Ion Selective Electrode-Copper(II) Based on EDTA as Ionophores in Poly(vinyl chloride) Matrix

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A research on the preparation and characterization of ion selective electrode Cu(II) based poly(vinyl chloride) (PVC) by using ethylenediaminetetraacetate (EDTA) as ionophores has been done. The physical strength of the membrane can be improved with used poly(vinyl chloride) as matrix and dioctylphenylphosphonate (DOP) as plasticizer. The result showed that the optimum composition of the membrane with comparison was EDTA:PVC:DOP (60:30:10). The optimum dopant concentration of Cu^{2+} was 1 M with conductivity value was 4.62×10^{-2} Ohm^{-1} m^{-1}. The electrode exhibited an excellent potentiometric response over a wide concentration range of 1.0×10^{-5} - 1.0×10^{-1} M with a Nernstian factor of 28.8 mV/decade, detection limit was 3.02×10^{-6} M. The sensor works well in the pH range 3-7, can be used for a period of 4 weeks and demonstrated good selectivity towards analyte in the presence of several ions.

Keywords: Membrane, Ion selective electrode, EDTA, Cu^{2+}.

INTRODUCTION

Copper(II) is essential trace element in the human body. It is a cofactor for a variety of oxidative enzymes and plays an important role in various fundamental biological processes in organisms. The World Health Organization (WHO) has set the limit of copper in drinking water to be 2 mg/L (31 μM). Therefore, it is very important to monitor copper levels in various samples for environment safety and human health [1]. Copper(II) ion is a significant metal pollutant due to its widespread use and the toxic impact of its excess on microorganisms even at submicromolar concentrations [2]. The effects of pollution of Cu^{2+} ions are able to cause a decline of IQ and brain damage in children. Copper(II) ion consumption in large quantities can cause copper are toxic and cause acute symptoms [3].

Several analytical methods have been used for the determination of Cu^{2+} ions such as polarography, gravimetry and spectrophotometry methods. Copper could be determined by inductively coupled plasma mass spectrometry (ICP-MS), or electrothermal atomic absorption spectrometry (ETAAS), which usually have a sufficiently low detection limit [4]. Flame atomic absorption spectrometry (FAAS) is available in most laboratories, but it requires the use of a preconcentration step in order to reach an appropriate level of sensitivity [5]. Another viable analytical methods used for analysis of Cu^{2+} ions are electrochemical techniques such as ion selective electrode (ISE).

Ion selective electrode is an electrochemical sensor that is very widely used, because ISE can be controlled in the laboratory and can be used in the daily work [6]. The ion selective electrode (ISE) term arises because none of the electrodes are specific to a particular ion and none of the electrodes are completely free of interferes [7]. Ion selective electrode was first made of glass membrane for used to measure the pH of the solution [8]. 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 [9]. Ion selective electrode can be used in environmental analysis.

Several researchers have reported the quantification and speciation of metal complexes with chelating agents, such as ethylenediaminetetraacetate (EDTA) [10] or diethyldithiocarbamate (DDC) [11]. EDTA is one kind of amine polycarboxylic acid is often used as a titrant in complexometric titration. EDTA is actually hexadentate ligand that can be coordinated with a metal ion both nitrogen and fourth carboxyl group [12]. EDTA can be made into a membrane using PVC matrix as reinforcement and adding a certain amount of plasticizer. The conductivity of EDTA membranes can be improved by adding a certain amount of metals into the membrane. Metals added are referred to as a dopant metal [13]. There are two ways to

dopp 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. The optimum concentration for each metal were added to the membrane are specific and can be distinguished from the other metals [14].

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

EXPERIMENTAL

The materials used in this research are ethylene diamine tetra acetate, tetrahydrofuran (THF), copper sulfate, cadmium nitrate, zinkum chloride, nickel nitrate, ferric chloride, potassium nitrate, potassium chloride, potassium sulphate (E'Merck), polyvinylchloride (PVC), dioctylphthalate (DOP) (Sigma), araldite glue (RS Components) and distilled water.

