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Potentiometric sensors selective for Cu(II) determination in real water samples and biological fluids based on graphene and multi-walled carbon nanotubes modified graphite electrodes

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Three newly synthesized Cu(II) ion selective electrodes based on 1,8-dihydoxyanthraquinone (DHAQ), as an ionophore, have been developed. Carbon paste electrode has been modified with DAHQ (sensor I), graphene and DHAQ (sensor II) and multi-walled carbon nanotubes (MWCNTs) and DHAQ (sensor III), in order to improve the conductivity and transduction of chemical signal to electrical signal. Under optimized conditions, the electrodes I, II and III revealed Nernstian slopes of 29.78 ± 0.17, 30.25 ± 0.12, and 30.55 ± 0.19 mV $decade^{-1}$, respectively, at 25±1 °C covering a wide concentration range from 1×10^{-6} to 1×10^{-1} mol L^{-1} for sensors I and II and from 1×10^{-5} to 1×10^{-1} mol L^{-1} for sensor III with detection limit values of 8×10^{-7}, 5×10^{-7}, and 3.3×10^{-6} mol L^{-1}, respectively. The response of the proposed electrodes is very fast and independent of pH in the range of 2.4–6.5 and the response mechanism is studied using IR, SEM and EDX analyses. Selectivity coefficients have been determined by applying separate solution method and matched potential method, where the obtained values indicated the good discrimination of Cu(II) from other cations by the proposed sensors. The developed sensors have been used successfully for quantitative determination of Cu(II) ions in different matrix of spiked real water samples and biological fluids (urine and serum). These sensors have also been used successfully as indicator electrodes in the potentiometric titration of Cu(II) with EDTA.

Keywords: Carbon paste electrode, 1,8-dihydroxyanthraquinone (DHAQ), Cu(II) ion, Graphene, Multi-walled carbon nanotues (MWCNTs), Potentiometric titration

Heavy metals are widespread pollutants of great ecological concern as they are not biodegradable and thus persisting. This highlights the importance of not exceeding the permissible limit for each metal, above which they are generally toxic and some are even hazardous[1]. Industrial wastes which contain copper are common because copper is ranked as third after iron and aluminum regarding the consumed amounts for industrial uses such as piping for water supplies, refrigeration and air conditioning as well as in wires, electromagnets, dye manufacture, as a mordant for textile dyes, petroleum refining, electrical relays and switches[2]. Copper (Cu) plays an important role in both humans and animals as it is a co-factor of many redox enzymes such as Ceruloplasmin with a Cu-dependent oxidation activity being involved in many biological processes like antioxidant defense, immune function and neuropeptide synthesis. The average level of copper in the blood should not exceed 100–150 μg/dL and if Cu is deficient, an impaired development of the cardiovascular system, bone malformation, neurologic and immunologic abnormalities and alternations in cholesterol metabolism can result[2,3]. On the other hand, long term exposure of human to copper can result in health problems such as irritation of the nose, mouth and eyes as well as headache problems. Moreover, its excessive intake results in certain human diseases such as Menke's syndrome and Wilson's disease[4].

In consequences, the determination of copper is important regarding its utilization and toxicity. A number of instrumental methods, such as atomic absorption spectrometry (AAS), inductively coupled plasma (ICP), anodic stripping voltammetry (ASV), and flame photometry[5-9] were employed for its estimation, but these methods, generally, required sample pretreatment and infrastructure backup and were not very convenient for routine analysis of large number of environmental samples. On the other hand, ion sensors are the analytical tools which are convenient, fast, required no sample pretreatment and also suitable for 'on-line' analysis[10]. Among the various potentiometric methods, carbon paste electrodes (CPEs) were distinct in terms of response stability, renewability and low ohmic resistance without using internal solution[11].

In view of enhancing the sensitivity of sensors, graphene and MWCNTs, built from sp^2 carbon units, can be used. The aberrant characteristics of graphene result from the 2p orbitals which form the π state bands that delocalize over the sheets of carbon constituting graphene. MWCNTs contain concentric graphite tubules with multiple layers of graphite sheets[12,13]. Because of their unique structure as well as extraordinary physical properties[14,15], they have been one of the most commonly studied materials in carbon paste electrodes[4,16-20].

The purpose of this work was the development of new carbon paste Cu(II) ion selective electrode based on application of DHAQ with high selectivity toward Cu(II) ion as the active ingredients. In this research the role of nano scale materials such as graphene nanoplatelets and MWCNTs on the response properties (slope, linear range, detection limit, regression and response time) of novel Cu(II) ion selective electrodes was discussed. The selectivity for a variety of ions and the effect of the carbon paste matrices composition, amount of ionophore, plasticizer type, pH and temperature on the potentiometric response properties of the proposed electrodes were investigated and optimized. The limit of detection and quantification, precision and accuracy of the method were optimized according to the ICH guidelines.

Material and Methods

Materials and Reagents

Analytical grade reagents were used in this study. Distillated water was used throughout all experiments. Copper sulphate [$CuSO_4.5H_2O$] was supplied from Merck and 1,8- dihydroxyanthraquinone (DHAQ) was supplied from L. Light & Co. Ltd., Colnbrook, England. Disodium salt of ethylene diamine tetraacetic acid (Na_2EDTA) was purchased from Adwic. *o*-Nitrophenyloctyl ether (*o*-NPOE) was purchased from Fluka while dioctyl phthalate (DOP), dibutyl phthalate (DBP) and dioctyl sebacate (DOS) were purchased from BDH. 2-Fluorophenyl-2-nitrophenyl ether (FFNE), tricresyl phosphate (TCP) and graphite powder (synthetic 1–2 μm) were purchased from Sigma Aldrich. Graphene nanoplatelets (6–8 nm thick × 5 microns wide) were supplied from Strem Chemicals while multi-walled carbon nanotubes (MWCNTs) from Egyptian Petroleum Research Institute, Egypt. Chloride salts of manganese, cadmium, zinc, nickel, calcium, magnesium, lead, barium, cobalt, chromium and aluminum used as interfering materials were purchased from El Nasr Company.

Samples

Water samples

Water samples used in investigation were collected from different sources. They included underground tap water supplied from Manshat El-Kanater network (sample 1), Nile water supplied from El-Hager station (sample 2), Nile water which was the intake of Nekla station (sample 3) and tap water which was the output of Nekla station (sample 4). The pH of each sample was adjusted by NaOH or HNO_3 to the desired pH (pH = 4.5) and known amounts of Cu(II) were spiked to each sample.

Biological Fluids

Human serum was taken from patient 1 (infant) with age 2 years and urine was taken from Patient 2 (male) with age 30 years of Wilson disease patients. For determination of Cu(II) in human serum, the absorbance of the colored complex formed by the treatment of the serum sample with 4-(3,5-dibromo-2-pyridylazo)-N-ethyl-N-sulfopropylaniline reagent and incubated at 37 °C for 5 min, was measured at λ = 580 nm[21].

