Trace level monitoring of Cu(II) ion using CuS particles based membrane electrochemical sensor

Dipak Kumar Gupta a,b, Shova Neupane b,*, Harish Chand Yadav a, Vivek Subedi b, Sanjay Singh b, Ram Jeewan Yadav c, Anju Kumari Das b, Brahamedeo Yadav d, Krishna Badan Nakarmi e, Nabin Karki b, Amar Prasad Yadav b,**

a Tri-Chandra Multiple Campus, Tribhuvan University, Kathmandu, Nepal
b Central Department of Chemistry, Tribhuvan University, Kirtipur, Kathmandu, Nepal
c Prithvi Narayan Campus, Tribhuvan University, Pokhara, Nepal
d Ramsworup Ramsagar Multiple Campus, Tribhuvan University, Janakpur, Nepal
e Patan Multiple Campus, Tribhuvan University, Kathmandu, Nepal

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ABSTRACT

Cu(II) monitoring is a matter of great interest to researchers due to its toxicity and adverse environmental effects. Among different methods for detecting Cu(II), ion-selective electrode (ISE) is more advantageous as they are low-cost, easy to fabricate, and highly selective. Here, we report a simple, inexpensive, and reproducible procedure for the fabrication of Cu(II) ion-selective electrodes using CuS particles and polyvinyl chloride (PVC) as a matrix. CuS particles, obtained by chemical precipitation, were characterized using X-ray diffraction (XRD), Fourier-transform infrared (FTIR) spectroscopy, ultraviolet-visible spectroscopy (UV-Vis), scanning electron microscopy (SEM), and energy-dispersive X-Ray spectroscopy (EDX). Optimization of the membrane compositions was done to get a well-behaved sensor by varying amounts of CuS, PVC, and acetophenone (AP). A membrane composition of 0.4 g CuS, 0.5 g PVC, and 1.0 mL AP in 5.0 mL tetrahydrofuran (THF) gave a Nernstian slope of 27.31 mV per decade change of Cu(II) ion over a wide range of concentration down to 64 ppb (1 \times 10^{-6} M). The sensor gave a fast response time of 25 s, and it indicated the endpoint in a potentiometric titration of Cu(II) with standard EDTA solution. A pH-independent potential response was obtained in the pH 4.0–6.0.

1. Introduction

Cu(II) is an essential trace element present in all land and marine organisms. It is a cofactor for various oxidative enzymes and plays an important role in different biological processes. World Health Organization (WHO) has set the limit of Cu(II) in drinking water at 2.0 mg/L [1, 2]. The increased accumulation of Cu(II) in the environment from numerous industrial sources poses a danger to public health. Excessive Cu(II) intake causes diseases such as gastrointestinal catarrh, Wilson disease, Menke’s syndrome, hypoglycemia, dyslexia, and Alzheimer’s [3, 4]. Thus, the determination of trace amount of Cu(II) has gained more attention as it directly affects human health and the environment.

Several instrumental techniques such as atomic absorption spectrometry (AAS), inductively coupled plasma-mass spectrometry (ICP-MS), flow injection analysis, liquid chromatography, gravimetric, and voltammetric techniques are used for the determination of Cu(II) in environmental samples [5]. They can monitor and detect miscellaneous trace pollutants in the exposed environment, but unfortunately, their maintenance and operational cost is high [6, 7]. Thus, a portable, sensitive, and selective analytical technique is highly demanding. Electrochemical sensors or ion-selective electrodes (ISEs) can account for the aforementioned requirements to a greater extent [8, 9]. Such sensors even do not require sample pre-treatment conditions and can also be suitable for online analysis.

The critical part in designing an ion-selective electrode is finding a suitable and selective sensing element [10]. Various researchers have made numerous publications on neutral carrier and ion-exchange based ISEs [11, 12, 13, 14, 15, 16, 17, 18]. However, most of them suffer
drawbacks such as narrow concentration range, high detection limit, and substantial interferences from cations such as Fe$^{3+}$, Co$^{2+}$, Ni$^{2+}$, Sb$^{3+}$, Na$^+$, Cs$^+$ and K$^+$. CuS–Ag$_2$S all solid state Cu(II) ion-selective electrodes have been reported to give a good response to Cu(II) ion [19, 20]. Such electrodes have been limited by the leaching of Cu(II) ion from the membrane and poor mechanical properties of the pellet [10, 19, 20]. This has given rise to the development of PVC matrix membrane ion-selective electrodes [21]. This idea has been further expanded by using nanoparticles trapped PVC membrane ion-selective electrodes to detect Cu(II) ion with mixed success in obtaining reproducible and reliable sensor response [7, 22, 23]. However, more study is needed to get information concerning nanoparticle characterization and its effect on the response and stability of the fabricated sensor.