Equipment used in the manufacture of membrane is glass plate, glass equipment such as flask, measuring cup, pipette volume and beaker glass (E-Merck), digital multimeter to measure resistance, to determine the amount of ion Cu^{2+} was absorbed by the membrane used atomic absorption spectrophotometers (GBC Avanta 6506), to observe a shift wavenumber of functional groups that can form a complex after didop membrane with a metal ion Cu^{2+} used FT-IR spectroscopy (Prestige 21-D) and surface morphology used scanning electron microscope (SEM).

Membrane preparation: Poly(vinyl chloride) was dissolved in 20 mL of THF after the DOP added while stirring using a stirrer, then added EDTA that has been mashed into the mix gradually, stirring until homogeneous at room temperature. The mixture is poured into a glass plate and left until all the solvent evaporates and EDTA-derived membrane of PVC-DOP. Making the membrane is made with several variations of composition for each membrane EDTA-PVC-DOP was 50:40:10; 55:35:10; 60:30:10; 65:25:10. This variation is done to determine the optimum composition of the membrane [15,16].

Membrane doped: EDTA-PVC membrane-DOP is cut into several circular with a diameter of 1.5 cm. Membranes dipped in a solution of $CuSO_4$ at various concentrations 0.25 - 1.5 M for 5 days, removed and dried in oven at 40 °C for 0.5 h.

Characterization of membrane EDTA-PVC-DOP: Determination of percentage absorption of membrane by AAS to observe the most optimum membrane composition performed by AAS analysis. A total of 10 mL of 10 ppm Cu^{2+} prepared in the vial bottle. EDTA-PVC-DOP membrane in various compositions comparison that has been prepared was inserted into each of the standard solution of Cu^{2+} and soaked for 24 h. Membranes were separated and the filtrate was measured by AAS, obtained data absorbance measurements.

Membrane conductivity measurements: Membranes have been soaked in a solution of $CuSO_4$ at various concentrations. Conductivity measurements carried out with four-point probe estimators 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 Cu^{2+} ion selective electrode [14].

FT-IR spectroscopy and scanning electron microscope (SEM) analysis: To observe the binding of Cu^{2+} dopant in the membrane is done by observing changes in the wavelength number of amine and carbonyl groups of EDTA compounds which may form complexes with Cu^{2+} ions by FT-IR spectroscopy. The surface morphology analysis was done by using scanning electron microscope (SEM) analysis.

Characterization of Cu^{2+} ion selective electrode: Characterization of Cu^{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 Cu^{2+} was provided as stock standard solution. From the above solution was diluted to make a solution of Cu^{2+} were 10^{-1} - 10^{-7} M of each of 20 mL. In each of the above solution of Cu^{2+} added 2 mL of 1 M KNO_3 as ionic strength adjusted buffer. Each solution was measured using the membrane electrode potential electrode Cu^{2+}-EDTA as the working electrode using a pH meter while stirring with a magnetic stirrer. Potential E (mV) measured against log $[Cu^{2+}]$. The Nernstian factors determined from the slope of the resulting curve. Detection limit values obtained from the extrapolation point of the curve log $[Cu^{2+}]$ against potential E (mV) [8]. The same procedures was done to determine the interval of pH measurement, response time, life time and the influence of interference ions *e.g.*, Zn^{2+}, Fe^{3+}, Ni^{2+}, Cd^{2+}, Pb^{2+}, Cl^- and SO_4^{2-}.

RESULTS AND DISCUSSION

Optimization of membrane composition: In this study, membrane materials used consisted of EDTA as an active ingredient in which the characteristics of ionophores has an active side which can be either free electrons and has a large surface area [6], PVC serves as a matrix which is a polymer non-polar and additives such as plasticizers DOP functioning. The solvent used to dissolve the PVC is THF [16].

Preparation of membranes is done by mixing EDTA, PVC and DOP in THF for 2 h at room temperature. The mixture is printed into the container glass plate and then the mixture was allowed to evaporate solvents and obtained a thin white membrane with a thickness of 1.33 mm. the mixing process is no reaction occurs between the PVC, EDTA and DOP. EDTA is only bound physically and stick to the PVC.

