four-point probe. For these measurements the current was varied from -35 nA to 35 nA. The measurement data were plotted on the graph as current, I (nA) against voltage, V (mV). Repetitive electrical measurements of the film with mercury solution were conducted at room temperature for various contact times, mercury solution concentrations and solution temperatures.

4. RESULTS AND DISCUSSION

Response to the chitosan film was first tested for a difference contact time, followed by concentration and temperature with mercury solution. To study the effect of different contact time of chitosan film with the mercury solution, the film was immersed in 8 ml of 0.5 ppm mercury solution at time interval of 1, 2, 4 and 8 minutes. The resistivity of the chitosan films, was calculated by using formula in Equation 2.

A. Contact Time

At soaking time of 1 to 4 minutes the resistivity of the film decreased as shown in measurement result in Figure 1. Reduction in resistivity of the film corresponded to higher numbers of mercury ions adsorb onto chitosan film. Where there are more metal ions adsorbed, it helps carry electrical charges and in turn decreased the resistivity of chitosan film.

However, at 8 minutes, the measurement shows an increment in resistivity. This might be contributed to the maximum adsorption of mercury ion has been obtained at time before 8 minutes. Table 1 shows the resistivity of chitosan film at different contact time.

Table 1: Resistivity of chitosan at different contact time with mercury solutions

Time (minutes)	Resistivity (MΩ.cm)
1	11.92
2	10.20
4	8.57
8	9.02

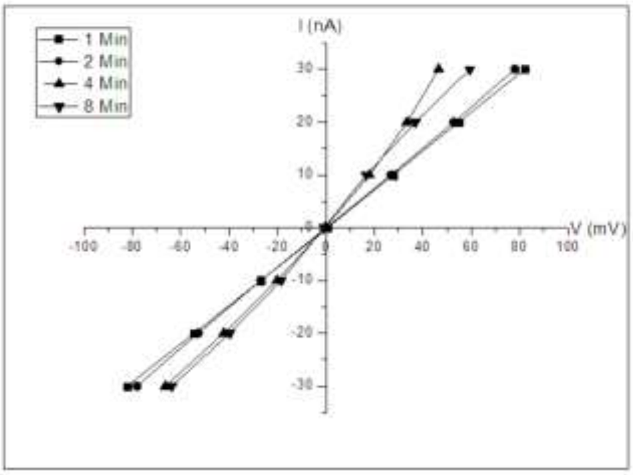

Figure 1: IV graph of chitosan at different contact time with mercury solution

B. Concentration

The response of the chitosan film towards various concentrations of mercury was also tested. For the relationship of resistivity of chitosan film with the concentration of mercury solution, the chitosan film was soaked into 8 ml of four different concentrations of mercury solution which are 0.5, 1, 2 and 2.5 ppm for 1 minute. The film was dipped into 8 ml mercury with concentration ranging from 0.5 to 2.5 ppm for one minute. The measurement result is shown in Figure 2.

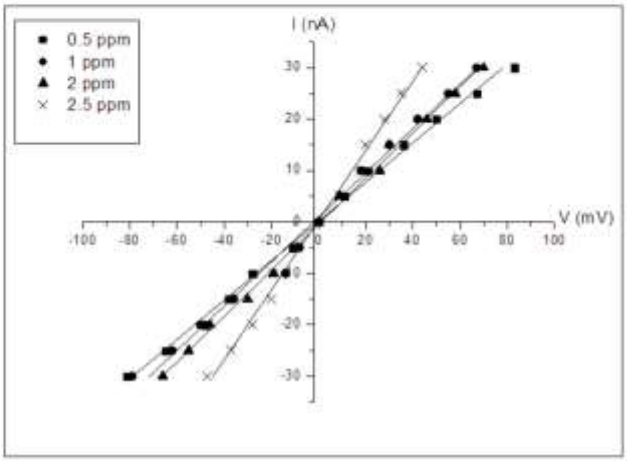

Figure 2: IV graph for chitosan at different concentration of mercury solution

Table 2 shows that the resistivity of the film decreased as the concentration of mercury ions is increased. Increasing the concentration of mercury will provide more ions to the solution, therefore more ions to be adsorbed by the chitosan film (Bamgbose, Adewuyi, Bamgbose, & Adetoye, 2010). This result also indicates that the film will have a higher adsorption rate in high concentrations of mercury compared to at the lower concentration (Lin, Chang, & Lin, 2012). Good sensitivity in the measurement was also observed with the ability to detect low concentrations of mercury, which is 0.5 ppm, which is the minimum limit of mercury in drinking water allowed by the Ministry Health of Malaysia (Alina et al., 2012).

Table 2: Resistivity of chitosan film soaked into different mercury concentration

Concentration(ppm)	Resistivity(MΩ.cm)
DI water	18
0.5	11.92
1	10.52
2	10.20
2.5	6.62

C. Temperature

The effect of temperature on resistivity was explored at 40, 50, 60 and 70˚C by soaked the chitosan film into the 8 ml of mercury solution for 1 minute for each temperature. To investigate the influence of temperature on the film's ability to adsorb ions, 8 ml of mercury solution was heated to the required temperature. The film was then soaked in the solution for 1 minute. The relationship between film resistivity and mercury temperature is shown in Figure 3.

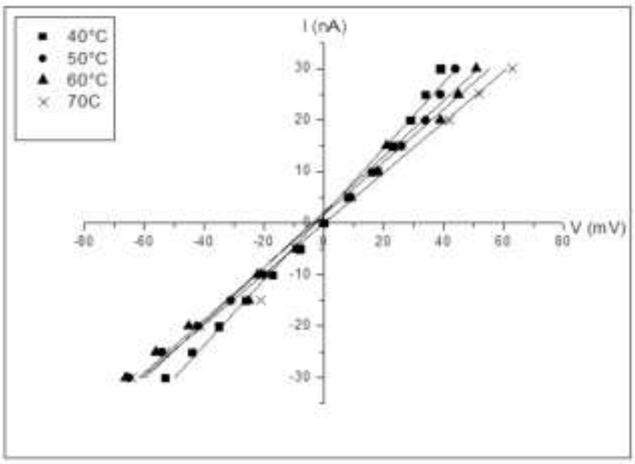

Figure 3: IV graph for chitosan at different temperatures of mercury solutions

From Figure 3, it is evidently shown that the resistivity value of chitosan film towards the heavy metal solution increased with temperature. As temperature increases, the chitosan will convert into chitin like material (Adikary & Lanka, 2001). Chitin is polysaccharide material that has less amino groups compared to chitosan (Sağ & Aktay, 2000). Amine group is the one which is responsible in chelating the heavy metal ions. Having a less amine group will result in fewer amounts of mercury ions adsorb onto chitosan films and produced higher resistivity. The resistivity of chitosan film at different temperature is given in Table 3.

Table 3 Resistivity of chitosan film with different temperature of mercury solution

Temperature (°C)	Resistivity (MΩ.cm)
40	7.07
50	8.38
60	8.70
70	9.25

5. CONCLUSION

This study has shown the capability of chitosan to bind mercury ions by chelation as one of its main properties. The results show that the resistivity of the chitosan film varies at different heavy metal concentration, contact time and solution temperature. The variation of resistivity values is attributed to the different amount of ions binding onto the chitosan. The present study will be extended in future such that the ability of chitosan film to be used as part of electronic sensor for mercury ion detection.

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