

Selective Determination of Copper(II) Based on Cu(II)-Metal-Organic Framework in different Water Samples

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Four new modified electrodes are carbon pasted (*o*-NPOE; electrode I and DOS; electrode II); and screen-printed electrodes (*o*-NPOE; electrode III and DOS; electrode IV) based on Cu(II)-metal-organic framework ionophore were constructed for determination of copper ion (Cu(II)) over wide concentration ranges. The prepared electrodes exhibit Nernstian slope of 28.81 ± 0.31 , 29.43 ± 0.74 , 29.61 ± 0.20 and 30.04 ± 0.22 mV decade⁻¹ towards Cu(II) ion over a wide concentration range of 10^{-6} - 10^{-2} and 4.9×10^{-7} - 1.0×10^{-2} mol L⁻¹ with a detection limit of 1.0×10^{-6} and 4.9×10^{-7} mol L⁻¹ at pH range from 3.0 - 8.0, 3.0 - 8.5, 3.0 - 8.0 and 2.5 - 8.5 for electrodes I, II, III and IV, respectively. Updated electrodes exhibited a stable and repeatable potential throughout 86, 103, 195 and 205 days for electrodes I, II, III and IV, respectively. The modified electrodes showed strong selectivity for Cu(II) ion against a large variety of cations. The suggested electrodes were effectively used for the identification of Cu(II) ion in various samples of water and the produced data were well compared to the results obtained using inductively coupled plasma atomic emission spectrometry (ICP-AAS).

Keywords: Cu(II)-metal-organic frameworks; ionophore; Potentiometric; copper ions.

1. INTRODUCTION

The importance of copper is due to its relevance to both humans and the environment. In humans, copper plays an important biological role [1, 2] where it is the third most abundant trace element after iron and zinc present in the human body. It presents in at least 30 enzymes. Also, it plays a fundamental role in many metabolic processes [3-6]. It is known that copper must be present in a balanced quantity in human beings so its deficiency may lead to anemia and its accumulation in a high concentration results in Wilson's disease [7, 8]. On the other hand, copper may be a pollutant or even

toxic to the environment when present as free ion Cu(II) in a high amount. This toxic quantity results from using copper in several industries, such as electrodeposition, painting, metal processing, fertilizers, wood and pigment industries. But the most hazardous side of copper being as a water pollutant [9] where the tolerance limit for copper in drinking water is 0.005 mg L^{-1} [10]. It is therefore of great importance to track copper concentrations in different water samples, and so there was a serious need to develop a simple, reliable, and low-cost technique for copper determination. Several methods for determination of copper are now available, including; normal atomic absorption spectroscopy [11, 12], flame and cold vapor atomic absorption spectroscopy, electro-thermal atomization [13], (ICP-OES) [14], anodic stripping voltammetry [15] and gravimetric detection [16]. However the previous methods have an accurate result but it requires so many time-consuming modulation steps, specialized devices, sample pretreatment, and unique training curriculum [17]. An alternative method that comes into existence uses electrodes of modified carbon paste (MCPEs) as sensors for the quantitative determination of different species. These electrodes called Ion-selective electrodes (ISEs) [18-22].

Ion-selective electrodes (ISEs) have been studied more than three decades and are now routinely employed for direct potentiometric determination of various metal ion species in environmental samples, especially in water samples [23-27].

These (ISEs), designed to insert ionophores into solvent polymeric surfaces or carbon paste electrodes, have been used for the specific and immediate determination of many ion species in clinical, chemical, and environmental research [28]. The application of chemically modified electrodes (CMEs) in analytical chemistry had attracted considerable attention [21, 29]. A few numbers of CMEs had been demonstrated as potentiometric sensors.

Recently, several papers focusing mainly on sensors, based on carbon paste, have been published in the electrochemical analysis [18]. Although considerable attention has been paid to the preparation of MCPEs so far, the applications of these MCPEs focused mainly on the field of voltammetric determination, and only very few of these electrodes were used in potentiometry [30].