Determination of absorption percentage of membrane by AAS: Comparison of the composition of materials in the manufacture of the membrane may be striving in the process of absorption of Cu^{2+}, the greater the amount of active ingredient, the greater the absorption performed by the membrane. AAS measurement data can be known concentration of dopant ions are bound by membranes, by measuring the absorbance of the filtrate is the result of soaking the membrane with a solution of 10 ppm Cu^{2+} dopants for 24 h. The measurement results can be seen in Fig. 1.
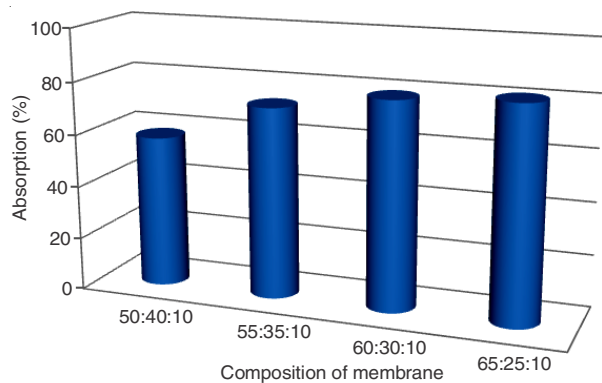
Fig. 1. Absorption percentage of EDTA-PVC-DOP membrane againts Cu^{2+}

The optimum composition selected is in the membrane with a composition ratio of EDTA:PVC:DOP 60:30:10. In this composition, percentage absorption of Cu^{2+} ion by membrane already above 75 % and it has been possible to use as a working electrode ESI [17]. For the membrane composition above 60:30:10 cannot be used, because visually and physically very weak and fragile, although percentage absorption for Cu^{2+} ions are also high.

Membrane conductivity: Doping EDTA-PVC-DOP membrane with Cu^{2+} aims to reduce the resistance of the membrane. Immersion of metal ions to EDTA-PVC-DOP membrane can increase the conductivity value of membranes. The purpose of the conductivity measurement is to determine the optimum dopant concentration of Cu^{2+} for optimum dopant concentration is typical for each metal type dopant and the active membrane and doped membrane performed at the optimum concentration [14]. The measurement results can be seen in Fig. 2.
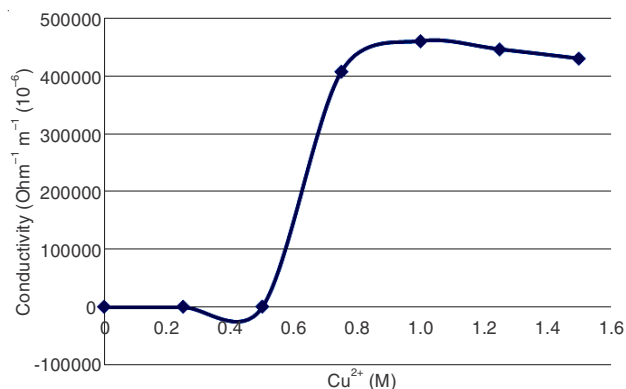

Fig. 2. Membrane conductivity at various dopant concentrations

The optimum dopant concentration was 1 M, with a value of conductivity was 4.62×10^{-2} Ohm^{-1} m^{-1}. In this state the resistivity of the membrane decreases to the minimum value and increased membrane conductivity. Dopant concentration above 1 M indicates a decrease in the value of conductivity of the membrane. This is due to excess Cu^{2+} ions that enter the membrane is much larger compared to the number of N atoms in the amine group of EDTA. This excess Cu^{2+} ions form ionic atmosphere that enhances the degree of irregularity in the membrane, even an excess of these ions form a separate phase that is not tied to one another so that the resistivity of the membrane will increase [18,19].

