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Construction of Chemically Modified Electrode for the Selective Determination of Copper(II) Ions in Polluted Water Samples Based on new β-cyclodextrine and 1,4-bis(6-bromohexyloxy)benzene Ionophores

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Novel chemically modified carbon paste ion-selective electrodes (CMCPEs) for copper(II) ions determination based on β-cyclodextrin (β-CD) and β-cyclodextrin/1,4-bis(6-bromohexyloxy)benzene (β-CD/BHOB) as new ionophores have been prepared and studied. The proposed potentiometric method was based on the fabrication of modified β-cyclodextrin-chemically modified carbon paste sensor (β-CD-CMCPEs; electrode III) and modified β-cyclodextrin/1,4-bis(6-bromohexyloxy)benzene-chemically modified carbon paste sensor (β-CD/BHOB-CMCPEs; electrode VI) sensors. CMCPEs have been successfully used for the potentiometric titration of Cu(II) in the analytical grad solutions, with a potential jump amounts to 125 and 214 mV for electrode (III) and electrode (VI), respectively. These sensors have wide linear dynamic range from $3.1 \times 10^{-7} – 1 \times 10^{-2}$ and $1 \times 10^{-7} – 1 \times 10^{-2}$ mol L^{-1} with a Nernstian slope of 28.90 ± 0.92 and 29.94 ± 0.12 mV $decade^{-1}$ and low detection limit of 3.1×10^{-7} and 1×10^{-7} mol L^{-1} for electrode (III) and electrode (VI), respectively. They have fast response time (9 and 6 s) and good selectivity with respect to different metal ions. β-CD and β-CD/BHOB based sensors were suitable for aqueous solutions of pH range from 3.5 to 7 and 3.0 to 8. They can be used for about 3 and 4 months without any considerable divergence in potential for electrode (III) and electrode (VI), respectively. The frequently used Cu(II) solution of analytical and technical grade as well as Cu(II) ion in different water samples has been successfully titrated and the results obtained agreed with those obtained with inductively coupled plasma atomic absorption spectrometry (ICP-AES).

Keywords: Chemically modified carbon paste sensors; β-Cyclodextrins; 1,4-bis(6-bromohexyloxy)benzene ionophere; Determination of copper(II).

1. INTRODUCTION

Copper is an important element either for all plants or animals. It functions at low concentration as bacteriostatic substances, fungicides, and wood preservatives. In addition, it is found in a variety of enzymes [1-5]. Copper is widely used in many industries, such as electroplating, paint, metal finishing, electrical, fertilizer, wood manufacturing and pigment industries. As Cu(II) is a highly toxic ion, the removal of Cu(II) from wastewater has been the subject of many researches. Copper ion (Cu(II)) is a common hazardous pollutant in wastewater and is often released by metallurgical, plating, printing circuits, fertilizer and refining industries. The tolerance limit for Cu(II) for discharge into inland surface waters is 3.0 mg/L and in drinking water is 0.05 mg/L [5-9]. Higher concentrations in wastewater can be easily decreased by various methods including electrochemical operations, reverse osmosis, or adsorption by porous adsorbent such as zeolite or activated carbon [10,11]. There are several techniques, which have been used for determination of copper in solution including flame atomic absorption spectroscopy (FAAS) [12,13], stripping voltammetry [14], inductively coupled plasma-optical emission spectrometry (ICP-OES) [15-17], electrothermal atomic absorption spectrometry (ET-AAS) [5,18], spectrophotometry [19] and inductively coupled plasma-mass spectrometry (ICP-MS) [15-17]. In spite of the fact that these methods provide accurate results, they are not very convenient for analysis of the large number of environmental samples because of the requirement of sample pre-treatment and sufficient infrastructure backup. Ion-selective electrodes (ISEs), especially those with neutral carrier-based solvent polymeric membranes, have been studied for more than three decades, and are now routinely employed for direct potentiometric measurements of various ionic species in environmental, industrial and clinical samples [5,13,16,17,20-26]. Potentiometric detection based on ISEs is a simplest method, offers several advantages such as fast and easy preparation procedures, simple instrumentation, relatively fast response time, wide concentration range, reasonable selectivity, low cost and may also be suitable for online analysis [5,13,16,17,20,21,27-30].

In this paper, new chemically modified carbon paste sensors (CMCPEs) were fabricated for rapid and sensitive quantification of Cu(II) ions in both pure and water samples. The new β-CD and β-CD/ BHOB were used as excellent ionophores in the construction of CMCPEs (electrodes (β-CD and β-CD/ BHOB)). These modified electrodes were utilized as electrochemical sensors for Cu(II) determination. The characteristics and analytical performance of CMCPEs like influence of different plasticizers, ionophores content, pH range, temperature and effect of the interfering ions have been investigated.

2. EXPERIMENTAL

2.1. Apparatus

Laboratory potential measurements were performed using Jenway 3505 pH-meter. Silver-silver chloride double-junction reference electrode (Metrohm 6.0726.100) in conjugation with different ion selective electrode was used. Digital burette was used for the field measurement of Cu(II) ion under investigation. pH measurements were done using Thermo-Orion, model Orion 3 stars, USA. Prior to analysis, all glassware used were washed carefully with distilled water and dried in the oven before use.