Copper sulfide (CuS) nanoparticles have attracted tremendous interest due to their quantum size effect [24, 25, 26]. The constituents of CuS nanoparticles (Cu and S) are abundant in nature; they are non-toxic and cheap. It is alluring as it exists in different stoichiometric compositions with varying crystalline phases [24, 27, 28]. It behaves as a p-type semiconductor with a bandgap of 2 eV. The bandgap matches with ultraviolet and visible light energy so that CuS can be used in a wide range of applications such as electro-conductive electrodes, solar cell devices, IR detectors, Li-ion batteries, and other optoelectronic devices [29, 30].

CuS nanoparticles in a polymer matrix show excellent applications [21, 31, 32, 33]. This paper describes an electrochemical sensor fabricated using CuS nanoparticles in the matrix of polyvinyl chloride (PVC) and acetophenone (AP) plasticizer for selective and sensitive detection of Cu(II) ions. CuS particles were prepared by chemical precipitation routes using dimethylformamide (DMF) as a stabilizing agent. The effects of parameters such as membrane composition, pH of the solution, internal solution concentration, and response time have been studied. The selectivity coefficients were determined by using the match potential method. Finally, fabricated CuS ion-selective electrode (ISE) was used as an indicator electrode for the titration of Cu(II) ion with hexadentate ligands EDTA.

2. Experimental

2.1. Chemicals and reagents preparation

Analytical reagent grade copper nitrate (Cu(NO$_3$)$_2$.3H$_2$O), sodium sulfide (Na$_2$S), dimethylformamide (DMF), potassium nitrate (KNO$_3$), ferric chloride (FeCl$_3$), ethylene diamine tetracetic acid (EDTA), Tetrahydrofuran (THF), Acetophenone (AP), cadmium nitrate (Cd(NO$_3$)$_2$.4H$_2$O), potassium nitrate (KNO$_3$), silver nitrate (AgNO$_3$), cobalt nitrate (Co(NO$_3$)$_2$.6H$_2$O), nickel nitrate (Ni(NO$_3$)$_2$.H$_2$O), ammonium nitrate (NH$_4$NO$_3$), and sodium nitrate (NaNO$_3$) were purchased from Sigma-Aldrich, India. A commercial-grade polyvinyl chloride (PVC), laboratory-grade sodium hydroxide (NaOH), and nitric acid (HNO$_3$) were used. All the chemicals of required concentrations were prepared in double-distilled water.

2.2. Preparation of CuS particles

CuS particles were synthesized by chemical precipitation method using DMF as a stabilizing agent [26, 28, 30]. For this, 100 ml of 0.1 M Cu(NO$_3$)$_2$.3H$_2$O solution was mixed with 20 ml of DMF and stirred for 10 minutes. Then, 100 ml of 0.1 M Na$_2$S solution was added to the mixture dropwise with constant stirring for 3 hours and left overnight. The reaction mixture was decanted, and the precipitate was washed with distilled water, filtered through Whatman 42 filter paper, and dried in an oven at 60°C for 8 hours. Eq. (1) represents the precipitation of CuS particles.

$$\text{Cu(NO}_3\text{)}_2 + \text{Na}_2\text{S} \rightarrow \text{CuS} \downarrow + 2\text{NaNO}_3$$  (1)

2.3. Characterization of CuS particles

The crystalline phase of the synthesized CuS particles was characterized by a Bruker X-ray diffractometer using Cu-Kα radiation having a wavelength ($λ$) of 1.5406 Å in the range of 2θ, 20–80. The Fourier-transform infrared (FTIR) spectrum of the CuS particles was recorded on a Shimadzu-tracer-100 spectrophotometer in the wavelength range of 400–4000 cm$^{-1}$. UV-Visible spectrum of CuS dispersed in water was recorded on double beam Labtronics LT-2802 spectrophotometer in the wavenumber range of 200–400 nm. The surface morphology and elemental characterization of the synthesized CuS particles were observed by scanning electron microscopy (SEM) [Merlin, Zeiss Microscopy, Germany] and energy dispersive x-ray spectrophotometer (EDX) [Hitachi H-7100].