For determination of Cu(II) content in urine sample, the following procedure was followed. The 24 h urine sample was collected in a clean bottle. Then after measuring urine volume, sodium dodecyl sulfate (SDS)-ascorbic acid was used to extract copper from proteins in pH of 3.2 adjusted by acetate buffer and then a colored complex was formed by the treatment of the sample with the ligand 2-(5-nitro-2-pyridylazo)-5-(N-propyl-N-sulfopropylamino) phenol (nitro-PAPS) reagent[22].

All experiments were performed in compliance with the relevant laws and institutional guidelines (Profession and Ethics Regulations, Resolution of the Ministry of Health and Population No. 238/2003). The protocol was approved by Faculty of Science (Cairo University) institutional committee(s) and all participants provided written informed consent to approve the experiments done with human subjects.

Apparatus

The potential measurements were carried out using a digital Hanna pH/mV meter (model 8417). Silver-silver chloride double-junction reference electrode (HANNA, HI 5311) in conjugation with the prepared sensors under study was used. Jenway 3505 pH meter was used for pH measurements. Digital burette was used for the potentiometric titration of Cu (II) against EDTA. Automatic pipettes Socorex Swiss (50–200 µL and 200–1000 µL) were used to measure the very small volumes whereas glass micropipettes were used to measure the large volumes. The energy dispersive X ray analyzer (EDX), (National research center, Egypt) and scanning electron microscope (SEM) (National Research Center Quanta FEG250) were used for surface analysis. The FTIR spectra were measured on a Perkin-Elmer 1650 spectrometer (4000–400 cm^{-1}) in potassium bromide pellets at the Microanalytical Center, Cairo University Egypt.

Procedure

Carbon paste electrodes preparation

A Teflon holder (12 cm length) with a hole at one end (7 mm diameter and 3.5 mm deep) for the carbon paste filling served as the electrode body. Electrical contact was made with a stainless steel rod through the center of the holder. This rod can move up and down by screw movement to press the paste down when renewal of the electrode surface was needed. DHAQ based carbon paste electrodes were prepared by thoroughly mixing the 1,8-dihydroxyanthraquinone (5-20 mg) as an ionophore with 250 mg graphite powder and different plasticizers (0.1 mL of DOP, TCP, DBP, DOS, FFNE or *o*-NPOE). Very intimate homogenization was achieved by careful mixing using agate pestle and mortar and afterwards rubbed by intensive pressing with the pestle. The ready prepared paste was then packed into the hole of the electrode body and then, the carbon paste was smoothed onto a wet filter paper until it had a shiny appearance[23]. Graphene and DHAQ based carbon paste electrodes and MWCNTs and DHAQ based carbon paste electrodes were prepared in similar fashion with the addition of different amounts of graphene and MWCNTs, respectively, along with the ionophore, graphite powder and plasticizer.

Potential measurements

The calibration of the prepared sensors under investigation was established by immersion of carbon paste electrode in conjugation with Ag /AgCl reference electrode in a 25 mL beaker containing 5.0 mL aliquots of 1.0×10^{-8}–1.0×10^{-1} mol L^{-1} of Cu (II) solution. The response of the sensors for copper ion was examined by measuring the potentials which were plotted against –log [Cu(II)]. The obtained calibration plots were used for posterior detection of unknown copper(II) concentrations.

Surface analysis

The energy dispersive X ray analyzer (EDX) and scanning electron microscope (SEM) were used for surface analysis of the paste at 4000X magnifications for sensors I , II and III before and after the interaction with Cu (II) ions.

Results and Discussion

Influence of the carbon paste composition on the electrodes response

Different carbon paste compositions by changing the amount of ionophore, type of plasticizer, ratios of graphene/graphite powder and MWCNTs/graphite powder ratios has been prepared according to Table 1. Subsequently, the influence of these different paste compositions on the response feature of proposed electrodes was investigated in the range of 1×10^{-8}–1×10^{-1} mol L^{-1}. The obtained results are shown in Table 1.

Optimization of the amount of the ionophore in the paste

The ionophore has the principal effect on the selectivity of the ion selective electrodes (ISEs). The potential developed at the electrode surface is the result of either an ion exchange process or an ion transport process occurring at each interface between the paste and solution. In this work, this ion transport depends on complexation between the used ionophore (DHAQ) and Cu(II) ions. In addition the plasticizer plays an important role in extraction of Cu(II) ions from solution into the paste[24]. The ionophore used in ISEs should have fast exchange kinetics and suitable formation constants as well as good solubility in the paste matrix and sufficient lipophilicity as not to lose the ionophore by leaching deteriorating the analytical signal over time[25].

DHAQ was tested for its suitability as Cu(II) selective ion ionophore. It was applied for construction of carbon paste electrodes of the same composition as electrode (No. 2), given in Table 1 and