2.2. Reagents

All chemicals used were of analytical reagent grade unless otherwise stated and doubly distilled water was used throughout. Copper sulphate [$CuSO_4.5H_2O$] was supplied from Merck. While sodium tetraphenylborate (NaTPB, Fluka), tricresylphosphate (TCP; Alfa-Aesar) were used. Other types of plasticizers, namely dioctylphthalate (DOP), dibutylphthalate (DBP), *o*-nitrophenyloctylether (*o*-NPOE) and dioctylsebacate (DOS) were purchased from Sigma, Merck, Fluka and Merck, respectively. 1,4-bis(6-bromohexyloxy)benzene (BHOB) was newly prepared by the authors and β-cyclodextrin (β-CD) was purchased from Merck and graphite powder (synthetic 1–2 μm) (Aldrich) was used for the fabrication of different electrodes. Chloride salts of iron, magnesium, cadmium, bromide, zinc, silver, potassium, manganese, lead, barium, lithium, sodium and aluminum are used as interfering ions.

2.2.1. Samples

Water samples ((formation water (Badr 3, Western Desert, Badr Petroleum Company (sample1) and Amry deep (10), Western Desert, Agiba Petroleum Company (sample2) and Karama, al-Wahhat-al-Bahhriyah, Qarun Petroleum Company (sample 3), Egypt) and (tab water (sample 4) and river water samples (sample 5), Giza, Egypt) and sea water (Marsa Matrouh in Mediterranean Sea area, (sample 6) and red sea (sample 7), Egypt).

2.3. Procedures

2.3 1. Preparation of chemically modified carbon paste sensor (CMCPEs)

A 500 mg pure graphite powder and 5-12.5 mg (β-CD or β-CD/BHOB) ionophore are transferred to mortar and mixed well with plasticizer (0.2 mL of DOP, TCP, DBP, DOS or *o*-NPOE). The modified paste is filled in electrode body and kept in distillated water for 24 h before use [17,21,27]. A fresh surface was obtained by gently pushing the stainless-steel screw forward and polishing the new carbon-paste surface with filter paper to obtain a shiny new surface.

2.3.2. Calibration of the new CMCPEs

The new CMCPEs (electrodes III and VI) were calibrated by immersion in conjunction with a reference electrode in a 25-mL beaker containing a 2.0 mL of acetate buffer solution of pH 4. Then 10 ml aliquot of copper solution of concentration ranging from 1×10^{-7} to 1×10^{-2} mol L^{-1} was added with continuous stirring and the potential was recorded after stabilization to ±0.3 mV. A calibration graph was then constructed by plotting the recorded potentials as a function of -log [Cu(II)]. The resulting graph was used for subsequent determination of unknown copper concentration [5,16,27].

2.3 3. Potentiometric determination of copper ion

The double junction Ag/AgCl reference electrode and the chemically modified CPE sensors were conjugated and immersed in a 50 mL beaker containing the prepared sample solution and then titrated using NaTPB solution.

2.3.4. Determination of copper ion in water samples

Add 2 mL of water samples, 1 mL acetate buffer, complete to 10 mL with bidistilled water, mix well and adjust the pH to 4. Copper (II) is determined potentiometrically as described above.

3. RESULTS AND DISCUSSION

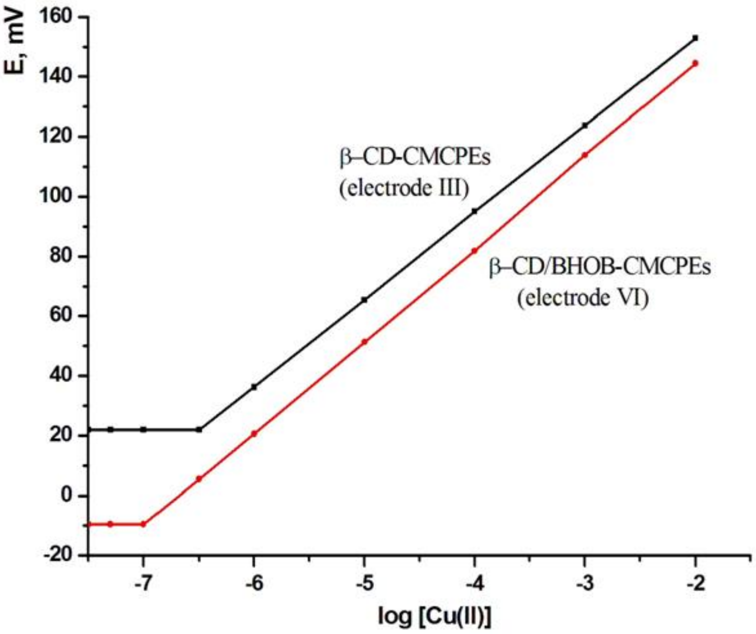

Figure 1. Calibration curve for Cu(II)-chemically modified carbon paste based on β-CD (electrode III) and β-CD/BHOB (electrode VI).

β-CD and β-CD/BHOB compounds are used as effective ionophores for the construction of Cu(II) selective chemically modified carbon paste electrode (III) and electrode (VI), respectively. The effect of paste composition, selectivity, working range, pH of the media and life time of electrodes were investigated. The sensors plasticized with TCP were calibrated against a double junction

Ag/AgCl reference electrode, at 25± 1°C, using the direct calibration technique. The potential response of the electrodes is determined and they found to have a linear response over wide concentration range from $3.1\text{x}10^{-7}$ to $1\text{x}10^{-2}$ and 1×10^{-7} to 1×10^{-2} mol L^{-1} of Cu(II) with a divalent cationic slope of 28.90±0.92 and 29.94±0.12 mV decade^{-1} and exhibit detection limit of 3.1×10^{-7} and 1×10^{-7} mol L^{-1} for electrode (III) and electrode (VI), respectively (Figure 1).