2.4. Preparation of CuS-PVC membrane and electrode

CuS-PVC sensor membrane was prepared by mixing CuS with PVC in the presence of AP as a plasticizer. The amount of PVC was fixed at 0.5 g, while the amount of CuS was 0.2, 0.3, 0.4, and 0.5 g. Each mixture of CuS and PVC was put into a Petri dish containing 10.0 ml of THF and 1.0 ml of AP. Finally, the mixture was homogenized and left overnight at room temperature for the evaporation of the organic solvent to get a thin CuS-PVC membrane.

An inner filling CuS-PVC membrane electrode was prepared by fixing the membrane in a polyethylene (PE) tube. The tube was filled with an internal solution of Cu(NO$_3$)$_2$.2H$_2$O, and a self-made miniaturized silver/silver chloride reference electrode (SSE) was inserted in the inner filling solution by adopting the established procedure [34]. The fabricated electrode was then equilibrated for 24 h in a 0.01 M Cu(NO$_3$)$_2$.2H$_2$O solution for performance measurement. The cell assembly given below was used to calibrate the electrode

Ag/AgCl, Cu(II) (aq.), PVC membrane/test solution/SCE

The cell electromotive force (EMF) was measured by a digital multimeter (BK TEST BENCH 389).

2.5. CuS-PVC electrode response characterization

The cell assembly thus prepared was used for direct potentiometry measurements of Cu(II) ion concentration in the range of 10$^{-6}$ M to 10$^{-3}$ M. A saturated calomel electrode (SCE) was used as an outer reference electrode, and cell EMF was measured within ±2.0 mV accuracy in all the measurements. The cell assembly of Ag/AgCl, Cu(II) (aq.), sensor membrane/test solution/SCE was used to measure the Nernstian response of thus fabricated CuS-PVC membrane electrode. The cell EMF dependency on pH of the Cu(II) ion solution was measured in the pH range 1–8 at a fixed Cu(II) ion concentration of 1.0 × 10$^{-3}$ M. The pH of the test solution was adjusted by dropwise addition of an appropriate volume of either 2 M HNO$_3$ or 2 M NaOH solution for lowering and raising the pH of the test solution.

The CuS-PVC membrane electrode response time was evaluated by effecting a tenfold increase of Cu(II) ion concentration and recording the cell EMF every 5s till 80s. A plot of measured cell EMF against elapsed time was made to determine the time taken by the sensor to produce an equilibrium cell EMF.

Potentiometric titration between the Cu(II) ion solution and a standard EDTA solution was monitored using the fabricated Cu-PVC membrane as an indicator electrode combined with an external SCE reference. Both electrodes were connected through a salt bridge of potassium nitrate in agar-agar gel. Cell EMF was measured after the addition of a known volume of EDTA (10$^{-2}$ M).

Finally, the selectivity coefficient of the membrane electrode was calculated by the match potential method [5]. The concentration of
interfering ions (secondary ion) producing the same potential change
effected by Cu(II) ion (primary ion) was estimated by using Eq. (2)
\[ K^{\text{tot}} = (\Delta E)/B \]  
(2)
Where \( \Delta E \) is the concentration difference of primary ion producing an
EMF change equivalent to Nernstian slope, \( B \) is the concentration of
interfering ions producing EMF change equivalent to Nernstian slope.
The interfering ions used for the purpose were Co^{2+}, Ni^{2+}, Cd^{2+}, K^+,
NH_4^+, Na^+.

3. Results and discussion

3.1. Characterization of CuS particles

Figure 1 shows the X-ray diffraction pattern of CuS particles. The obtained
diffraction patterns at 2\( \theta \) = 29.83, 32.20, 48.52, 52.91, and
59.70 correspond to the (102), (103), (110), (108), and (116) planes of
CuS, respectively [35, 36, 37]. The diffraction patterns and interplanar
spacing of the CuS particles was in good agreement with the standard
hexagonal structure of CuS (JCPDS 06-0464). An average crystallite size
of the CuS particles was estimated using Debye-Scherer Eq. (3) [38]:
\[ D = \frac{0.94}{\beta} \frac{\lambda}{\cos \theta} \]  
(3)
Where \( D \) is average crystallite size, \( k \) is Scherer constant, \( \lambda \) is the wave-
length of X-ray, \( \beta \) is peak width of half maximum, and \( \theta \) is Bragg
diffraction angle.