Carbon paste electrodes (CPEs) therefore continued to play a vital role in the evolution of laboratory analytical techniques or in the evaluation of new methodologies [31]. Creating new groups of compounds such as metal-organic MOFs frameworks enabled us to use this type of compounds as new potentiometric sensors for metal detection. Metal-organic structures (MOFs) have been witnessing exponential growth over the past two decades. MOFs exhibit a broad range of potentiometric applications, catalysis, gas storage and separation, luminescence and drug delivery [32] due to their unique characteristics, such as structural variability, stability, strong porosity, high specific surface area, and exceptional adsorption inclinations. The MOF-based chemical sensor is obviously a successful method among the various M/OF implementations, because MOFs which exhibit varying degrees of response to interactions between the host species and the system. Extra features of MOFs include: 1) high surface area concentrate high-level analytes enhancing detective sensitivity; 2) specific functional sites (open metal sites, Lewis acid / basic sites and tunable pore sizes) capable of achieving specific recognition with unprecedented selectivity through host-guest interactions or size exclusion.; and 3) Flexible porosity allowing the reversible absorption and release of substrates to promote regeneration and recycling. The synthetic versatility of MOFs enables the tuning of their

intrinsic electrical and optical properties, which has been suggested by theoretical predictions to be simpler [33]. Here, we have sought to summarize the sensing applications of MOFs through most current studies. Different receptive signal mechanisms are addressed in each part based on two observable changes caused by the guest molecules adsorbed inside the MOF cavity: 1) a shift in the emission spectrum or a change in the emitting color; and 2) a change in the fluorescent strength, including luminescent enhancement or quenching which is described, respectively, as "turn-on" and "turn-off" responses.

MOFs detect small molecules, cations, and anions as well as variations in pH, humidity, and temperature [34]. In recent years, (MOFs) have grown rapidly as chemical sensors. A number of studies have been reported on this subject, and attention continues to grow. The explanation is that the particular merits of M/OFs can be used to boost sensitivity and selectivity across a wide range of energy / charge transfers between different ligands and metal centers, such as from ligands to metal centers or metal centers to ligands; and from MOF skeletons to guest species. This paper intends to provide a newfangled update on recent progress in using MOFs as ionophore potentiometric sensors in ISEs on the basis of their electrochemical responses towards metal ions specifically Cu(II). MOF-based sensors function by utilizing different mechanisms, including electrochemical responses. (Cu(II)-MOFs/CPEs) and (Cu(II)-MOFs/SPEs) based on (MOFs) for copper detection in different water samples. Also, characterization of the electrodes is studied such as pH, response time, temperature, linear response range, detection limit, and selectivity to copper in the presence of other interfering ions.

2. EXPERIMENTAL

Potentiometric measurements were performed at 25 ± 1 °C using Jenway 3505 pH-meter. Silver-silver chloride double-junction reference electrode (HANNA-HI5415-Italy). Thermo-Orion, model Orion 3 stars, USA, was used to calculate pH. Before examination, all the glassware used was carefully washed with distilled water and dried in the oven prior to usage.

The reagents used were with the analytical grade as well as the deionized water used throughout the tests was twice deionized. (MOF) ionophor was processed using the recently reported procedure [35]. Carbon graphite powder (synthetic 1–2 μm , Aldrich, Germany). Sodium dioctyl sebacate (DOS), dibutyl phthalate (DBP), dioctyl phthalate (DOP), *o*-nitrophenyl octylether (*o*-NPOE) and tricresyl phosphate (TCP) were purchased from Fluka, Merck, Sigma, Fluka, and Alfa-Aesar, respectively. All chloride salts of ammonium, lithium, cadmium, thorium, cobalt, ferrous, ferric, barium, calcium, manganese, strontium and potassium, or sulfate salts of magnesium, aluminum, sodium, cerium, nickel, lead and zinc are used as interfering materials to test the selectivity of the electrodes.

The various water types used in this analysis involved tap water (New Cairo (sample 1) and Cairo University (sample 2)), formation water (Badr2, Western Desert, Badr Petroleum Company (sample3) and (Gemsa Petroleum Company (sample4)) and seawater (Alexandria in Mediterranean Sea area, (sample 5).