3.1. Composition and characteristics of the sensors.

Preliminary experiments showed that chemically modified carbon paste sensors which do not contain ionophores have no response or low response towards Cu(II) ion. For this purpose, a new ionophores like β-CD and β-CD/BHOB were investigated as modifier for the present electrodes. It is known that the sensitivity and linearity obtained with a given electrode depend significantly on the amount of ionophore in the electrode composition. Thus, for this purpose, four chemically modified carbon paste electrodes (CMCPEs) were prepared to determine the best electrode contents. The proportion of β-CD and β-CD-BHOB ionophores were varied as 5, 7.5, 10 and 12.5 mg (w/w)%. The potentiometric titration was carried out for each electrode and the resulting potential breaks at the end point were found to be 95, 115, 125 and 109 mV mL^{-1} and 190, 214, 209 and 182 mV mL^{-1} for β-CD (electrode III) and β-CD/BHOB (electrode VI) ionophores, respectively. These electrodes give sharp and reproducible inflection at the end point (125 and 214 mV mL^{-1} for electrode III and electrode VI, respectively). These results indicate that the highest potential break at the end point was evaluated using 10 and 7.5 mg of CMCPEs for electrode III and electrode VI, respectively. But increasing the amount of ionophore over 10 and 7.5 mg, the total potential change decreased as shown in Table 1 and Figure 2.

Table 1. Effect of ionophore content on the performance characteristics of Cu(II)-CMCPEs based on β-CD and β-CD/BHOB ionophores.

Electrode type	Ionophore content β-CD (mg)	Ionophore content β-CD/ BHOB (mg)	End point (mL)	Recovery (%)	Total potential change, mV	Potential break at the end point, (mV)	ΔE/ΔV (mV/mL)
I	5	-	3.927	98.17	102	95	245
II	7.5	-	3.946	98.65	126	115	300
III	10	-	3.987	99.67	132	125	323
IV	12.5	-	3.946	98.65	115	109	280
V	5	5	3.932	98.30	196	190	480
VI	7.5	7.5	3.988	99.70	221	214	540
VII	10	10	3.972	99.30	216	209	527
VIII	12.5	12.5	3.923	98.07	189	182	460

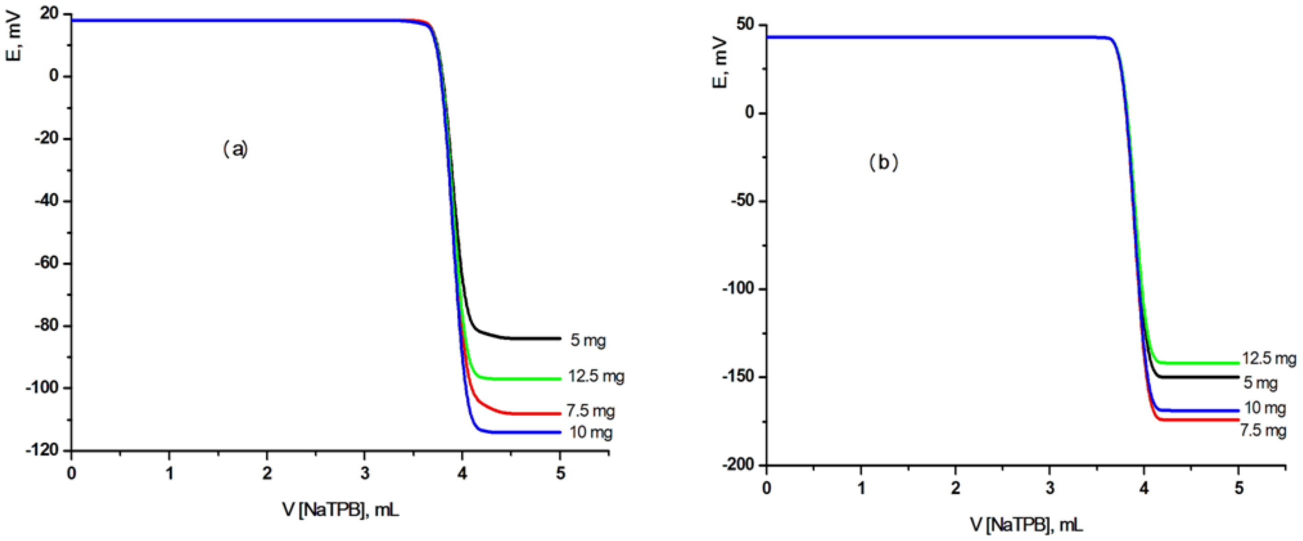

Figure 2. Effect of ionophore content on the performance characteristics of Cu(II)-CMCPEs in the potentiometric titration of 2 mL of 1×10^{-2} mol L^{-1} Cu(II) with 1×10^{-2} mol L^{-1} NaTPB solution based on (a) β-CD and (b) β-CD/BHOB ionophores.