For the most intense peak at 48.52\( ^\circ \), substituting a value of 0.94 for
\( k \), and 0.63 for \( \beta \) gave crystallite size of 13.2 nm. Therefore, the X-ray
diffraction pattern confirmed the formation of CuS particles in the nano
range.

FTIR spectrum of CuS particles is depicted in Figure 2. The peaks
observed at 478 cm
–1 and 669 cm
–1 were attributed to Cu-S stretching.
These bands were in agreement with the peak reported in the literature
[39].

UV-Visible spectrum of CuS particles dispersed in water is shown in
Figure 3. The spectrum exhibited an absorption band edge centered at
about 300 nm, which is blue-shifted. The blue shift in the absorption
band edge shows that the smaller crystallite size of CuS particles exhibit a
remarkable quantum size effect on its optical properties [24]. The ab-
sorption peak is consistent with a smaller crystallite size of the synthe-
sized particles [24].

The bandgap of CuS particles was calculated by using the following
Eq. (4) [40].
\[ \alpha h \nu = A(h \nu - E_g) \]  
(4)

Where \( \alpha \) is the coefficient of absorption, \( h \) is the Planck’s constant, \( E_g \) is the
optical energy gap of material, \( \nu \) is the frequency of light, \( A \) is con-
stant, \( r \) depends on the nature of the electron transition (1/2 for direct
transition and 2 for indirect transition band gaps), and \( h \nu \) is the energy of
the photon. By extrapolating the plot of \((\alpha h \nu)^2\) with energy as shown in
Figure 3b, the bandgap energy of CuS particle was calculated as 3.8eV,
which is higher than that of bulk CuS (2.2eV) and as expected for
nanoparticles. The larger bandgap is due to the quantum size confine-
ment effects, and there is wide variation in the reported band gap values
of CuS nanoparticles [24, 28, 41].

3.2. SEM-EDX analysis

The SEM image of the synthesized CuS particles is shown in Figure 4a,
which is a representative image taken over several locations. The image
shows the granular shape with some degree of agglomeration. The average size
ranged from 80 to 750 nm in diameter. The irregular size distribution could be attributed to the uncontrolled nucleation of CuS.

EDX patterns were used to evaluate the composition and purity of the
resulting CuS particles, as shown in Figure 4b. It shows the presence of Cu
and S peaks with the presence of O peaks. The existence of oxygen is
taken as impurities due to surface contamination. The average atomic
ratio of CuS, calculated from the quantification of the peaks (O element
excluded), gave the value of 24.5:20.9. This indicates that the surface of
the samples was rich in Cu. The deviation of atomic ratio from 1:1 was
believed to be originated from the absorption of excessive Cu(II) on the
surface of the nanoparticles.

3.3. Response of the CuS-PVC membrane

Four CuS-PVC membranes with different compositions were prepared
to evaluate the best performance of the membrane. The ratio of CuS, PVC,
THF, and acetophenone were varied as shown in Table 1 to make a
membrane of CuS entrapped in the matrix of PVC.

The response of the membrane towards Cu(II) ion concentrations was
evaluated in a direct potentiometry. For this, the internal filling solution
of \( 1 \times 10^{-3} \) M Cu(NO_3)_2 solution was used, and the external solution was
varied from \( 1.0 \times 10^{-6} \) to \( 1.0 \times 10^{-1} \) M by the standard addition method
[8]. The plots of cell EMF of all four CuS-PVC membrane as a function of
the concentration of Cu(II) thus obtained are shown in Figure 5. The cell
EMF of a Cu(II) ion-selective membrane can be given by Eq. (5),
\[ E_{\text{cal}} = E_0 + 0.0295 \log [\text{Cu}^{2+}] \]  
(5)
Figure 5 shows the EMF of the cell increases with decrease in Cu(II) ion concentration that is dictated by the constant, $E_0$, which includes the contributions of both the reference electrodes. The linear concentrations range and slope, evaluated by linear regression analysis, for different membranes are compared in Table 2. All the membranes show linearity in the cell EMF over a concentration range from $10^{-6}$ to $10^{-1}$ M. However, the Nernstian slope was greatly affected by the composition of the membrane. Only membrane 3 electrode showed the Nernstian slope of 27.31 mV per decade change in concentration of Cu(II) ion. All the other membranes did not show satisfactory slopes and, therefore, were discarded for further study. It is clear that the composition of the membrane profoundly affects the response and performance of the membrane electrode. The low Nernstian slopes in membrane electrode other than electrode 3 show the sluggish establishment of ionic equilibrium at the PVC membrane-solution interface, which is affected by the surface distribution of the CuS particles in the PVC matrix [22]. These electrodes needed a relatively longer time to give higher Nernstian slope, which is not practical in real measurements. The result shows that membrane electrode 3 can be well used for monitoring Cu(II) ion concentration as low as 64 ppb with great accuracy, which fulfills the requirement of Cu(II) sensor for environmental monitoring of Cu(II) ion in drinking water, wastewater, and any such applications which discharge low amount of Cu(II) ion. Also, this sensor showed better Nernstian response and stability compared to all solid-state CuS electrode [20] without facing any problem of membrane crack unlike in all solid-state membrane.

To further understand the response of the 3rd membrane electrode towards Cu(II) ion, the effect of the internal filling solution was studied by varying its concentration viz., $10^{-3}$ to $10^{-6}$ M Cu(II), and measuring the cell EMF in the range of $10^{-6}$ to $10^{-1}$ M external Cu(NO$_3$)$_2$ solutions. The internal filling solution results on cell EMF are presented in Figure 6, and slopes and linear concentration range are tabulated in Table 3. Figure 6 and Table 3 show that the best working range ($10^{-1}$ to $10^{-6}$ M Cu(II)), as well as the Nernstian slope (27.31 mV/decade Cu(II)) against a theoretical Nernstian slope of 29.16 mV), is obtained for internal filling solution of $10^{-3}$ M Cu(II). Another internal filling solution has resulted in
poor Nernstian slope and working concentration range. The role of internal filling solution is to charge up the outer surface of the membrane and helps attain the ionic equilibria as fast as possible. At higher concentration of internal filling, the outer surface of the membrane is highly charged up so that fast ionic equilibrium is established and therefore a higher Nernstian slope is obtained. However, when the concentration of internal filling solution is decreased (from \(10^{-3} \text{ M}\) to \(10^{-6} \text{ M}\)), the outer surface of the membrane has low charge build up and therefore it could not maintain ionic equilibrium quickly. This also results in decrease in linearity in the outer Cu(II) ion solution (to \(10^{-4} \text{ M}\)) due probably to disturbance in the ionic flux at the outer surface. Therefore, the best membrane composition and internal filling solution were finally obtained to study the membrane electrode response towards Cu(II) further.

### 3.4. Effect of pH

The pH effect of the test solution on the EMF response of the 3rd CuS-PVC membrane was studied in the pH range of 1–8, as shown in Figure 7. Cu(II) ion concentration of \(1.0 \times 10^{-3} \text{ M}\) was used as both external and internal solution to study the pH effect on the cell EMF. The cell EMF remained independent of pH in the range 4–6. In the acidic solution below pH 4, effected by adding 2 M HNO₃ dropwise, the cell EMF increases drastically due to the adsorption of H⁺ ions. On the other hand, as the pH shifted to higher values than 6 the cell EMF decreases due to the adsorption of OH⁻ ions on the membrane surface. The results show that the cell EMF responded to H⁺ and OH⁻ concentrations at low and high pH, respectively, and therefore for application of this membrane electrode for the measurement of Cu(II) ion, a pH range of 4–6 should be maintained. The pH response of solid-state Cu-ISE has been reported to be almost similar [37].

### 3.5. Potentiometric titration

The analytical utility of the membrane electrode has been established using it as an indicator electrode in the potentiometric titration of Cu(II) with a standard solution of EDTA as titrant. 30 mL of \(1 \times 10^{-3} \text{ M}\) Cu(NO₃)₂ was titrated against \(1 \times 10^{-2} \text{ M}\) standard EDTA solution, and the titration curve is shown in Figure 8. As the EDTA solution was added to the Cu(II) solution, the EDTA-Cu complex was formed and resulted in a gradual decrease in cell EMF value due to the decrease in Cu(II) concentration. Unlike in other potentiometric titration, a sharp breakpoint was not found that could indicate a precise estimation of Cu(II). But, from a certain point, the cell EMF increased gradually. Therefore, at the intersection of two regions of EMF change, the endpoint was located at 3.2 mL of EDTA solution (Figure 8), which was about 107% of the theoretical values and within the experimental error. The concentration of Cu(NO₃)₂ solution was calculated using a well-known formula, as

### Table 2. Various parameters evaluated from plots in Figure 5 for different membrane compositions.

| Membrane no. | Intercept (mV) | Concentration range (M) | Slope mV/decade |
|--------------|---------------|-------------------------|-----------------|
| 1            | 305.67        | \(10^{-1} - 10^{-6}\)   | 8.20            |
| 2            | 376.12        | \(10^{-1} - 10^{-6}\)   | 2.92            |
| 3            | 290.73        | \(10^{-1} - 10^{-6}\)   | 27.31           |
| 4            | 301.89        | \(10^{-1} - 10^{-6}\)   | 9.22            |

### Table 3. Effect of internal solution on the slope of the 3rd membrane electrode.

| Internal (Cu(II)) (M) | Slope (mV) | Linearity in external (Cu(II)) (M) |
|----------------------|------------|-----------------------------------|
| \(10^{-3}\)          | 27.31      | \(10^{-1} - 10^{-6}\)             |
| \(10^{-4}\)          | 21.30      | \(10^{-1} - 10^{-4}\)             |
| \(10^{-5}\)          | 12.97      | \(10^{-1} - 10^{-6}\)             |
| \(10^{-6}\)          | 14.85      | \(10^{-1} - 10^{-4}\)             |

Figure 6. Cell EMF vs. concentration plots for 3rd membrane electrode with different internal reference solutions of Cu(NO₃)₂.

Figure 7. Effects of pH on the EMF of the 3rd membrane electrode immersed in \(10^{-3} \text{ M}\) external Cu(II) solution containing the same internal solution concentration.

Figure 8. Potentiometric titration of 30 mL of \(1 \times 10^{-3} \text{ M}\) Cu(NO₃)₂ solution vs. \(1 \times 10^{-2} \text{ M}\) EDTA solution using 3rd electrode.
shown in Table 4. The increase of cell EMF after endpoint indicates that the membrane electrode also responds to the EDTA. The result shows that the CuS-PVC membrane electrode could be successfully used for the potentiometric determination of Cu(II) ions with an EDTA solution as a titrant.

3.6. Response time

The practical time required for the Cu-sensor membrane to reach a potential of equilibrium value after a rapid change in the concentration of Cu(II) ions brought about by the standard addition method to effect a 10-fold difference in concentration was measured. The cell EMF vs. time is shown in Figure 9. As seen in the figure, the cell EMF reaches its equilibrium value in about 25–30 seconds in most cases, except at low concentration. In 10⁻⁶ M Cu(II) ion concentration, the electrode was not allowed to remain in the test solution for too long a period as this leads to deterioration of the membrane. The estimated response time of the membrane electrode suggests it could monitor the Cu(II) ion concentration inflow system such as sewage and drainage from industry.

3.7. Potentiometric selectivity

Selectivity studies were carried out by the potential match method. Ions like Pb²⁺ and Ag⁺ showed little interference at concentration <10⁻² M. Table 5 shows that the selectivity coefficient values are less than 1.0, which indicates that these ions could not affect the response of the CuS-PVC membrane for Cu(II) ions in the concentration range over which it showed linearity. The selectivity coefficient values are minimal, so the membrane can be used to determine Cu(II) ions with the same accuracy.

4. Conclusion

This study shows that a Cu(II) ion-selective electrode has been successfully fabricated using CuS particles trapped in a PVC matrix. Formation of CuS particles are confirmed by the XRD pattern showing an average crystallite size of 13.2 nm. The FTIR spectrum shows the presence of Cu-S stretching peaks around 669 and 478 cm⁻¹. The surface image by SEM indicates the granular but irregular distribution of particle size. The membrane electrode prepared with 0.4 g CuS, 0.5 g PVC with 1 ml AP shows the best response towards Cu(II) ion in the concentration range of 10⁻¹ M to 10⁻⁶ M (64 ppb) with a Nernstian slope of 27.31 mV in the pH range 4–6. The membrane electrode performs well as an indicator electrode in the potentiometric titration of Cu(II) with EDTA solution. The prepared Cu-PVC electrochemical sensor is portable, inexpensive, and shows good response time. However, it cannot be used for more than 3 months.

Declarations

Author contribution statement

Dipak Kumar Gupta, Shova Neupane: Analyzed and interpreted the data; Wrote the paper.
Harish Chand Yadav, Vivek Subedi: Performed the experiments.
Sanjay Singh, Ram Jeewan Yadav, Anju Kumari Das, Brahamdeo Yadav, Krishna Badan Nakarmi, Nabin Karki: Contributed reagents, materials, analysis tools or data.
Amar Prasad Yadav: Conceived and designed the experiments; Wrote the paper.

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Data availability statement

Data included in article/supplementary material/referenced in article.

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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