The Cu(II)-MOF/CPEs were fabricated by transferring 500 mg of pure graphite powder in addition to 7.5-12.5 mg of Cu(II)-MOF as ionophore and mixed well with (0.2 ml of *o*-NPOE (electrode I), TCP, DOP, DBP, or DOS (electrode II)) as a plasticizer into a mortar and stirred to be in a uniformed shape. The obtained paste was loaded into the electrode body and stored for 24 hours in distilled water before use [36-39]. A regenerated surface can be obtained by screwing the upper tip of the electrode to produce a fresh surface every time we use it. A smooth and shiny surface can be produced by polishing the regenerated surface area with filter paper.

The Cu(II)-MOF/SPEs were designed just use a handheld screen printer. A series of 12 electrodes was printed on an elastic X-ray film, which forced the prepared conductive ink to penetrate the screen stencil through the mesh. A panel made of heavy-duty polyester fabric (I 003 M Sefar Pet 1000 with 36 mesh count) was pre-tensioned to a wooden frame of 30x40 cm. A steel sheet was pre-tensioned to a steel frame that includes grooves of the same electrode dimensions for the stainless steel template [5, 38-45]. The home-made printing ink was formulated by a comprehensive blend of 450 mg binding material (*o*-NPOE (electrode III) and DOS (electrode IV)), 1.25 g polyvinyl chloride, 0.75 g of the carbon powder with mixture of acetone: cyclohexanone (1:1, v / v) as a solvent and 7.5-15 mg of Cu(II)-MOF was added after stirring for 15 min. The ink was sonicated and applied for printing of the electrodes [5, 38-45]. The Cu(II)-MOF/SPEs were stored at room temperature in a dry place.

The new electrodes were calibrated using a series of standard solutions of concentration ranges from 1×10^{-2} to 1×10^{-7} mol L⁻¹. These standard solutions transferred into 25 ml beakers, Cu(II)-MOF/CPEs and Cu(II)-MOF/SPEs electrodes in conjunction with reference electrode were immersed in this solutions starting from lower concentration 10^{-7} mol L⁻¹ to higher concentration 10^{-2} mol L⁻¹ and stirred continuously. The recorded potentials results plotted as a function of $-\log [\text{Cu(II)}]$. For subsequent determination of Cu(II) in various samples of water, the received curve is being used.

The different water samples were allowed to be filtered using filter paper then 5 ml of the filtrate was transferred into 25 ml beaker and a series of known concentrations of Cu(II) were spiked in the filtrated water samples.

3. RESULTS AND DISCUSSION

Cu(II)-metal-organic framework (Cu(II)-MOF) is used as an efficient ionophore for the building of a Cu(II)-selective Cu(II)-MOF/CPEs and Cu(II)-MOF/SPEs. Response properties of modified Cu(II)-MOF/CPEs and Cu(II)-MOF/SPEs have been studied and reported as seen in Table 1.

The Cu(II)-MOF/CPEs were found to have a linear response over a large concentration range of 1.0×10^{-6} - 1.0×10^{-2} molL⁻¹ of a copper ion with divalent cationic slopes of 28.81 ± 0.31 and 29.43 ± 0.74 mV decade⁻¹ for electrodes I and II, respectively. The Cu(II)-MOF/SPEs were found to have linear response over the concentration range of 4.9×10^{-7} - 1.0×10^{-2} mol L⁻¹ with slopes of 29.61 ± 0.20 and 30.04 ± 0.22 mV decade⁻¹ for electrodes III and IV, respectively.

Table 1. Obtained characteristics of Cu(II)-MOF/CPEs (Electrodes I, II) and Cu(II)-MOF/SPEs (Electrodes III, IV) at T = 25 °C, pH = 6..