3.2. Effect of plasticizer

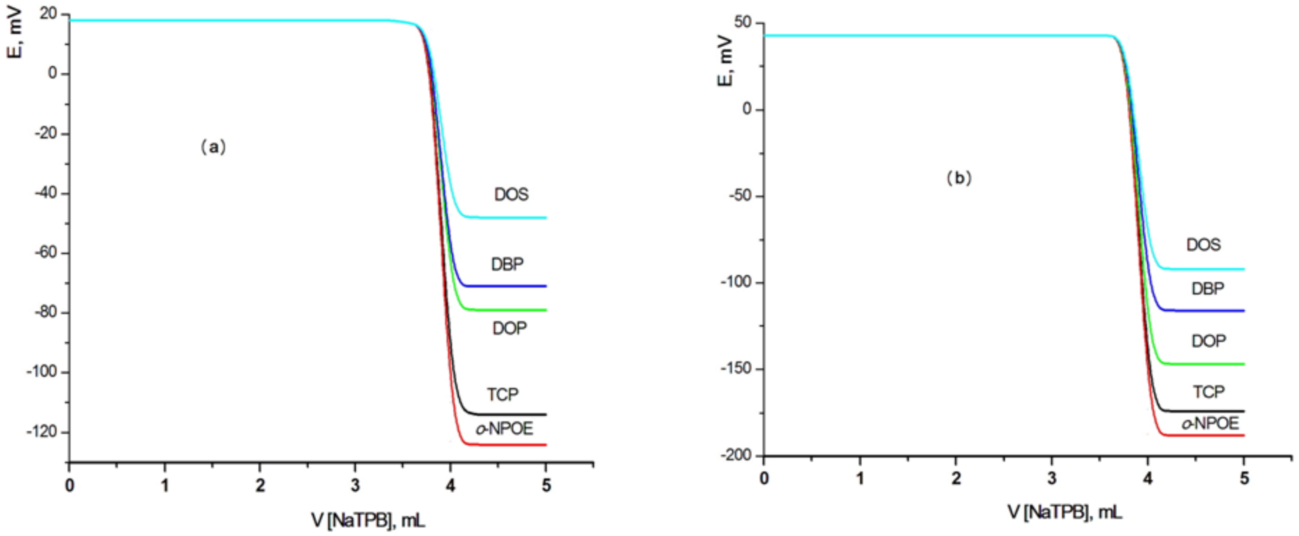

Figure 3. Effect of plasticizer on the performance characteristics of Cu(II)-CMCPEs in the potentiometric titration of 2 mL of 1×10^{-2} mol L^{-1} Cu(II) with 1×10^{-2} mol L^{-1} NaTPB solution based on (a) electrode (III) and (b) electrode (VI).

The influence of solvent mediator (plasticizer) type and concentration on the characteristics of the Cu(II) chemically modified carbon paste sensors (Cu(II)-CMCPEs) were investigated using five solvents with different polarities *o*-NPOE, TCP, DBP, DOP and DOS. The presence of plasticizers not only improves the workability of the sensor, but also contributes significantly to the improvement of the working concentration range, stability and life span of the electrode. It is found that the highest total potential change (145 and 236 mV) and the highest potential break at the end point (138 and 228 mV) are obtained using *o*-NPOE which may be attributed to its high dielectrical constant and the high extractability of the β-CD (electrode III) and β-CD/BHOB (electrode VI) ionophores, respectively (Figure 3), compared with other tested plasticizers (ε values were 24, 3.88, 5.2, 4.7 and 17.6, for *o*-NPOE, DOS, DOP, DBP and TCP, respectively) [20,21]. Due to the high extractability of the formed ionophores in the *o*-NPOE, no electrode preconditioning is needed before applying the electrode in the potentiometric titration and an excellent titration curve can be achieved from the second titration process. While, electrodes fabricated using other plasticizers need either to operate the titration process at least 4-8 times or to soak in the aqueous suspension of the ion pair before using these electrodes in the titration process.

3.3. Dynamic response time

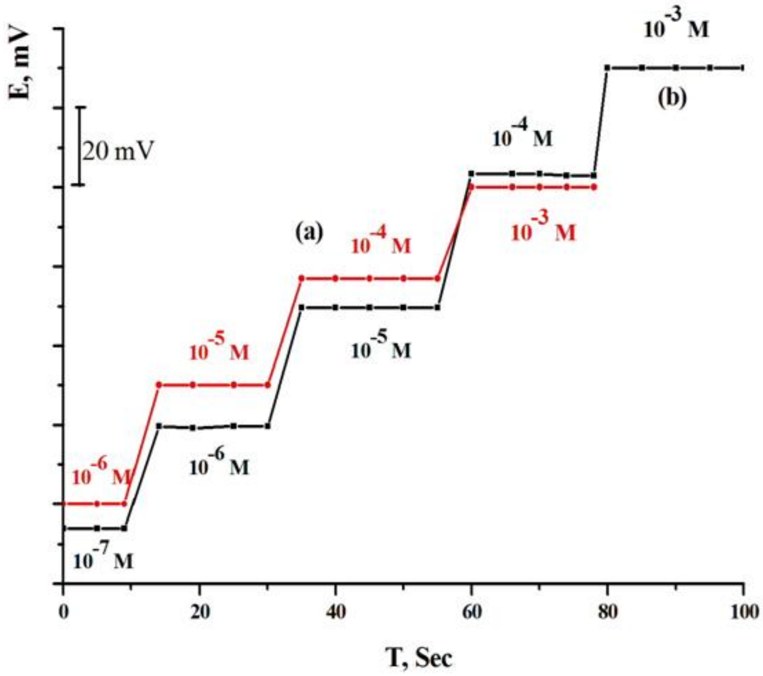

Figure 4. Dynamic response time of copper(II) sensors (a) electrode (III) and (b) electrode (VI).

For analytical applications, the response time of an electrode is of critical importance. The response time is defined as the time elapsed from the dropping of the electrode in the solution until the equilibrium potential was reached. Also the average time required for the electrode to reach a steady potential response within ± 1 mV of the final equilibrium value. After successive immersion of a series of Cu(II) solutions, each having a 10-fold difference in concentration was investigated. Response time inherent to CMCPEs are only measurable if the overall response time of the potentiometric system is governed by the properties of the paste of electrode, i.e. if the time constant of the response function of the electrode is much larger than the time constant of the electrochemical cell and the electronic EMF–measuring device. Indeed, the overall response time is affected by a series of factors, for example the constant of the measuring instrument, the impedance of the equivalent electric circuit of the paste, the rate of the ion transfer reaction across the paste – sample interface, the establishment of a liquid–

junction potential at the reference electrode [13,16]. The results clearly indicate that all the potentiometric response times of the electrode in the concentration range of 1×10^{-6}–1×10^{-3} and 1×10^{-7}–1×10^{-3} mol L^{-1} Cu(II) were less than 9 and 6 s for electrode III and electrode VI, respectively, (Figure 4). These fast response times can be explained by the fact that these electrodes contain carbon particles surrounded by a very thin film of *o*-NPOE and acting as a conductor [30] and the absence of the internal reference solution.

3.4. Lifetime

The average lifetime for most of the reported potentiometric sensors is in the range of 3–4 and 4-5 months. After this time, the slope and detection limit of the sensor will decrease and increase, respectively [21,27,28]. The lifetime of the proposed modified Cu(II) sensors was evaluated by periodically recalibrating the potentiometric response to Cu(II) ion in a series of standard copper sulphate solutions. After conditioning step the sensors repeatedly calibrated five times during a period of 100 and 133 days for electrode III and electrode VI, respectively, and their responses are depicted in Figure 5. The sensors were gently washed with distilled water, dried and stored at room temperature when not in use. As it can be seen from Figure 5, before 3 and 4 months for electrode III and electrode VI, respectively, no significant change in the performance of the sensor was observed (there is a slight gradual decrease in the slopes from 28.90 to 26.52 and 29.94 to 26.84 mV decade^{-1} and an increase in the detection limit from 3.1×10^{-7} and 1×10^{-6} to 1×10^{-7} and 5.0×10^{-7} mol L^{-1} for electrode III and electrode VI, respectively. This shows that the lifetime of the proposed Cu(II) sensors was more than 4 months. The reason for this limited life time of the modified electrode can be attributed to one of the following factors namely the loss of plasticizer, carrier, or ionic site from the polymeric film due to leaching into the sample.

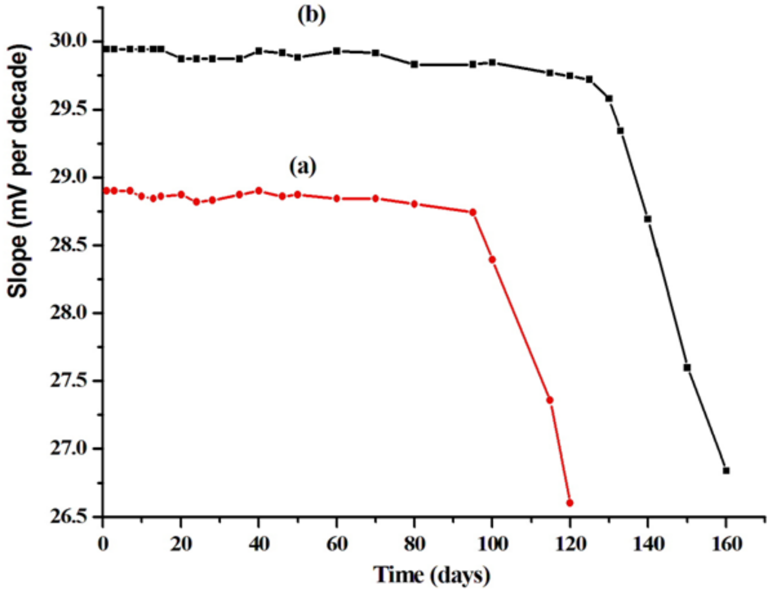

Figure 5. Lifetime of the Cu(II) chemically modified carbon paste electrodes (a) electrode (III) and (b) electrode (VI).

3.5. Effect of pH

The influence of pH of the test solution on the potential response of the paste sensor was tested in the pH range from 1 to 9 and the results are shown in Figure 6. As can be seen, potential remains constant over a pH range of 3.5–7.0 and 3.0-8 for electrode III and electrode VI, respectively, beyond which the potential changes considerably. The observed drift at higher pH values could be due to the formation of some hydroxyl complexes of Cu(II) ion in solution [20,21,27-29]. The observed decrease in potential at low pH values indicates that the protonated ionophore possesses a poor response to the copper ions in solution.

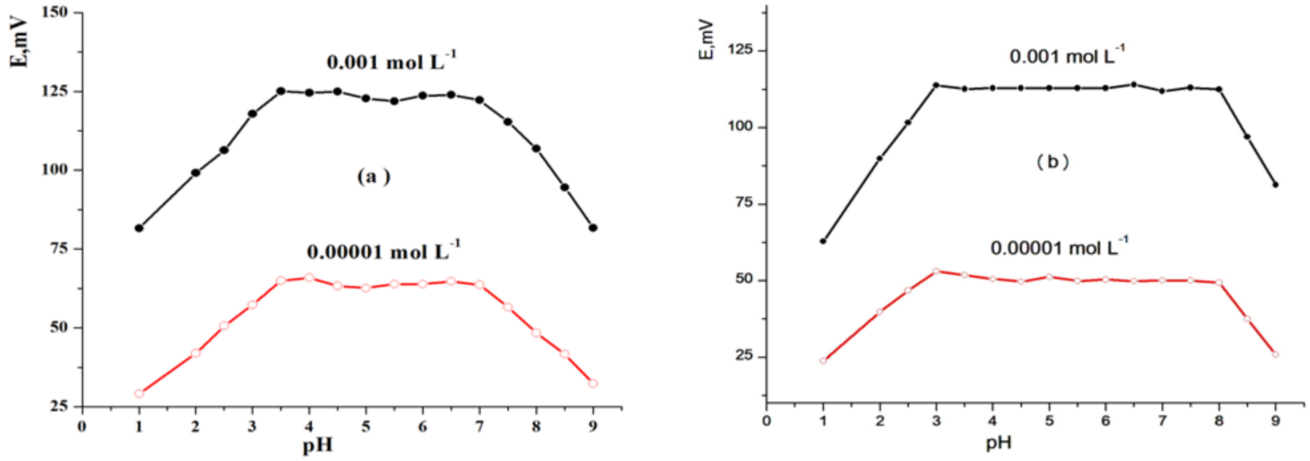

Figure 6. Effect of pH on the performance characteristics of Cu(II)-CMCPEs (a) electrode III and (b) electrode IV.

3.6. Effect of temperature

Trend of changes of electrode performance with temperature, at test solution temperatures 10, 20, 30, 40, 50 and 60 ºC for the Cu(II) electrode was studied. The electrode exhibits good Nernstian behavior in the temperature range (10–60 ºC). At higher temperatures, the slope of electrode did not show a good Nernstian behaviour. This behaviour may be due to the disturbances occurring in phase boundary equilibrium at the CMCPEs layer-test solution interface produced by the thermal agitation of the solution. The standard cell potentials (E^{o}_{cell}), were determined at different temperatures from the respective calibration plots as the intercepts of these plots at *p*Cu(II) = 0, and were used to determine the isothermal temperature coefficient (dE^{o}/dt) of the cell with the aid of the following equation [27,29]:

$$E^{\circ}_{Cell} = E^{\circ}_{Cell(25)} + (dE^{\circ}/dt)_{Cell}\,(t-25)$$

Plot of E°_{cell} versus (t−25) produced a straight line. The slope of this line was taken as the isothermal temperature coefficient of the cell. It amounts to 0.00047 and 0.00038 V/°C for electrode III and electrode VI, respectively (Figure 7). The standard potentials of the reference electrode ($Ag/AgCl_2$, KCl (saturated)) were calculated using the following equation:

$E^{o}_{Ag/AgCl2} = 0.198\text{-}0.00032(t\text{-}25)$

The values of the standard potentials of Cu(II) electrodes were calculated at different temperatures from the following relation:

$E^{o}_{cell} + E^{o}_{reference} = E^{o}_{electrode}$

Plot of E° electrode versus (t−25) gave a straight line. The slope of the line was taken as the isothermal temperature coefficient of the Cu(II) electrode. It amounts to 0.00065 and 0.00015 V/°C for electrode III and electrode VI, respectively. The small values of (dE^{o}/dt) cell and $(dE^{o}/dt)_{electrode}$ reveal the high thermal stability of the electrode within the investigated temperature range.

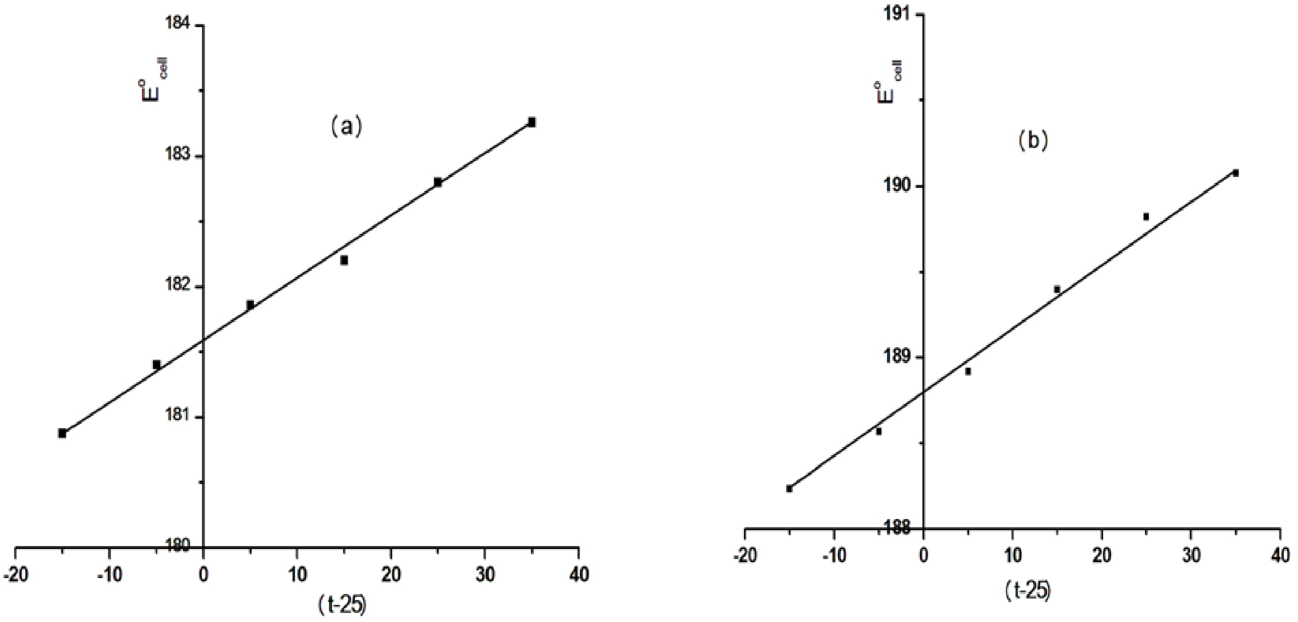

Figure 7. Effect of temperature on the performance characteristics of Cu(II)-CMCPEs (a) electrode (III) and (b) electrode (VI).

3.7. Potentiometric selectivity

The selectivity behaviour is one of the most important characteristics of an ion-selective electrode, and it is usually described in terms of selectivity coefficient, which reflected the relative response of the membrane sensor for the primary ion over other ions present in the solution. To investigate the selectivity of the proposed Cu(II) selective electrodes, their potential response was investigated in the presence of various cations using both the matched potential method (MPM) [5,13,16,17,31] and the fixed interference method (FIM) [16,31]. In the matched potential method, the selectivity coefficient was determined by measuring the change in potential upon increasing the primary ion activity from an initial value of a_A to a'_A and a_B represents the activity of interfering ion added to the reference solution of primary ion of activity a_A which also brings the same potential change. It is given by the expression:

$$K^{MPM}_{A,B} = \frac{a'_A - a_A}{a_B}$$

In the present study, a_A and a'_A were kept at 1.0 × 10^{-3} and 1.0 × 10^{-5} mol L^{-1} Cu(II) and a_B was experimentally determined. However, in the FIM, the selectivity coefficient was evaluated from potential measurement on solutions containing a fixed concentration of interfering ion (1.0 × 10^{-2} mol L^{-1}) and varying amount of Cu(II) ions. The selectivity coefficient is calculated from the following equation:

$$K^{FIM}_{A,B} = \frac{a_A\,(DL)}{(a_B)^{Z_A/\,Z_B}}$$

where a_A is the activity of the primary ion A (Cu(II)) at the lower detection limit in the presence of interfering ion B, a_B, the activity of interfering ion B and z_A and z_B are their respective charges. The values of selectivity coefficient so determined are compiled in Table 2. As can be seen, the selectivity coefficients determined by both methods are sufficiently smaller than 1.0 indicating that the present sensors are significantly selective to copper ion over all the interfering ions.

Table 2. Selectivity coefficients of various ions using electrode (III) and electrode (VI).

Interfering ions	$K^{MPM}_{A,B}$ (a) electrode (III)	$K^{MPM}_{A,B}$ (a) electrode (VI)	$K^{FIM}_{A,B}$ (b) electrode (III)	$K^{FIM}_{A,B}$ (b) electrode (VI)
K^+	4.27×10^{-2}	5.19×10^{-2}	8.25×10^{-2}	7.12×10^{-2}
Na^+	9.34×10^{-4}	4.35×10^{-4}	5.43×10^{-4}	6.23×10^{-4}
NH_4^+	6.19×10^{-4}	4.42×10^{-4}	3.73×10^{-4}	2.64×10^{-4}
Ag^+	5.76×10^{-2}	7.11×10^{-2}	3.27×10^{-2}	1.74×10^{-2}
Li^+	6.28×10^{-3}	3.54×10^{-3}	9.44×10^{-4}	7.90×10^{-4}
Cd^{2+}	8.71×10^{-2}	8.03×10^{-2}	5.45×10^{-3}	3.55×10^{-3}
Hg^{2+}	1.25×10^{-4}	2.67×10^{-4}	6.27×10^{-4}	4.32×10^{-4}
Pb^{2+}	7.31×10^{-4}	6.76×10^{-4}	7.11×10^{-4}	5.43×10^{-4}
Mg^{2+}	4.54×10^{-5}	6.77×10^{-5}	4.90×10^{-5}	8.12×10^{-5}
Zn^{2+}	1.97×10^{-1}	2.40×10^{-1}	0.78×10^{-1}	0.95×10^{-1}
Fe^{3+}	6.43×10^{-5}	4.81×10^{-5}	3.45×10^{-5}	7.53×10^{-5}
Al^{3+}	5.41×10^{-4}	7.35×10^{-4}	1.54×10^{-4}	2.22×10^{-4}
Cr^{3+}	7.21×10^{-2}	6.62×10^{-2}	7.11×10^{-2}	1.62×10^{-2}
Cl^-	4.89×10^{-4}	4.62×10^{-4}	7.66×10^{-4}	3.27×10^{-4}
SO_4^{-2}	1.05×10^{-5}	3.44×10^{-5}	7.20×10^{-6}	9.00×10^{-6}
Br^-	8.23×10^{-4}	5.40×10^{-4}	1.52×10^{-4}	1.09×10^{-4}
NO_3^-	0.89×10^{-3}	1.44×10^{-3}	0.77×10^{-3}	2.30×10^{-3}
I^-	9.11×10^{-2}	7.82×10^{-2}	6.20×10^{-2}	7.95×10^{-2}

3.8. Potentiometric determination of copper ion in real samples

The Cu(II)-CMCPEs were used successfully for determination of Cu(II) ions in different environmental samples including formation water, tap-, and river-Nile water. Determination of Cu(II) in the previously mentioned samples was performed using the standard addition method. The assay method for Cu(II) ions over the concentration range of $1 \times 10^{-7} – 1 \times 10^{-2}$ mol L^{-1} was achieved using three batches (three determinations each) for the statistical treatment of the results. Water samples of very low concentration of Cu(II) (below the detection limit of the electrodes) were spiked by adding aliquots of standard solution of Cu(II) ion to the samples. The samples were acidified with HNO_3 acid to dissociate the metal-complexes then adjusted to pH 4.0-5.0 using acetate buffer.

The amount of copper was measured by the proposed copper selective electrode and by inductively coupled plasma atomic absorption spectrometry (ICP-AES). It is clear from the results, given in Table 3, that there is good agreement between the results of the proposed sensor and those obtained from ICP-AES method. The recovery ranges are between 96.00 and 101.0%.

3.9. Comparison study

In Table 4, some important characteristics of the proposed electrodes are compared with the corresponding values previously reported for Cu(II)-selective electrodes based on different modifiers [5,32-37]. It is evident from this table that in many cases, the performances of the proposed electrode show superior behaviour if compared with the best previously reported Cu(II) sensors.

4. CONCLUSION

The chemically modified carbon paste electrodes incorporating β-CD (electrode III) and β-CD/BHOB (electrode VI) ionophores as electroactive phase can be used in the development of copper ion-selective electrodes. The electrodes having the composition of 50.0% graphite, 40.0% TCP and 10.0% β-CD or β-CD/BHOB ionophores responds to Cu(II) ions in a Nernstian behaviour with slope of 28.90 ± 0.92 and 29.94 ± 0.12 mV decade^{-1} and low detection limit of 3.1×10^{-7} and 1×10^{-7} mol L^{-1} for electrode (III) and electrode (VI), respectively. The electrodes are characterized by a relatively fast response, reasonable long-term stability and responsive potential stability. Most of metal ions do not affect the selectivity of the copper electrodes. The electrodes were applied to direct determination of Cu(II) ions in water samples as indicator electrodes using potentiometric titration. Table 4 shows the comparison of the performance characteristics of the proposed sensors with those of the best previously prepared copper sensors. From the interference study it is obvious that the proposed sensor has no interference from many ions. Wider working concentration range and lower limit of detection were also offered by the proposed sensors compared to some of those previously suggested [5, 32-35]. The response time of the present sensors is smaller than many of the reported electrodes [5, 34-37].

Table 3. Determination of copper ions in spiked water samples using electrode (III) and electrode (VI).

Samples	[Cu(II)] (mg L^{-1})									
		(Electrode III)			(Electrode VI)			ICP-AES		
	Added	Found	R.S.D (%)	Recovery (%)	Found	R.S.D (%)	Recovery (%)	Found	R.S.D (%)	Recovery (%)
1	7.5	7.42	0.561	98.93	7.45	0.436	99.33	7.39	0.967	98.53
	10	9.88	0.499	98.80	10.01	0.308	100.1	9.78	1.032	97.80
	12.5	12.40	1.001	99.20	12.47	0.880	99.76	12.42	0.966	99.36
2	7.5	7.36	1.021	98.13	7.38	1.00	98.40	7.33	1.210	97.73
	10	9.77	1.325	97.70	9.80	1.015	98.00	9.69	1.401	96.90
	12.5	12.41	0.863	99.28	12.52	0.399	100.2	12.38	1.025	99.04
3	7.5	7.29	1.486	97.20	7.40	1.025	98.66	7.27	2.004	96.93
	10	9.77	1.303	97.70	9.90	1.098	99.00	9.79	1.671	97.90
	12.5	12.44	1.141	99.52	12.46	0.756	99.68	12.42	0.895	99.36
4	2.5	2.43	1.342	97.20	2.46	1.105	98.40	2.4	1.621	96.00
	5	4.96	0.747	99.20	4.98	0.312	99.60	4.95	1.007	99.00
	7.5	7.49	0.658	99.86	7.5	0.007	100.0	7.47	0.255	99.60
5	2.5	2.45	1.075	98.00	2.52	0.081	100.8	2.46	1.009	98.40
	5	5.04	0.010	100.8	5.05	0.011	101.0	4.99	0.088	99.80
	7.5	7.52	0.017	100.3	7.55	0.024	100.7	7.5	0.243	100.0
6	6	5.9	1.002	98.33	5.98	0.065	99.66	5.88	1.128	98.00
	8	7.93	0.798	99.13	8.02	0.205	100.3	7.95	1.074	99.37
	11	10.88	1.015	98.90	11.04	0.081	100.4	10.97	0.880	99.73
7	6	5.85	1.321	97.50	5.92	0.573	98.67	5.79	1.366	96.50
	8	7.89	1.631	98.63	7.95	0.153	99.38	7.90	1.107	98.75
	11	10.9	0.957	99.09	10.88	0.501	98.91	10.85	1.011	98.64

Table 4. Comparing some of the Cu(II)-CMCPs (electrode VI) characteristics with some of the previously reported Cu(II)-ISEs.

References	Slope (mV decade^{-1})	Response time (s)	pH	Life time (months)	Linear range (mol L^{-1})	DL (mol L^{-1})
Proposed electrode	29.94	6	3.0 – 8	4	$1 \times 10^{-7} – 1 \times 10^{-2}$	1×10^{-7}
5	29.45	8	3.8 – 5	3	1×10^{-6} - 1.0×10^{-2}	1×10^{-6}
32	26.20	2–18	-	-	$1.0 \times 10^{-5} – 1.0 \times 10^{-2}$	2.5×10^{-6}
33	28.10	6	5.3 - 7.2	2	$1.0 \times 10^{-7} – 1.0 \times 10^{-3}$	6.3×10^{-8}
34	29.40	8	2.8 - 7.9	4	6.3×10^{-6} - 1.0×10^{-1}	6.3×10^{-6}
35	30.30	<15	4.5 – 7	< 1	1.0×10^{-6} - 1.0×10^{-1}	7.5×10^{-7}
35	25.90	<15	4.5 – 7	< 1	$3.1 \times 10^{-6} – 1.0 \times 10^{-2}$	2.1×10^{-6}
36	29.50	10	1.8 – 5.8	<2	$5.0 \times 10^{-8} – 1.0 \times 10^{-1}$	4.0×10^{-8}
37	29.34	<10	2 – 5	1	$6.0 \times 10^{-8} – 1.0 \times 10^{-1}$	4.0×10^{-8}

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