Table 1 — Optimization of the carbon paste ingredients

Electrode No.	Composition of various components in carbon pastes (amount in mg)							Electrode characteristics		
	Ionophore (mg)	Plasticizer (mg)	GP (mg)	Graphene (mg)	MWCNTs (mg)	Graphene/ GP ratio	MWCNTs/ GP ratio	Linear range (mol L^{-1})	Slope (mV $decade^{-1}$)	R^2
Effect of the amount of ionophore										
1	5	100-TCP	250	–	–	–	–	1×10^{-6}–1×10^{-1}	26.32 (±0.46)	0.9987
2	**10**	**100-TCP**	**250**	**–**	**–**	**–**	**–**	**1×10^{-6}–1×10^{-1}**	**29.78 (±0.17)**	**0.9994**
3	15	100-TCP	250	–	–	–	–	1×10^{-6}–1×10^{-1}	27.85 (±1.15)	0.9992
4	20	100-TCP	250	–	–	–	–	1×10^{-6}–1×10^{-1}	26.72 (±0.20)	0.9989
Effect of different plasticizers										
2	**10**	**100-TCP**	**250**	**–**	**–**	**–**	**–**	**1×10^{-6}–1×10^{-1}**	**29.78 (±0.17)**	**0.9994**
5	10	100-*o*-NPOE	250	–	–	–	–	1×10^{-6}–1×10^{-1}	26.00 (±1.80)	0.9991
6	10	100-DOP	250	–	–	–	–	1×10^{-6}–1×10^{-2}	28.55 (±1.60)	0.9992
7	10	100-DOS	250	–	–	–	–	1×10^{-5}–1×10^{-1}	29.84 (±1.43)	0.9990
8	10	100-DBP	250	–	–	–	–	1×10^{-6}–1×10^{-1}	25.10 (±2.62)	0.9968
9	10	100-FFNE	250	–	–	–	–	1×10^{-6}–1×10^{-1}	25.50 (±0.70)	0.9942
Effect of different graphene/graphite weight ratios										
10	10	100-TCP	225	25	–	0.11	–	1×10^{-6}–1×10^{-1}	26.40 (±0.60)	0.9991
11	**10**	**100-TCP**	**200**	**50**	**–**	**0.25**	**–**	**1×10^{-6}–1×10^{-1}**	**30.25 (±0.12)**	**0.9996**
12	10	100-TCP	150	100	–	0.67	–	1×10^{-6}–1×10^{-1}	26.33 (±0.87)	0.9981
13	10	100-TCP	125	125	–	1	–	1×10^{-6}–1×10^{-1}	23.00 (±0.87)	0.9970
14	10	100-TCP	100	150	–	1.5	–	5×10^{-6}–1×10^{-1}	22.02 (±1.26)	0.9964
15	10	100-TCP	50	200	–	4	–	5×10^{-6}–1×10^{-1}	20.30 (±1.07)	0.9963
16	10	100-TCP	–	250	–	–	–	1×10^{-5}–1×10^{-1}	19.90 (±0.87)	0.9954
Effect of different MWCNTs/graphite weight ratios										
17	10	100-TCP	245	–	5	–	0.02	5×10^{-5}–5×10^{-2}	32.25 (±1.39)	0.9986
18	10	100-TCP	235	–	15	–	0.06	3×10^{-5}–5×10^{-2}	27.21 (±0.73)	0.9995
19	**10**	**100-TCP**	**225**	**–**	**25**	**–**	**0.11**	**1×10^{-5}–1×10^{-1}**	**30.55 (±0.19)**	**0.9998**
20	10	100-TCP	215	–	35	–	0.16	3×10^{-5}–1×10^{-1}	27.20 (±0.25)	0.9991
21	10	100-TCP	200	–	50	–	0.25	5×10^{-5}–1×10^{-1}	26.23 (±0.20)	0.9991
22	10	100-TCP	150	–	100	–	0.67	5×10^{-5}–1×10^{-1}	24.00 (±1.32)	0.9990
23	10	100-TCP	125	–	125	–	1	1×10^{-4}–1×10^{-1}	23.36 (±2.68)	0.9986
24	10	100-TCP	100	–	150	–	1.5	1×10^{-4}–1×10^{-1}	20.80 (±2.70)	0.9950

MWCNTs: Multi-walled carbon nanotubes, GP: Graphite, TCP: Tricresyl phosphate, *o*-NPOE: ortho-Nitrophenyloctyl ether, DOP: Dioctyl phthalate, DOS: Dioctylsebacate, DBP: Dibutyl phthalate, FFNE: 2-Fluorophenyl-2-nitrophenyl ether, R^2: Regression (correlation factor).
Values in parentheses are SDs based on four replicate analyses and optimized values are bold.

applied for measuring a variety of metal ions and their potential responses were shown in Fig. 1. It was shown that among all investigated cations, Cu(II) ion showed the Nernstian potential response and this can be attributed to the selective behavior and more interaction of the ionophore for Cu(II) over other metal ions as well as the rapid exchange kinetics of the resulting complex[23].

The response of the electrodes containing constant ratio of the plasticizer and graphite and comprising different amounts of 5 mg, 10 mg, 15 mg and 20 mg of DHAQ were studied in solutions containing different activities of the Cu(II) ions ranging from 1.0×10^{-8} to 1.0×10^{-1} mol L^{-1} for each composition to spot the adequate electrode. The results were

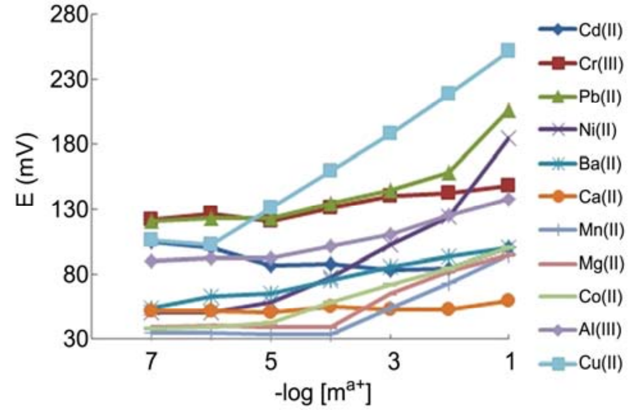

Fig. 1 — Potential response of carbon paste ion-selective electrode (electrode with composition No. 2) over concentration range of 1.0×10^{-7}–1.0×10^{-1} mol L^{-1} of different metal ions.

compiled in Table 1. The slope of the electrode was increased with increasing the amount of the ionophore until the value of 10 mg (electrode No. 2) which gave the best slope, regression and standard deviation (SD) value. However, further increase in the amount of the ionophore decreased the slope and this can be explained by the change of the ratio of the ionic sites to the ionophore in the paste and hence the deterioration of the electrode response from Nernstian to sub-Nernstian[26].

Effect of soaking time on this electrode was studied. As shown in Fig. 2, without soaking the slope was super-Nernstian. However, by increasing the soaking time the slope became more Nernstian reaching 29.7 ± 0.22 mV decade^{-1} after soaking in 1.0×10^{-3} mol L^{-1} Cu(II) solution for 10 min. Further increase in soaking time had an opposite effect of decreasing the slope to sub-Nernstian value and this may be due to saturation of the paste with Cu(II) ions or leaching of active ingredients into the bathing solution.

Effect of different plasticizers

An adequate plasticizer must have the following criteria: sufficient lipophilicity, no crystallization in the paste, no oxidation, selectivity properties and mechanical stability, high molecular weight, low tendency for exudation from the paste matrix, low vapor pressure and high capacity to dissolve the substrate and other additives present in the paste[27,28]. The use of plasticizers will give some permeable properties to the paste and will improve its mechanical stability by promoting binding between grains[29]. The proportion of plasticizer must be optimized in order to minimize the electrical asymmetry of the paste, to keep the sensor as clean as possible, and to stop leaching to aqueous phase.

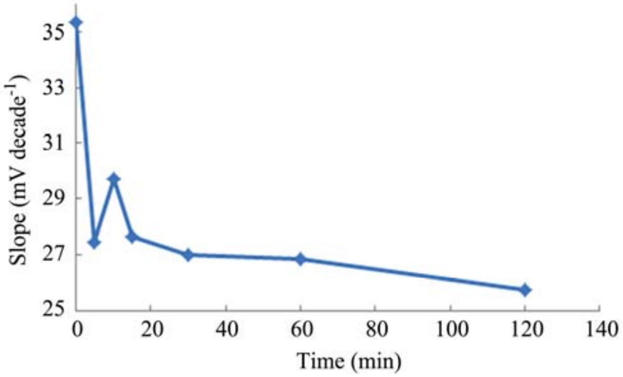

Fig. 2 — Effect of soaking time on electrode I with composition No. 2.