FT-IR spectroscopy: To obtain an overview of the groups what ion Cu^{2+} bound to the membrane EDTA-PVC-DOP, it can be seen from the data measurement FT-IR spectrum by comparing the FT-IR spectrum before and after interaction with the ion Cu^{2+} (Fig. 3).
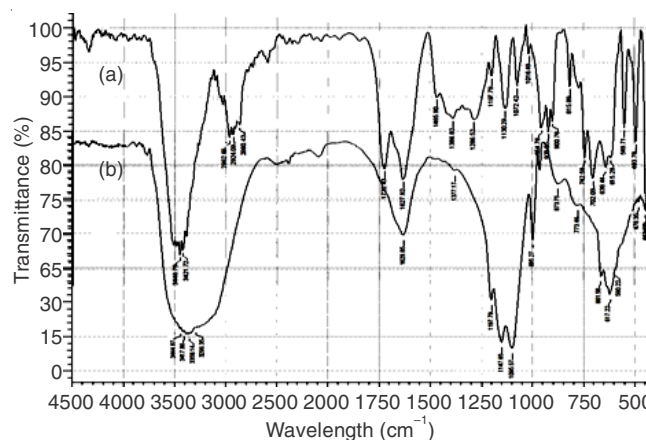

Fig. 3. FT-IR spectra EDTA-PVC-DOP membrane (a) before (b) after doped with Cu^{2+}

FT-IR spectra in Fig. 3a. show the absorption band at wavenumber: 1016.14, 1072.42, 1130.29 and 1197.79 cm^{-1}, indicate the presence of C-O- stretching vibration. Absorption band at wave number 1627.92 cm^{-1}, indicate the presence of vibration N-H of secondary amide and 1722.43 cm^{-1}, indicate the presence of vibration of C=O originating from EDTA. An absorption band at wavenumber 3421.72 cm^{-1} and 3446.79 cm^{-1} is the stretching vibration -OH derived from EDTA.

FT-IR spectra of membrane after the drop with Cu^{2+} ions (Fig. 3b) shows the change in the intensity of the absorption band and slightly shift wave number when compared with the FT-IR spectra of the membrane before doped. These changes can be seen with loss absorption band group C=O at wave numbers 1722.43 cm^{-1} and a decrease in the intensity of the absorption band N-H of secondary amide at wave number 1627.92 cm^{-1}, shows the Cu^{2+} ion which is electropositive and has a relative atomic mass of a large ion can disturbing vibrations by pulling electrons from the N so that the N-H bond becomes weaker and the C atom attract free electrons owned O atoms resulting C-O bond being lost and several absorption bands shifted wave numbers.

Scanning electron microscope (SEM): A PVC-EDTA-DOP membrane obtained in optimum composition of the surface morphology was analyzed by scanning electron microscope (SEM). The surface morphology analysis membrane compared before and after interaction with metal Cu^{2+} with magnification of 1000 times. The measurement results can be seen in Fig. 4.

The surface morphology of PVC-EDTA-DOP membrane [Fig. 4(a)] show a pattern of regular structure with nodes are round with a uniform size and is still empty. Spherical shape node of the membrane surface is the structure of the membrane pores are not binding or loaded with Cu^{2+}. This indicates that the membrane surface has a surface structure having cavities the same size and can be filled with metal ions are charged electropositive. From Fig. 4(b) it can be seen that the change
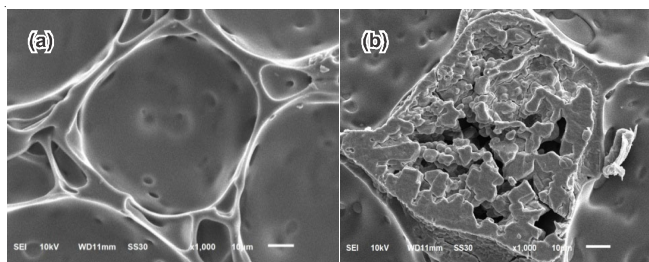
Fig. 4.   Surface morphology PVC-EDTA-DOP membrane (a) before, (b) after interaction with Cu^{2+}

of morphology of the membrane surface after doped with Cu^{2+} ions. Surface morphology spherical membrane has been filled by nodes that form a uniform, which allegedly is a Cu^{2+} bonding on cavities or pores contained in PVC-EDTA-DOP membrane. This indicates that the Cu^{2+} ions have formed a bond with EDTA through coordination bond formation with carboxyl group (-OH) and an amine group (-NH) contained in EDTA ionophores, forming a complex compound structure EDTA-Cu(II).