Parameter	Cu(II)-MOF/CPEs		Cu(II)-MOF/SPEs	
	I	II	III	IV
Slope (mV decade ⁻¹)	28.81±0.31	29.43±0.7 4	29.61±0.20	30.04±0.22
Relative standard deviation (RSD%) ^a	1.21	0.94	1.05	0.72
Concentration range (mol L ⁻¹)	1.0×10 ⁻⁶ – 1.0×10 ⁻²		4.9×10 ⁻⁷ – 1.0×10 ⁻²	
Lower detection limit (mol L ⁻¹)	1.0×10 ⁻⁶		4.9×10 ⁻⁷	
Upper detection limit (mol L ⁻¹)	1.0×10 ⁻²		1.0×10 ⁻²	
Working temperature range (°C)	(10-60)		(10-60)	
Working pH range	3.0-8.0	3.0-8.5	3.0-8.0	2.5-8.5
Response time (s)	8	7	5	4
Correction coefficient, r	0.991	0.995	0.998	0.999
Life time (days)	86	103	195	205
Accuracy (%)	99.88	99.90	99.92	99.94
Precision (%)	0.97	0.98	0.98	0.99

3.1. Impact of ionophore content

The composition of the sensing part of the electrode was optimized from 7.5 to 15 mg to get the appropriate ionophore (Cu(II)-MOF) content. Firstly, four electrodes were prepared including the previous concentration ranges using the Cu(II)-MOF/CPEs and Cu(II)-MOF/SPEs. The weights of Cu(II)-MOF were differed as 7.5, 10, 12.5 and 15 mg. The potentiometric adjustment was completed for every electrode and the subsequent slope were discovered to be 22.34 ± 0.56, 27.21 ± 0.32, 29.43 ± 0.74 and 24.85 ± 0.91 mV decade⁻¹ and 25.45 ± 0.28, 27.53 ± 0.12, 30.04 ± 0.22 and 28.69 ± 0.16 mV decade⁻¹ for Cu(II)-MOF/CPEs and Cu(II)-MOF/SPEs, respectively. These outcomes demonstrate that the best slope was accomplished utilizing 12.5 mg of Cu(II)-MOF for Cu(II)-MOF/CPEs and Cu(II)-MOF/SPEs electrodes, respectively (Figure 1).

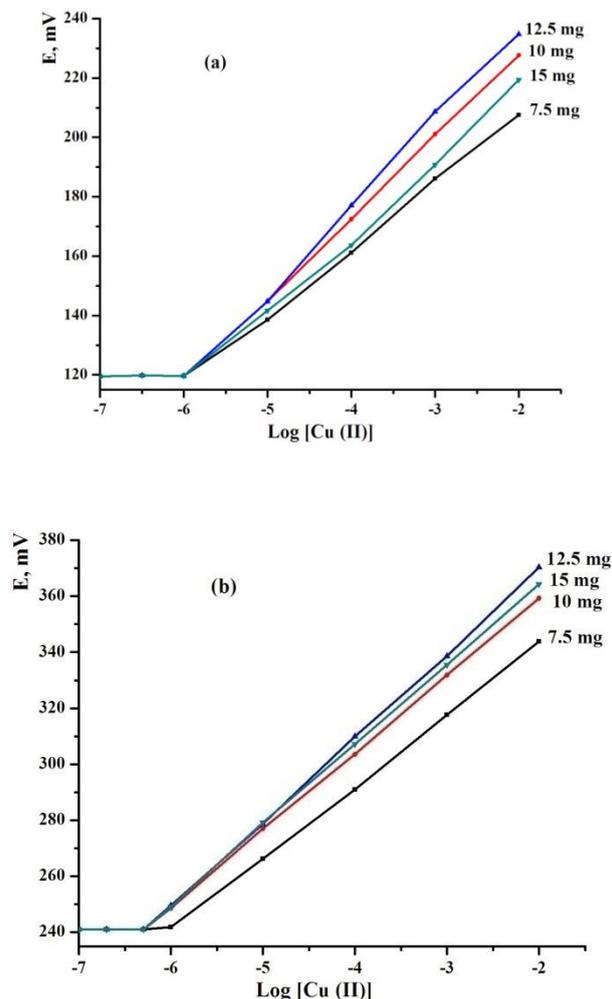


Figure 1. Influence of ionophore contents on the response of (a) Cu(II)-MOF/CPEs (electrodes I and II) and (b) Cu(II)-MOF/SPEs (electrodes III and IV) at $T = 25^{\circ}\text{C}$, $\text{pH} = 6$.