In exploration for a suitable plasticizer, six plasticizers, namely, TCP, *o*-NPOE, DOS, DOP, DBP and FFNE were studied to figure out the plasticizer with the best response. The carbon paste electrode with TCP as a solvent mediator produced the best response concerning slope, linear range, repeatability and regression as shown in Table 1. Electrode No. 2, composed of 250 mg graphite, 10 mg DHAQ and 100 mg TCP, gave the best sensitivity, with a Nernstian slope of 29.78 ± 0.17 mV decade^{-1} and detection limit of 8.0×10^{-7} mol L^{-1} over a relatively wide dynamic range from 1.0×10^{-6} to 1.0×10^{-1} mol L^{-1} of Cu(II) ions. Therefore, this composition was used to study various operation parameters of the electrode and this sensor will be referred to as electrode I.

Effect of graphene content

Graphene has zero effective mass and displays high mobility of charge carriers and hence high conductivity[30]. Every atom is on the surface and is accessible from both sides, so there is more interaction with surrounding molecules which means that it has high surface area[14].

Due to the mentioned advantages of graphene, a study of impregnation of it in different weight ratios with graphite powder was made, while keeping the amount of ionophore and binder to (graphite powder + graphene) weight ratio constant. Increasing graphene/graphite powder ratio improved the slope, regression, and detection limit due to the increase in transduction property of the sensor, as shown in Table 1. Anyway, increasing the graphene/graphite ratio higher than 1:4 in the composition of the carbon paste led to sub-Nernstian values and thus decreased its sensitivity. It is probably due to the high surface area formed on the electrode surface that may offer special opportunities for the capturing ions on the surface of the paste and the decrease in binder to graphene ratio which can decrease the extractability of the sensor. The electrode modified with graphene and DHAQ with the composition of 200 mg graphite powder, 50 mg graphene, 10 mg DHAQ and 100 mg TCP with graphene/graphite powder ratio of 1:4 was selected as the one with optimal ingredient composition (electrode No. 11). It exhibited a Nernstian slope of 30.25 ± 0.12 mV decade^{-1} over a wide concentration range from 1×10^{-6} to 1×10^{-1} mol L^{-1} and provided an improvement in the slope, sensitivity with a detection limit of 5.0×10^{-7} mol L^{-1} and regression with respect to electrode (I). An important advantage of this electrode over electrode I was the no need for preconditioning step (soaking) before calibration.

Effect of MWCNTs content

Using MWCNTs leads to the expansion of the surface of paste by fabrication of three dimensional nanostructures, as well as diminishing the Ohmic resistance of the paste. The properties of MWCNTs, including their unique dimensions and their unusual current conduction mechanism make them ideal components in electrical circuits. Using MWCNTs in the composition of the carbon paste not only improved the conductivity of the sensor, but also increased the transduction of the chemical signal to electrical signal[16].

A study similar to that of graphene was made. Results obtained from Table 1 showed that the impregnation of MWCNTs in the paste, however, decreased the linear range and this may be due to the larger specific surface area of the MWCNTs that can offer special opportunities for the capturing ions on the surface of the paste. Our study showed that increasing MWCNTs to graphite powder weight ratio enhanced the sensitivity of the electrode and led to more Nernstian response and better regression until the value of 1:9 MWCNTs/graphite powder ratio (electrode No. 19) was obtained. However, the more increase in this ratio had an opposite effect of decreasing the linear range and causing the response to be sub-Nernstian and this can be due to the decrease in binder to MWCNTs ratio that can decrease the homogeneity and extractability of the paste. As it can be seen from Table 1, electrode No. 19 has the optimum content of MWCNTs with the paste composition of 225 mg graphite powder, 25 mg MWCNTs, 10 mg DHAQ and 100 mg TCP. In comparison with electrodes I and II, as it is shown in Table 1, this sensor which can be referred to as electrode III, exhibited an improvement in the regression and the response of the electrode to a more Nernstian slope of 30.55±0.19 mV decade^{-1} than electrodes (I) and (II) over a concentration range from 1×10^{-5} to 1×10^{-1} mol L^{-1} with a limit of detection of 3.3×10^{-6} mol L^{-1}.

SEM, EDX and IR analyses

The use of a suitable modifier content and plasticizer in the electrodes composition may lead to complex formation at the sensor surface by extraction of Cu(II) ions from the solution into the paste during the measurement. This was confirmed by energy dispersive X-ray analysis (EDX) and scanning electron microscope (SEM). The proposed electrodes (I, II and III) were prepared according to their optimum compositions No. 2, 11 and 19, respectively, as shown in Table 1, then they were soaked in Cu(II) solution of concentration of 1.0×10^{-3} mol L^{-1}. This soaking resulted in complex formation between Cu(II) ions and DHAQ modifier shown as illuminated spots filling the voids between carbon particles and also resulted in a change in the morphology of the surface, as shown in Fig. 3. Moreover, it can be seen that the

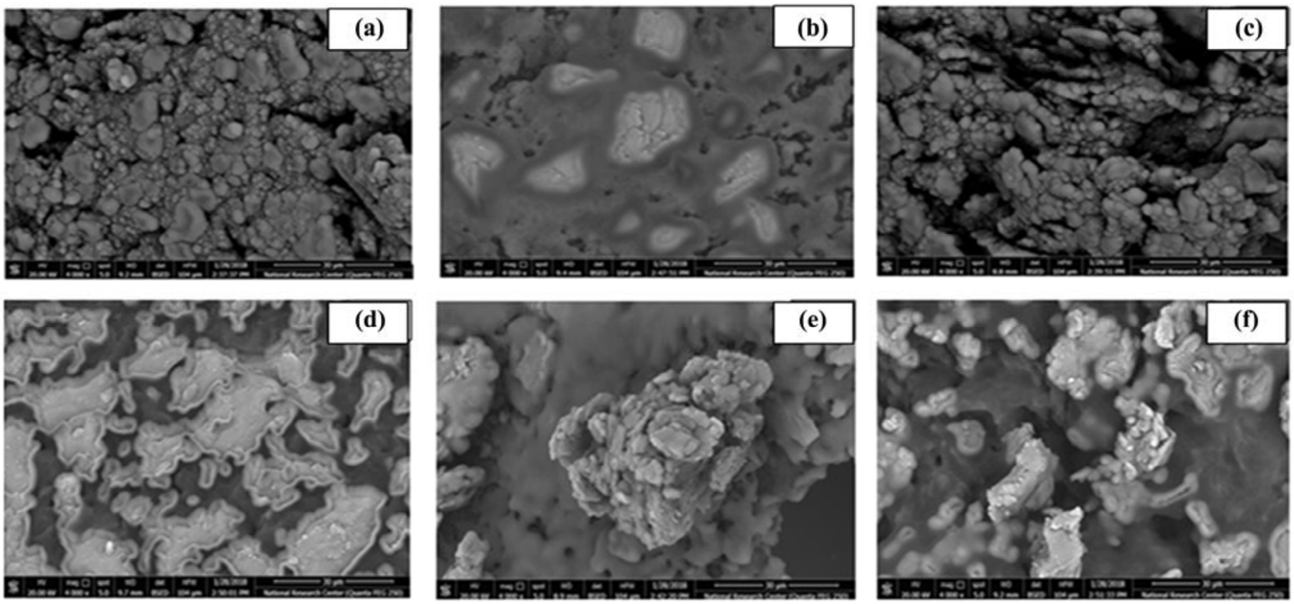

Fig. 3 — SEM image for surface of electrodes I (a) before soaking and (b) after soaking, electrode II (c) before soaking and (d) after soaking and electrode III (e) before soaking and (f) after soaking.

morphological structures of the three proposed sensors were different and the specific surface area and the homogeneity of the paste were noticeably increased from electrode I to electrode II (which contains graphene) and from electrode II to electrode III (which contains MWCNTs) and this in turn resulted in an increase in the extractability of Cu(II) ions from solution into the paste surface during the calibration time which explained the improvement in response time toward the low concentration of Cu(II) ions. This mechanism of extraction of Cu(II) ions and complex formation was supported by EDX analysis as shown in Fig. 4. IR spectra confirmed these data. It was showed that the phenolic group band at 3437 cm^{-1} disappeared and the band of carbonyl group was split and shifted to lower frequency[31,32] from 1616 to 1608 cm^{-1}and 1585 cm^{-1} which also confirmed the formation of complex between Cu(II) ion and DHAQ through coordination with the phenol and quinine oxygens (between positions 1 and 9, and between positions 8 and 9 of DHAQ).

Effect of pH of the test solution

The influence of pH on the potentiometric response of these new proposed electrodes in the pH range of 1.5–8.0 at 1.0×10^{-4} and 1.0×10^{-2} mol L^{-1} of Cu(II) ion solution was investigated and the operational range was studied by changing the pH of the test solution with dilute HNO_3 and/or NaOH. The data revealed that the potentials remain constant in the pH range of 2.4–6.5 for electrodes I, II and III, respectively. A drift in response was achieved at higher pH (pH> 7) because of simultaneous formation of hydroxy complexes or hydroxide precipitate of $Cu(OH)_2$ which diminishes the concentration of Cu(II) in solution. On the other hand, at pH< 2, the electrode response increased rather irregularly with increasing analyte acidity which can be attributed to the strong response of the ionophore to H_3O^+ ions in the solution[33].

Response time and reversibility

The average time required for the mentioned electrodes to reach a potential within ±1 mV of the final equilibrium value after successive immersion in Cu(II) ion solutions, each having a 10-fold difference in concentration, was investigated. The measurements of potential versus time were carried out at various concentrations from 1.0×10^{-6} to 1.0×10^{-1} mol L^{-1} for electrodes I and II, and from 1.0×10^{-5} to 1.0×10^{-1} mol L^{-1} for electrode III, of Cu(II) ion and typical results were presented in Fig. 5. It was pointed that, by increasing the surface area and homogeneity of the paste from electrode I to electrode II and from electrode II to electrode III, the response of the electrode to Cu(II) ions became faster. The average response times were 10 s, 6 s and 3 s for electrodes I, II and III, respectively. It was noticed that the response time increased when the concentration was lowered to 1.0×10^{-6} mol L^{-1} and 1.0×10^{-5} mol L^{-1} because of the longer equilibration time, whereas higher concentrations (≥1.0×10^{-4} mol L^{-1}) have faster response times due to fast exchange kinetics of the metal–ligand complexation–decomplexation at the paste surface[34]. The reversibility of the CPEs was evaluated by potential recording of these electrodes in the sequence high-to-low concentrations of Cu(II) ion from 1.0×10^{-1} to 1.0×10^{-6} mol L^{-1} for electrodes I and II and from 1.0×10^{-1} to 1.0×10^{-5} mol L^{-1} for electrode III. The results shown in Fig. 5 indicated that the potentiometric responses of these sensors were

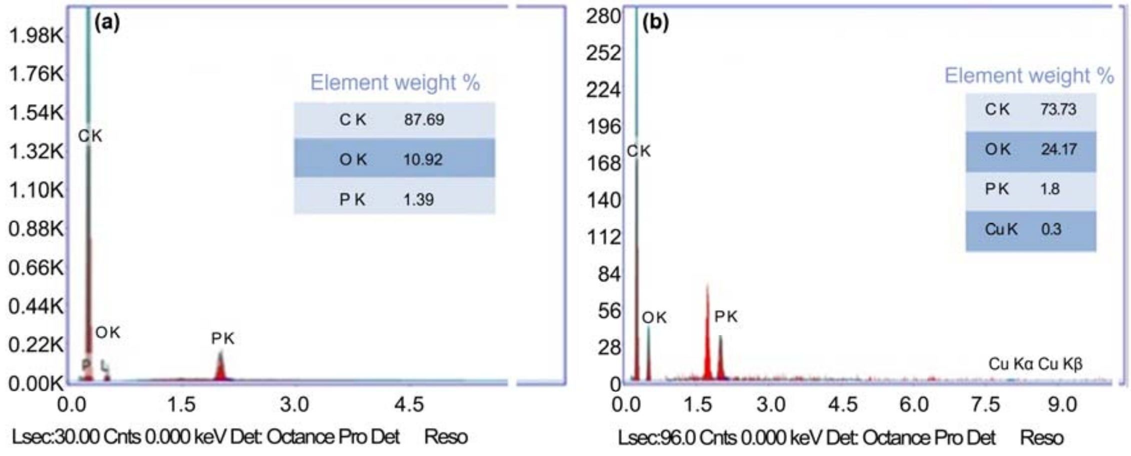

Fig. 4 — EDX analysis showing weight% of different elements present in the electrode I (with composition No. 2) (a) before soaking and (b) after soaking.

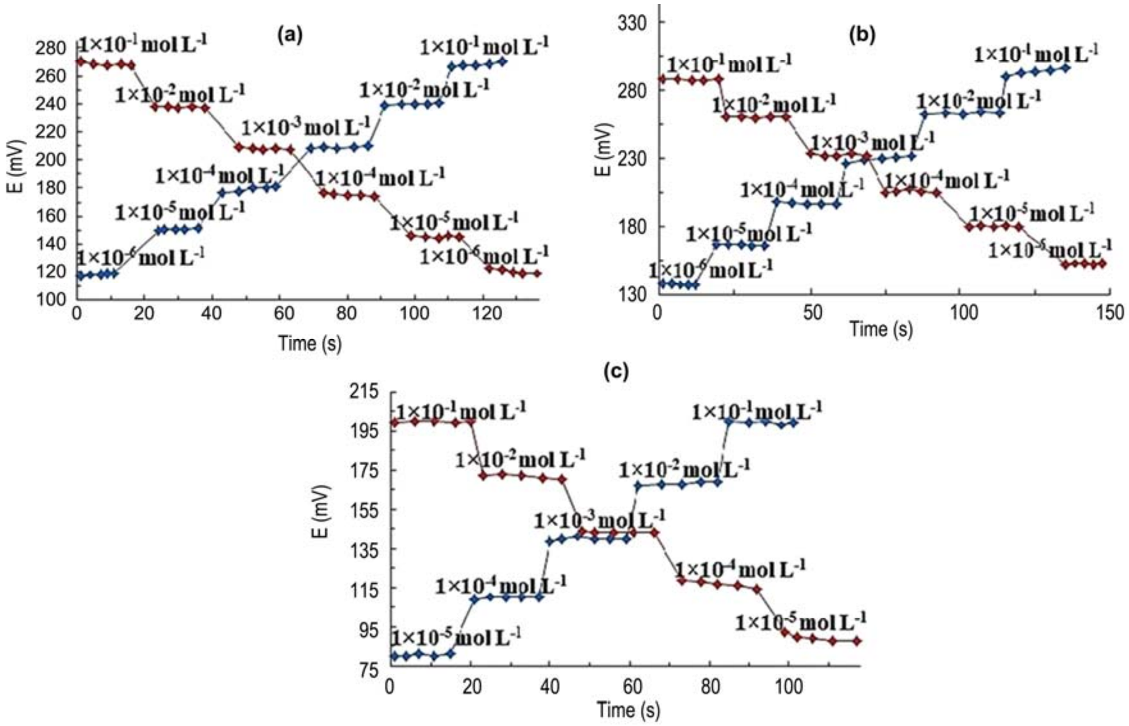

Fig. 5 — Dynamic response of proposed carbon paste electrodes; (a) electrode I: DHAQ based (b) electrode II: DHAQ and graphene based and (c) electrode III: DHAQ and MWCNTs based for step changes in Cu(II) concentration from high-to- low and low-to-high.

reversible; although the time needed to reach equilibrium values was longer (11 s, 9 s and 4 s for electrodes I, II and III, respectively) than that for low-to-high sample concentrations[26]. These observations indicated no memory effect on the electrode response was observed.

Lifetime, homogeneity and reproducibility of the proposed carbon paste electrodes

Lifetime is defined as the time span between the conditioning of the electrode and the moment of the decrease of the electrode slope of the response curve to 95% of the original slope[33] so, the same electrodes were prepared and they were tested on different days during which the electrodes were used extensively (1 h per day). The obtained results showed that the lifetime of the paste of electrodes I, II and III, with paste compositions No. 2, 11 and 19, were 40, 37 and 30 days, respectively, after which a deviation from Nernstian slope was observed. The observed decrease of the electrodes response may be due to the decomposition of DHAQ, used as an ionophore, and the deterioration of the mechanical stability of the paste.

From the literature, CPEs suffer from the memory effect so the surface of the electrodes must be renewed by polishing it on a filter paper before calibration process and rinsed carefully in distilled water to remove memory effects[35], but the developed electrodes showed a good repeatability of the results which confirmed the reversibility of the reaction between electroactive material and copper ions in the electrode surface, especially electrode III exhibits repeatability of Nernstian slopes up to 10 consecutive calibration runs after which the slope was decreased from 30.6 (±0.16) mV decade^{-1} to 25.87 (±0.3) mV decade^{-1} at the last measurement which means that the paste will be consumed at lower rate and this can be considered as an important advantage.

To test paste homogeneity, the proposed electrodes were applied for Cu(II) measurement in a 1.0×10^{-3} mol L^{-1} Cu(II) solution. The measurement was repeated five times and after each measurement the electrode surface was renewed. The RSD % values for the found potentials were 0.99, 0.95 and 0.86 for electrodes I, II and III, respectively, which were of reasonable values.

In order to evaluate the reproducibility of those electrodes, a series of pastes (five) for each electrode with their optimum compositions (No. 2, 11 and 19) were prepared and the responses of these electrodes were tested to Cu(II) ion concentration of 1.0×10^{-3} mol L^{-1}. The results showed that the proposed electrodes (No. 2, 11 and 9) have good reproducibility with RSD % values of 2.02, 1.98 and 1.02, respectively.

Selectivity studies

The selectivity behaviour is obviously one of the most essential characteristics of an ion-selective electrode, determining the feasibility of a reliable measurement in the target sample. In this work, selectivity coefficients of the proposed electrode towards different cationic species (M^{n+}) were evaluated by using both of the separate solution method (SSM)[36,37] and the matched potential method (MPM)[38-40]. The values in Table 2 reflected good selectivity of these electrodes for reliable quantification of Cu(II) ion over a wide variety of other metal ions and the main cause of this selectivity is the incorporation of DHAQ as an ionophore that complexes with Cu(II) ions more preferably than other metal ions. A comparison between the proposed sensors concerning analytical parameters is also given in Table 3.

Analytical Applications

The proposed electrodes were applied for the determination of different spiked Cu(II) ions concentrations in various real water samples containing different concentrations of other cations (Al^{3+}, total iron, Ca^{2+}, Mg^{2+} and Mn^{2+}). The pH of each sample was adjusted by NaOH and/or HNO_3 to the desired pH (pH = 4.5). An aliquot of standard solutions was added to the sample and the Cu(II)

Table 2 — Selectivity coefficients of various interfering species calculated by SSM and MPM methods for proposed sensors I (with composition No. 2), II (with composition No. 11) and III (with composition No. 19)

Foreign ions, B	$K^{SSM}_{Cu(II), B}$			$K^{MPM}_{Cu(II), B}$		
	Electrode I	Electrode I	Electrode II	Electrode III	Electrode II	Electrode III
Zn^{2+}	1.3×10^{-4}	2.0×10^{-2}	2.9×10^{-2}	1.4×10^{-2}	4.4×10^{-5}	2.4×10^{-5}
Pb^{2+}	4.0×10^{-2}	1.3×10^{-1}	1.6×10^{-1}	1.1×10^{-1}	6.0×10^{-2}	2.3×10^{-2}
Cd^{2+}	3.3×10^{-4}	1.3×10^{-2}	2.9×10^{-2}	8.3×10^{-3}	1.3×10^{-3}	2.2×10^{-4}
Cr^{3+}	2.7×10^{-3}	2.5×10^{-2}	2.8×10^{-2}	2.3×10^{-2}	3.8×10^{-3}	2.8×10^{-4}
Ba^{2+}	3.9×10^{-4}	5.3×10^{-2}	6.2×10^{-2}	8.1×10^{-3}	6.1×10^{-4}	8.9×10^{-6}
Ca^{2+}	3.1×10^{-5}	1.4×10^{-2}	3.0×10^{-2}	9.5×10^{-3}	2.0×10^{-5}	1.8×10^{-6}
Mn^{2+}	3.2×10^{-5}	5.5×10^{-3}	6.6×10^{-3}	3.0×10^{-3}	1.9×10^{-4}	6.6×10^{-6}
Mg^{2+}	7.6×10^{-5}	1.2×10^{-2}	8.3×10^{-2}	1.1×10^{-2}	4.3×10^{-4}	8.9×10^{-6}
Co^{2+}	1.3×10^{-4}	1.4×10^{-2}	1.6×10^{-2}	1.3×10^{-2}	9.7×10^{-5}	1.1×10^{-6}
Al^{3+}	2.7×10^{-4}	2.5×10^{-2}	3.3×10^{-2}	1.9×10^{-2}	3.0×10^{-3}	1.1×10^{-4}
Ni^{2+}	9.0×10^{-4}	1.5×10^{-2}	2.0×10^{-2}	1.2×10^{-2}	1.1×10^{-5}	8.0×10^{-5}

Table 3 — Specification of proposed electrodes based on DHAQ as an ionophore

Parameter	Values/Range		
	Electrode I	Electrode II	Electrode III
Optimized carbon paste composition (w/w%)	Graphite powder: TCP: DHAQ(69.44:27.78:2.78)	Graphite powder: graphene: TCP: DHAQ(55.56: 13.89: 27.78: 2.78)	Graphite powder: MWCNTs: TCP: DHAQ(62.50: 6.94: 27.78: 2.78)
pH range	2.4–6.5	2.4–6.5	2.4–6.5
Linear range (mol L^{-1})	1×10^{-6}–1×10^{-1}	1×10^{-6}–1×10^{-1}	1×10^{-5}–1×10^{-1}
Slope (mV $decade^{-1}$) ± SD	29.78 (±0.17)	30.25 (±0.12)	30.55 (±0.19)
Regression	0.9994	0.9996	0.9998
Average response time (s)	~10 s	~6 s	~3 s
Detection limit (mol L^{-1})	8.0×10^{-7}	5.0×10^{-7}	3.3×10^{-6}
Quantification limit (mol L^{-1})	2.64×10^{-6}	1.65×10^{-6}	9.9×10^{-6}
Isothermal coefficient (V °C^{-1})	1.5753×10^{-3}	1.1445×10^{-3}	1.0968×10^{-3}
Life time of the paste (days)	40	37	30
Soaking time	10 min	No need for soaking	No need for soaking
SD (intra day)	0.0003–0.01	0.0005–0.0512	0.0003–0.011
RSD % (intra day)*	0.4–2.8	1.79–2.79	0.4–2.82
SD (inter day)	0.0003–0.025	0.0005–0.039	0.0007–0.048
RSD % (inter day)*	0.48–2.04	1.59–2.43	1.73–2.79

*Average of five replicate analyses.

concentrations were determined. The results obtained for all of the water samples were summarized in Table 4 and the recovery % for all of the applied electrodes were satisfactory, in spite of the presence of other cations, because of the high selectivity and low detection limit of the constructed Cu(II) sensors. There was a very good correspondence between spiked and experimentally obtained results. In addition, these sensors were also used successfully for determination of Cu(II) in real biological samples (urine and serum) of Wilson disease patients and the obtained data showed an agreement with those obtained by spectrophotometer and the obtained RSD% values were 0.977, 0.999 and 0.862 and recovery % values were 99.01, 100.44 and 99.45 for electrodes I, II and III, respectively. Moreover, these sensors were used successfully as indicator electrodes in the potentiometric titration of 5.0 mL of 1.0×10^{-2} mol L^{-1} Cu(II) solution, adjusted at pH = 10 using ammoniacal buffer, against standard solution of 1.0×10^{-2} mol L^{-1} EDTA. Comparison between the proposed sensors was shown in Fig. 6. The obtained data showed that the investigated sensors can be successfully applied for potentiometric titration of Cu(II) with EDTA. It is clear from Fig. 6 that the DHAQ and MWCNTs based electrode (electrode III) had the highest performance in comparison with the other two electrodes. The titration curves were sigmoid in shape and showed good inflection point at the equivalence point.

Comparative studies

Comparison of the proposed electrodes with other Cu(II) ion selective electrodes[4,10,41-44] concerning the Nernstian slope, working ranges of Cu(II) determination, detection limit, pH, response time and life time was also made as shown in Table 5. The prepared solid contact sensors showed favorable

Table 4 — Determination of copper(II) in spiked water samples and comparison of the results with those obtained by ICP-AAS

Sample No.	Taken, mg mL^{-1}	Found, mg mL^{-1}				RSD%			Recovery%				t-test*		
		Sensor I	Sensor II	Sensor III	ICP	Sensor I	Sensor II	Sensor III	Sensor I	Sensor II	Sensor III	ICP	Sensor I	Sensor II	Sensor III
1	0.025	0.0250	0.0255	0.0248	0.0251	2.80	2.43	2.82	100.00	102.00	99.20	100.40	0.32	1.49	0.96
	0.125	0.1240	0.1233	0.1230	0.1248	1.77	2.03	2.11	99.20	98.64	98.40	99.84	0.89	1.34	1.55
	0.250	0.2520	0.2494	0.2480	0.2510	1.71	1.96	1.81	100.80	99.76	99.20	100.40	0.52	0.73	1.49
2	0.025	0.0248	0.0253	0.0250	0.0249	2.02	2.37	1.20	99.20	101.20	100.00	99.60	0.45	1.49	0.76
	0.125	0.1260	0.1240	0.1247	0.1251	1.98	2.02	0.80	100.80	99.20	99.76	100.08	0.80	0.98	0.90
	0.250	0.2525	0.2530	0.2520	0.2491	1.98	1.98	1.99	101.00	101.20	100.80	99.64	1.52	1.74	1.30
3	0.025	0.0250	0.0252	0.0248	0.0246	2.80	2.78	1.21	100.00	100.96	99.20	98.40	1.28	1.92	1.49
	0.125	0.1240	0.1240	0.1250	0.1238	1.85	1.77	1.60	99.20	99.20	100.00	99.04	0.19	0.20	1.34
	0.250	0.2480	0.2510	0.2480	0.2490	1.73	1.20	0.60	99.20	100.40	99.20	99.60	0.46	1.49	1.50
4	0.025	0.0251	0.0252	0.0248	0.0244	2.79	2.80	2.02	100.40	100.80	99.20	97.60	1.96	2.20	1.79
	0.125	0.1240	0.1250	0.1252	0.1224	1.85	2.64	2.40	99.20	100.00	100.16	97.92	1.56	1.76	1.90
	0.250	0.2491	0.2480	0.2492	0.2450	1.78	1.77	1.98	99.64	99.20	99.60	98.00	1.99	1.52	1.88

*Tabulated t- values at 95% confidence level is 2.571 (n = 5).

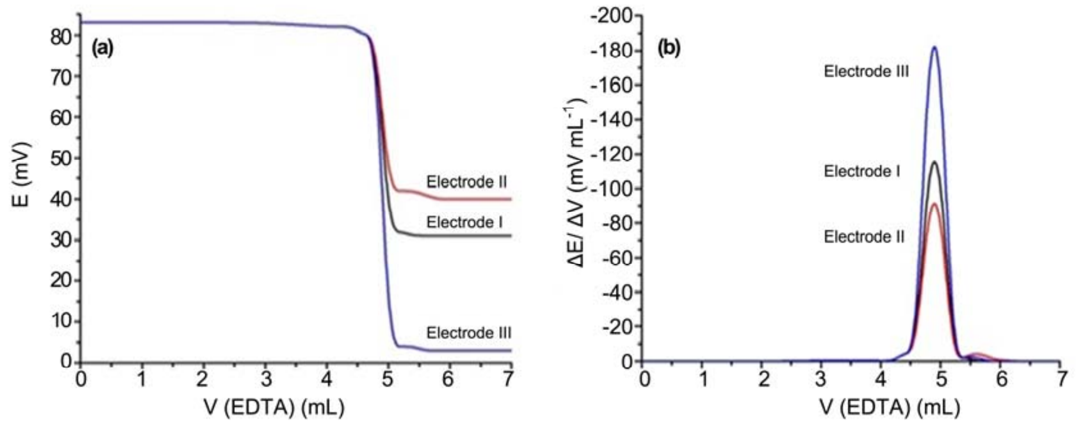

Fig. 6 — (a) First derivative and (b) S-shaped titration curves for comparison between performance characteristics of electrodes I, II and III in potentiometric titration of 5.0 mL 1.0×10^{-2} mol L^{-1} $CuSO_4.5H_2O$ solution with 1.0×10^{-2} mol L^{-1} of EDTA.

Table 5 — Comparison between the proposed electrodes and previously published methods

Ref.	Type of electrode	Modifier	Slope, mVdecade^{-1}	Detection limit, mol L^{-1}	Linear range, mol L^{-1}	pH range	Response time, s	Life time
[4]	CPEs I and II	I: MWCNT-SPAEIMP II: MWCNT-SPAEIMP+Ag-NP	I: 29.93 II: 29.11	I : 3.2×10^{-6} II: 2.5×10^{-7}	I: 5.0×10^{-6}–1.0×10^{-1} II: 5.0×10^{-7}–1.0×10^{-1}	2–5.5	<15	2 months
[10]	PVC membrane electrode	dimethyl 4, 4′ (o-phenylene) bis(3-thioallophanate)	30.30		9.8×10^{-6}–1.0×10^{-1}	3.1–7.6	20	2 months
[41]	CPE I and II SPE III and IV	*N,N′*-bis(salicylaldehyde)-*p*-phenylenediamine (SPD)	I: 29.62 II: 30.12 III: 29.91 IV: 30.70	1.0×10^{-6} 4.8×10^{-7}	1.0×10^{-6}–1.0×10^{-2} 4.8×10^{-7}–1.0×10^{-2}	I:3–6 II: 3–7 3–7	I: 13 II: 9 III: 8 IV: 6	I: 60 days II: 88 days III: 120 days IV: 145 days
[42]	Solid contact PVC membrane electrode	*o*-xylylenebis(N,N-diisobutyldithiocarbamate)	31.28	4.9×10^{-7}	1.0×10^{-6}–1.0×10^{-1}	4–6	<10	3 months
[43]	PVC membrane electrode	1-phenyl-2-(2-hydroxyphenylhydrazo) butane-1,3-dione.	28.86	6.3×10^{-7}	2.0×10^{-6}–5.0×10^{-3}	3–8	10	9 weeks
[44]	PVC membrane electrode	S,S'-bis(2-aminophenyl)ethanebis (thioate) (APhET)	29.50	4×10^{-6}	6.0×10^{-6}–5.0×10^{-2}	4–7	10	3 months
Proposed electrodes	CPEs I, II and III	DHAQ	I: 29.78 II: 30.25 III: 30.55	I: 8.0×10^{-7} II: 5.0×10^{-7} III: 3.3×10^{-6}	I and II: 1.0×10^{-6}–1.0×10^{-1} III: 1.0×10^{-5}–1.0×10^{-1}	2.4–6.5	I: 10 II: 6 III: 3	I: 40 days II: 37 days III: 30 days

SPAEIMP: 2-((3silylpropylaminoethylimino) methyl) phenol, NP: nanoparticle.

performance characteristics with short response time of 10 s, 6 s, 3 s and low detection limit of 8.0×10^{-7}, 5.0×10^{-7} and 3.3×10^{-6} mol L^{-1} for electrodes I, II and III, respectively, over wide pH range (2.4–6.5). The present electrodes were simple to construct due to the absence of internal reference solution which increases the system impedance and the electrode response time, moreover it makes the lifetime shorter as a result of leaching of the electroactive material throughout both solutions in contact with the membrane and finally due to the internal compartment, they couldn't with stand high pressure[45]. As it can be seen from Table 5, the disadvantages of the previously published methods can be due to the presence of internal solution and probability of deterioration of sensing membrane in case of PVC membrane electrodes[10,42-44] or the need for preparation of ionophore which can be time consuming and expensive[4,39,43,44]. The determination of copper in spiked water samples indicated that the constructed potentiometric sensors were capable of monitoring copper in real samples, providing a handy alternative for routine analysis without the need for preconditioning or pretreatment steps in addition to the advantages of simplicity and rapidity.

Conclusions

New Cu(II) ion carbon paste electrodes were developed by simple incorporation of 1,8-dihydroxyanthraquinone as an ionophore in carbon paste matrices. It was found that addition of nanomaterials as graphene nanoplatelets and multi-walled carbon nanotubes significantly enhances the response properties of the proposed electrodes. These sensors show an enhancement in the performance of the Cu(II) ion selective electrode in comparison to other previously reported electrodes[4,10,41-44]. These sensors were successfully applied for potentiometric determination of Cu(II) in real water samples with high agreement with data obtained from ICP method. Moreover, they were used as indicator electrodes in potentiometric titration of Cu(II) against EDTA.

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