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. 5.
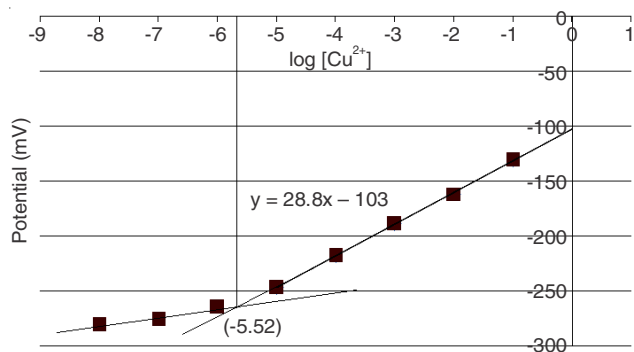

Fig. 5.   Determination of Nernstian factor and detection limit of ISE Cu^{2+}

An ideal value of Nernstian factor is 59.1/n (mV/decade), with n is the ionic charge. Its means for ISE Cu^{2+} with the value of n = 2 are 29.6 mV/decade. Nernstian factor values in this study was 28.8 mV/decade, which means any increase in the concentration of 10^{-1} M test solutions, the potential change of 28.8 mV/decade. This value indicates that the ISE Cu^{2+} still feasible for use in the analysis of Cu^{2+}, because the value allowed of Nernstian factor is 29.6 ± 5 mV/decade. In this research the detection limit is an extrapolation of the curve point log concentration (M) against potential (mV) [8]. From the curve extrapolated point value is -5.52, the detection limit value is -log -5.52 equal to 3.02×10^{-6} M.

Influence of pH: It is necessary to find the optimum pH range where the electrode without interference from the hydrogen ions. pH dependence of the membrane electrode works has been tested by using 1.0×10^{-3} M Cu^{2+} solutions over a pH range 2-10. The measurement results are shown in Fig. 6.

pH was adjusted by the addition of small drops of 0.1 M nitric acid or 0.1 sodium hydroxide. The potentials stay constant
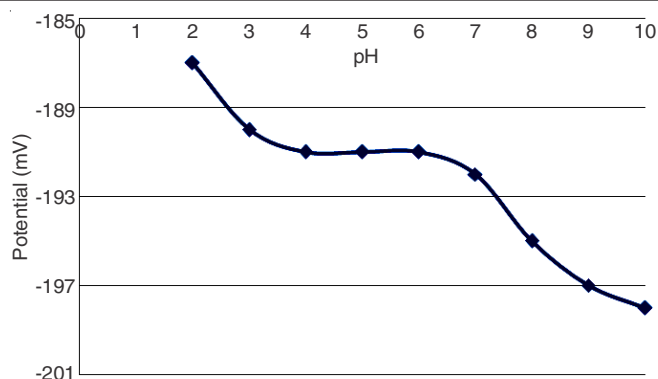

Fig. 6. Effect of pH measurements ISE with 10^{-3} M Cu^{2+}

from pH 3.0 to 7.0. The observed increase in the potential at low pH values indicates that the ionophore responds to the hydronium ions and a drift in potential is observed which is due to the formation of $Cu(OH)_2$ at pH greater than 7. On the other hand, the fluctuations below the pH value of 3.5 were attributed to the partial protonation of the employed ionophore [15,20].

Response time: Response time is the average time required for the manganese ion sensor to reach a potential within ± 1 mV of final equilibrium value [9]. The practical response time of the sensor was calculated by measuring the time required to attain the equilibrium potential by dipping the sensor in a series of Cu^{2+} ion solutions each having a tenfold difference in concentration. The results were obtained for response time measurement range 10-60 s, 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. The equilibrium potentials essentially remained constant for more than 1 min.

Life time: The life time of ESI Cu^{2+} was determined by measuring the Nernstian factor value changes for every week. Nernstian factor values are measured each week are shown in Fig. 7.
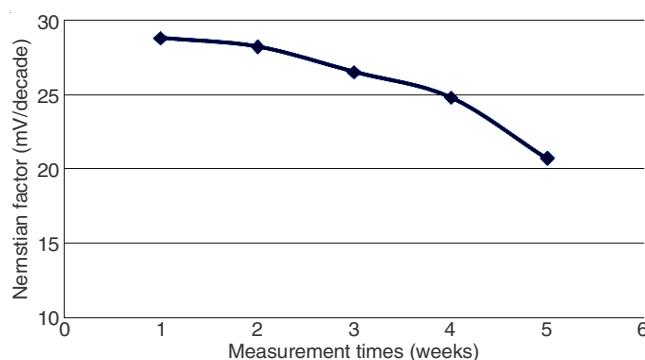

Fig. 7. Nernstian factor value changes from ESI Cu^{2+} for every weeks

Nernstian factor value obtained at 4-week was 24.8 mV/decade, while at 5-week, the Nernstian factor value have dropped dramatically become 20.7 mV/decade, assumed ISE Cu^{2+} is no capable use for analysis. Electrode can be used only during the life time of 4 weeks. It is well established that the loss of plasticizer, carrier, or ionic site from the polymeric film due to leaching into the sample is a primary reason for the limited lifetimes of the sensors [15].

Effect of interfering ions: An important parameter to assess performance of an ion-selective sensor is its selectivity towards a particular ion over other foreign ions. Selectivity is expressed as a selectivity coefficient $K_{Cu^{2+},B}^{pot}$. In this work, the potential responses of the proposed Cu^{2+} membrane sensor to a wide variety of cations and anions were investigated through the matched potential method (MPM) [21,22]. The concentration of interfere ions (a_j) 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:

$$K_{Cu^{2+},B}^{pot} = \frac{aCu^{2+}}{a_j}$$. The measurement results of selectivity

coefficient value of ISE Cu^{2+} for interfere ions can be seen in Table-1.

TABLE-1
SELECTIVITY OF COEFFICIENT VALUE
OF ISE Cu^{2+} FOR INTERFERE IONS

Interfere ions (B)	$K_{Cu^{2+},B}^{pot}$	Interfere ions (B)	$K_{Cu^{2+},B}^{pot}$
Ni^{2+}	0.1175	Cd^{2+}	0.0389
Fe^{3+}	0.1258	Cl^-	0.0212
Zn^{2+}	0.2376	SO_4^{2-}	0.0324

For the interfere ion Ni^{2+} obtained the selectivity coefficient value ISE Cu^{2+} was 0.1175. The value indicates the ISE Cu^{2+} 11.75 times more selective against the major ions Cu^{2+} compared with Ni^{2+} ion. The selectivity of coefficients value showed ESI Cu^{2+} with presence of Ni^{2+} ion at 10^{-3} M in the standard solution. All values are substantially lower than 1.0, indicate Ni^{2+}, Fe^{3+}, Cd^{2+}, Zn^{2+}, Cl^-, SO_4^{2-} ions toward concentration range 10^{-3} M was not interfere in the determination of Cu^{2+} ion and proves its applicability for determination of Cu^{2+} in the samples.

Conclusion

Membrane of PVC-DOP-EDTA can be made with optimum composition of 60: 30: 10, the membrane can absorb ion Cu^{2+} > 75 %. The optimum dopant concentration of Cu^{2+} are 1 M, the value of conductivity was 4.62×10^{-2} Ohm^{-1}m^{-1}. SEM analysis results indicate a change in the structure of the membrane surface morphology before and after doped with Cu^{2+} ions and FT-IR analysis results indicate a change in the wave number of carboxyl groups and NH groups of EDTA so it is possible the binding of Cu^{2+} ions. The measurement of the several parameters electrode characteristic are very good, shown by

the Nernstian factor value was 28.8 mV/decade, with a detection limit are 3.02×10^{-6} M. The sensor works well in the pH range 3-7, can be used for a period of 4 weeks and demonstrated good selectivity towards the analyte in the presence of several ions.

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