3.2. Impact of plasticizer

The quality of Cu(II)-MOF/CPEs and Cu(II)-MOF/SPEs for Cu(II) detection including Cu-MOF as ionophore was studied using five electrodes having different plasticizers DOS, *o*-NPOE, TCP, DBP and DOP. The data was graphically represented in Figure 2. Generally, it was discovered that the portability of the ionophore and its metal complex will be impacted by the lipophilicity of plasticizer likewise contributes fundamentally toward the improvement in the working concentration range, strength and time span of the sensor's usability [46, 47]. The resulting slopes were found to be 29.43 ± 0.74 , 28.81 ± 0.31 , 27.60 ± 0.08 , 25.40 ± 0.06 and 24.31 ± 0.38 mV decade^{-1} and 30.04 ± 0.22 , 29.61 ± 0.20 , 27.93 ± 0.23 , 25.69 ± 0.25 and 25.19 ± 0.37 mV decade^{-1} for Cu(II)-MOF/CPEs and Cu(II)-MOF/SPEs, respectively. The outcomes demonstrated that the best exhibition is obtained by the Cu(II)-MOF/CPEs and Cu(II)-MOF/SPEs prepared using DOS (electrodes II and IV) and *o*-NPOE (electrodes I and III).

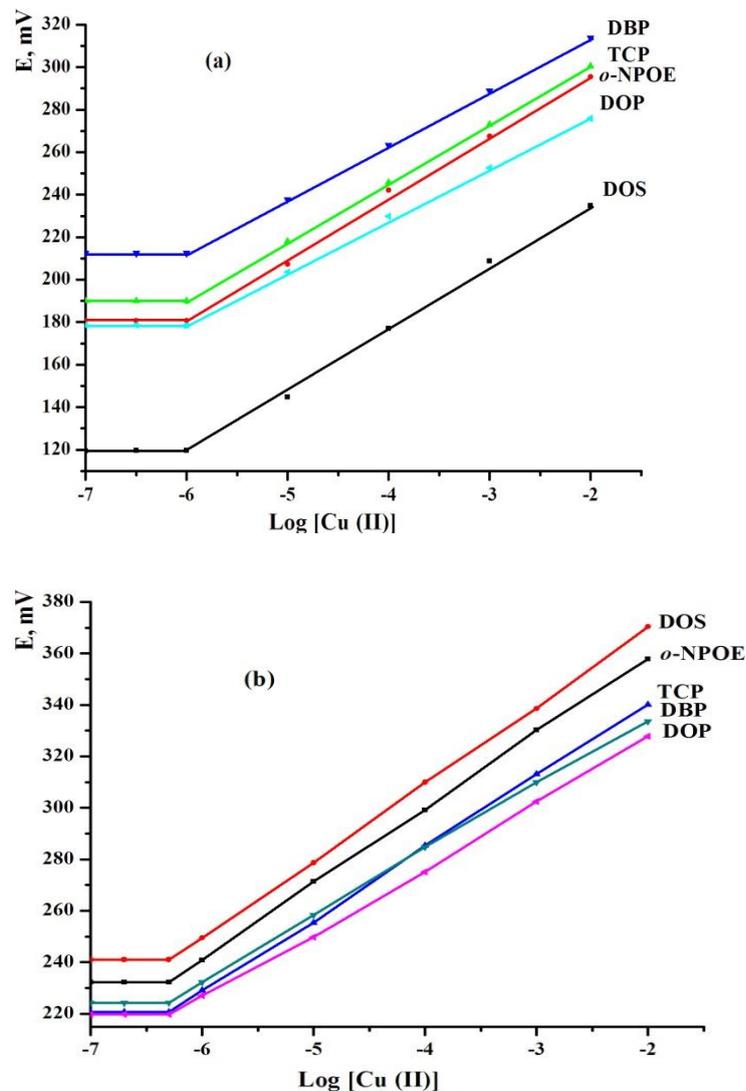


Figure 2. Impact of the type of plasticizer on the output of (a) Cu(II)-MOF/CPEs (electrodes I and II) and (b) Cu(II)-MOF/SPEs (electrodes III and IV) at $T = 25^\circ\text{C}$, $\text{pH} = 6$.

3.3. