PREPARATION AND CHARACTERIZATION ION SELECTIVE ELECTRODE Cd(II) BASED ON CHITOSAN IN PVC MEMBRANE

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Received August 15, 2011; Accepted October 10, 2011

ABSTRACT

Preparation of the chitosan membrane of ion-selective electrode for determination of cadmium ion has been conducted. Chitosan is a natural polymer containing nitrogen could coordinate with Cd^{2+} to increase the membrane conductivity value. Chitosan is a principal material and mixed with polyvinylchloride (PVC) as matrix dissolved previously to solvent tetrahydrofuran (THF) and dioctylphenylphosphonate (DOPP) is added as plasticizer by proportion chitosan:PVC:DOPP (6:3:1). To obtain the dopant optimum concentration, membrane was dipped in Cd^{2+} for 7 days and its conductivity value was measured using the four-point probe method. From FT-IR spectrum the peaks of amine, acetylamide and hydroxy groups wavelength number was observed to assure that Cd^{2+} bound to the chitosan. The optimum concentration of Cd^{2+} dopant was obtained at 1.00 M with conductivity value of 549.45 $ohm^{-1}m^{-1}$ wich gave a Nernstian factor of 32.03 mV/decade with the detection limit of 2.512×10^{-5} M. The electrodes work in the pH range 3 - 7. The life time of the electrode was 8 weeks. The ions of Ni^{2+}, Fe^{3+}, Pb^{2+}, Cu^{2+}, Zn^{2+}, Cl^- and SO_4^{2-} toward concentration range 10^{-3} M gave response did not interfere in the determine of Cd^{2+} ion.

Keywords: *Ion Selective Electrodes, Cadmium, PVC membrane, Chitosan*

INTRODUCTION

In recent years there has been a growing need or desire for constructing chemical sensors for fast and economical monitoring of our environmental samples especially for heavy metal ions in real time [1]. One of the chemical sensors that concerns researchers these days is ion selective electrode (ISE) which is a very wide electrochemical sensor usage. This is because ISE can be controlled in a laboratory and used in the daily work [2]. Potentiometric detection based on ISE, as a simple method, offers several advantages such as speed and ease of preparation and procedures, simple instrumentation, relatively fast response, wide dynamic range, reasonable selectivity, and low cost. These characteristics have inevitably led to sensors for several ionic species, and the list of available electrodes has grown substantially over the last few years [3]. ISE was first made of membrane glass, for used to measure the pH of the solution, further developed for determining concentrations of various metals such as Na^+, K^+, NH_4^+, Ca^{2+} and heavy metals such as Cu^{2+}, Pb^{2+}, and Cd^{2+} [4].

Chitosan is the molecular poliglucosamine obtained from deacetylation of chitin derived from crab shells, shrimp, squid, crustaceans and other animals, have been used as an absorbent metal Cu, Cr, Pb and Zn [5]. Chitosan can also be formed into thin membranes [6] and has made ISE Fe^{3+} using PVC as the matrix [7]. This is possible because chitosan has a lone pair of the amine and acetylamide groups which can form complexes with transition metals and post transition [8].

The conductivity of chitosan membranes can be improved by adding a certain amount of metals into the membrane. Metals added are referred to as a dopant metal. There are two ways to dope often performed by direct addition of dopants during the manufacture of membranes and with soaking in a solution of dopant. Doped by immersion will provide the membrane with a uniform conductivity in all parts of the surface so that the sensitivity increases and durable [9]. The optimum concentration for each metal were added to the membrane are specific, and can be distinguished from the other metals [10].

Weakness of the chitosan membrane electrode is easy to leak causing the solution may fall into the test solution. Chitosan membrane has a low tear resistance and to overcome them use PVC as a matrix by adding a little plasticizer [11].

In this research, ISE Cd^{2+} has been developed from the membranes of chitosan by adding dopants Cd^{2+} into the chitosan at matrix PVC through immersion, determining the concentration of optimum dopant and characterization ISE Cd^{2+} designed includes: Nernstian factor, detection limit, pH measurement, response time, life time and the influence of interfere ionic.

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EXPERIMENTAL SECTION

Materials

The materials used in this research were chitosan (Fluka), Polyvinylchloride (PVC) and dioctylphenylphosphonate (DOPP) (Sigma), cadmium nitrate, zinkum chloride, nickel nitrate, ferric chloride; cuprum sulfate, plumbum nitrate, potassium nitrate, potassium chloride, potassium sulphate and tetrahydrofuran (THF) (Merck), and araldite glue (RS Components).

Instrumentation

Equipment used in the manufacture of membrane is glass plate, glass equipment (E 'Merck), a digital multimeter to measure resistance, pH meter Orion model 420A to measure the electrical potential, to observe the shift in numbers wavelength of functional groups that can from complexes after membrane doped with Cd^{2+} used FT-IR spectroscopy (Prestige 21-Shimadzu).

Procedure

Membrane preparation

Chitosan was crushed to 400 mesh, 0.375 g PVC was dissolved in 20 mL of THF and added 1.0 mL DOPP, stirring with a magnetic stirrer, then the 0.750 g of chitosan was added gradually to the mixture and stirred for 2 h at room temperature. The mixture was poured into a glass plate and left until all the solvent evaporated and the obtained chitosan membranes. The same procedures are done also by comparison of the addition amount of chitosan, PVC and DOPP varied.

Membrane Doped

Chitosan membrane is cut into several circular with a diameter of 1.5 cm. Membranes dipped in a solution of $Cd(NO_3)_2$; 0.25, 0.5, 0.75, 1.0, 1.25 and 1.5 M for 5 days, removed and dried in oven at 40 °C for 30 min.

Membrane Conductivity measurements

Membranes that have been soaked in a solution of $Cd(NO_3)_2$ at various concentrations. Conductivity measurements carried out with four-point probe estimator's method by passing a current at two electrodes and measuring the resulting voltage at the other two electrodes. From the measurement results of the highest conductivity can be determined optimum concentrations of dopants, which in turn will be used on the assembly of Cd^{2+} ion selective electrode.

Characterization of Cd^{2+}-Chitosan Membranes

To observe the binding of Cd^{2+} dopant in the membrane is done by observing changes in the wavelength number amine, acetylamide and hydroxy groups of chitosan which may form complexes with Cd^{2+}. This is done by FT-IR spectroscopic analysis.

Working Electrode assembly

Membrane Cd^{2+}-chitosan that used as the working electrode is made by cutting the membrane glass, then the membrane Cd^{2+}-chitosan affixed using araldite glue, the electrode filled with 1M $Cd(NO_3)_2$ was added 1M KNO_3 as a ion strength adjusted buffer solution in the ratio 1:2.

Characterization of Cd^{2+} Ion Selective electrode

Characterization of Cd^{2+} ion selective electrode includes of the determination of the Nernstian factor, detection limit, pH measurement, response time, life time and the influence of interfere ion. The procedure works as follows: solution of 10^0 M Cd^{2+} is provided as stock standard solution. From the above solution was diluted to make a solution of Cd^{2+} were 10^{-1}, 10^{-2}, 10^{-3}, 10^{-4}, 10^{-5} and 10^{-6} M of each of 20 mL. In each of the above solution of Cd^{2+} added 2 mL of 1 M KNO_3 as ionic strength adjusted buffer. Each solution was measured using the membrane electrode potential electrode Cd^{2+}-chitosan as the working electrode using a pH meter while stirring with a magnetic stirrer. Potential E (mV) measured against log $[Cd^{2+}]$. The Nernstian factors determined from the slope of the resulting curve. Detection limit values obtained from the extrapolation point of the curve log $[Cd^{2+}]$ against potential E (mV). The same procedures was done to determine the interval of pH measurement, response time, life time, and the influence of interfere ions; Zn^{2+}, Fe^{3+}, Ni^{2+}, Cu^{2+}, Pb^{2+}, Cl^-, and SO_4^{2-}.

RESULT AND DISCUSSION

Optimum dopant concentration of Cd^{2+}

Membrane Cd^{2+}-chitosan has been conducted with a thickness membrane of 0.12 mm, with an optimum composition proportion of chitosan:PVC:DOPP (6:3:1) [12]. Chitosan membranes soaked in a solution of the dopant $Cd(NO_3)_2$ with various concentrations during 7 days, the conductivity value was measured using four-point probe method. The results of conductivity measurements are shown in Fig. 1.

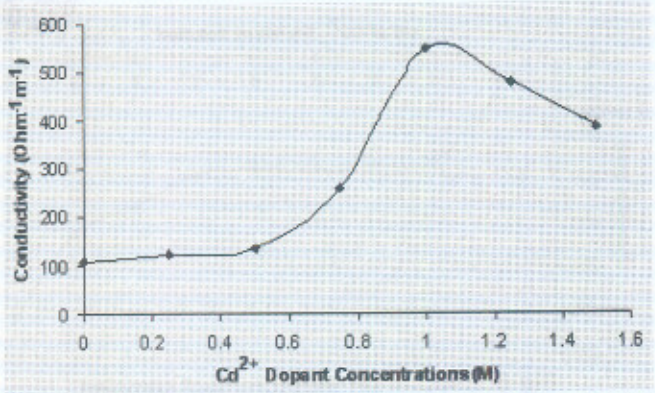

Fig 1. Membrane Conductivity at various dopant concentrations

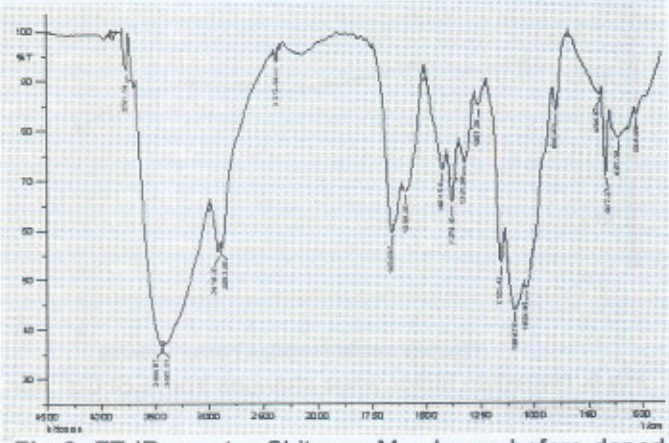

Fig 2. FT-IR spectra Chitosan Membrane before doped with Cd^{2+}

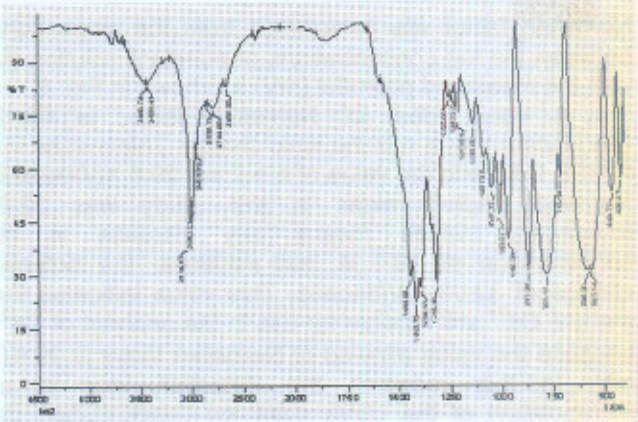

Fig 3. FT-IR spectra Chitosan Membranes after doped with Cd^{2+}

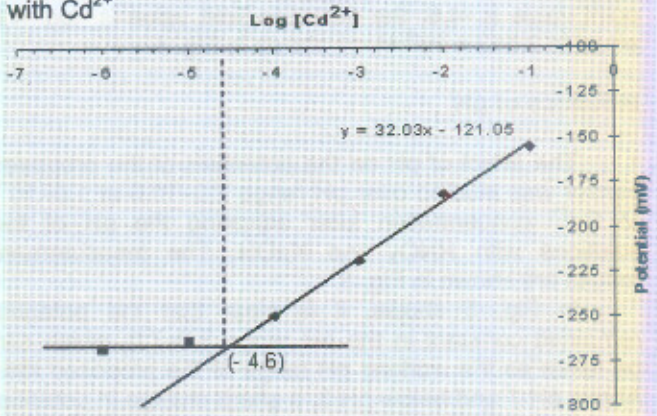

Fig 4. Determination of Nernstian factor and Detection limit of ISE Cd^{2+}

Immersion of metal ions to chitosan membrane can increase the conductivity value of membranes. The optimum dopant concentration is 1.0 M Cd^{2+} with the conductivity value is 549.45 $ohm^{-1}m^{-1}$. In this state the resistivity of the membrane decreased to the minimum value and increased membrane conductivity. The aim of conductivity measurement is to determine the optimum concentration of dopants, because the optimum concentration for each metal were added to the membrane are specific, and can be distinguished from the other metals [10].

Measurement of the Functional Groups Chitosan Membranes

There are two possibilities Cd^{2+} ion binds to the chitosan membrane is through the amine groups or amine and acetylamide groups or both [13]. Metal ion dopants provide special characteristics to form a complex with chitosan [8].

From FT-IR spectra in Fig. 2 prior to membrane before doped with Cd^{2+} showed that the N-H stretch of secondary amine (acetylamide group) at the wavelength 1652.85 cm^{-1} and N-H stretch of the primary amine at the wavelength 1589.34 cm^{-1}.

Fig. 3, the membrane after doped with Cd^{2+} showed peaks indicate the presence of N-H acetylamide and N-H stretch of primary amines group does not appear. While the peak of OH^- group at wavelength number ~3400 cm^{-1} decrease in intensity. This is made possible that the N and O atoms are the amine ligands and hydroxide will form a complex compounds bond with Cd^{2+} ions which are electropositive, by donating its lone pairs electron, the N-H bond become weakness and its peak did not reappear. From FT-IR spectral data above is known that Cd^{2+} ions form a complex with chitosan through primary amine groups, acetylamide groups and hydroxy groups.

Nernstian Factor and Detection Limits

Nernstian factor is an important parameter to determine electrodes are proper used in analysis.

Nernstian factor are determined from the slope curve between the log concentrations of standard solution (M) with the measured potential (mV) as shown in Fig. 4.

A value ideal of Nernstian factor is 59.1/n (mV/decade), with n is the ionic charge. This means that for ISE Cd^{2+} with the value of n = 2 are 29.6 mV/decade. Nernstian factor values in this study was 32.03 mV/decade, which means any increase in the concentration of 10^{-1} M test solutions, the potential change of 32.03 mV/decade. This value indicates that the ISE Cd^{2+} still feasible for use in the analysis of Cd^{2+}, because the value allowed of Nernstian factor is 29.6±5 mV. In this research the detection limit is an extrapolation of the curve point log concentration (M) against potential (mV). From the curve extrapolated point value is -4.6, the detection limit value is -log -4.6 equal to 2.512×10^{-5} M, as shown in Fig. 4.

Influence of pH

The effect of pH on the potentials of the proposed sensor was studied over pH range 2.0–10.0 at 1.0×10^{-3} M Cd^{2+} concentration after adjusting the pH of the solutions with HNO_3 and NaOH. The measurement results are shown in Fig. 5.

In Fig. 5 shows, it is clear that the potential remained constant in the pH range 3.0–7.0, which can be taken as the working pH range of the proposed ISE. Above pH 7 and below pH 3, a sharp change in potential may be attributed to the hydrolysis of Cd^{2+} become $Cd(OH)_2$ and disruption of H^+ ions from the test solution, respectively [14].

Response Time

The determination of the response time based on the provisions of international is the time required to reach 1 mV of final equilibrium potential after a sudden change in the primary ion activity [15]. The results were obtained response time measurement range 15-45 sec, the higher concentration of test solution the faster the response time. Agitation rate for each time the measurement should be constant. Different stirring speeds will give different response times, but the stirring speed is too high also interfering the measurement, because the magnetic stirrer hit the surface of the membrane.

Life Time

The life time of ESI Cd^{2+} is determined by measuring the Nernstian factor value changes for every week. Nernstian factor values are measured each week are shown in Fig. 6.

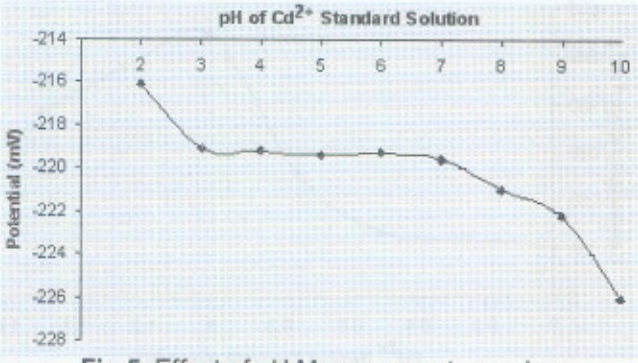

Fig 5. Effect of pH Measurement samples

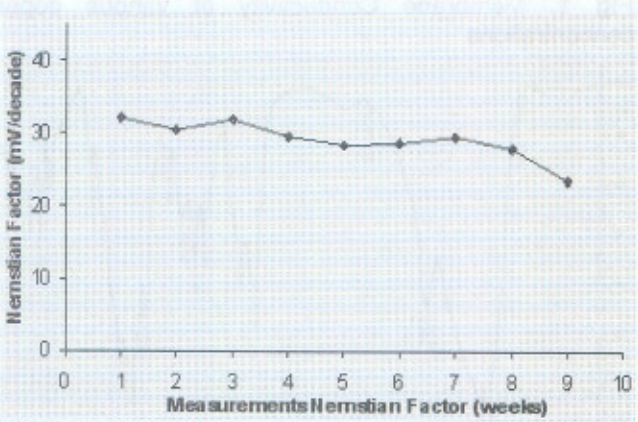

Fig 6. Nernstian factor value changes from ESI Cd^{2+} for every weeks

From Fig. 6, Nernstian factor value obtained at 8-week was 27.95 mV/decade, while at 9-week, the Nernstian factor value have dropped dramatically become 23.50 mV/decade, assumed ISE Cd^{2+} is no capable use for analysis. Electrode can be used only during the life time of 8-weeks. This is influenced by the aging process on the membrane resulted swelling both in the chitosan or the PVC as a matrix, and reduce the sensitivity of ISE showed by the decrease of the Nernstian factor value.

Effect of Ion Interfere

The selectivity coefficients, which reflect the relative response of the membrane sensor towards the primary ion over other ions present in solution, are perhaps the most important characteristics of an ISE. In this work, the potential responses of the proposed Cd^{2+} membrane sensor to a wide variety of cations and anions were investigated through the matched potential method (MPM) [16]. The concentration of interfere ions solution are 10^{-3} M. To determine the degrees of disorder of interfere ions in the test solution is done by calculating the coefficient selectivity:

Table 1. The selectivity of coefficient value of ISE Cd^{2+} for interfere ions

Interfere ions	K_{ij}^{pot}
Ni^{2+}	0.251
Fe^{3+}	0.025
Pb^{2+}	0.063
Cu^{2+}	0.158
Zn^{2+}	0.398
Cl^-	0.630
SO_4^{2-}	0.251

$$K = K_{ij}^{pot} = \frac{a_i}{a_j}$$

For the interfere ion Ni^{2+} obtained the selectivity coefficient value ISE Cd^{2+} was 0.251. The value indicates the ISE Cd^{2+} 25.1 times more selective against the major ions Cd^{2+} compared with Ni^{2+} ion. The selectivity of coefficients value showed ESI Cd^{2+} which made did not interfere with presence Ni^{2+} ion at 10^{-3} M in the standard solution.

The same calculations done also for interfere ions Fe^{3+}, Pb^{2+}, Cu^{2+}, Zn^{2+}, Cl^-, $SO_4^{2-}$and obtained the selectivity of coefficient value as shown in Table 1.

Interfere ions Ni^{2+}, Fe^{3+}, Pb^{2+}, Cu^{2+}, Zn^{2+}, $Cl^-$and SO_4^{2-} up to a concentration of 10^{-3} M did not provide responses that interfere with the measurement of Cd^{2+}. ISE Cd^{2+}- chitosan more selective than ISE from glass-CdS-AgI Sb_2S_3, this ESI is not selective for the ions Pb^{2+} and Cu^{2+} ions [17].

CONCLUSION

The optimum concentration of dopant solution Cd^{2+} on the membrane ISE Cd^{2+}-chitosan with a composition ratio of chitosan:PVC:DOPP (6:3:1) was 1.0 M at conductivity value was 549.45 ohm^{-1} m^{-1}. The measurement of the several parameters electrode characteristic very good, shown by the Nernstian factor value was 32.03 mV/decade, with a detection limit are 2.512×10^{-5} M. The electrodes work in the pH range 3–7. The life time of the electrode was 8 weeks. The ions of Ni^{2+}, Fe^{3+}, Pb^{2+}, Cu^{2+}, Zn^{2+}, Cl^-, and SO_4^{2-} toward concentration range 10^{-3} M was not interfere in the determination of Cd^{2+} ion.

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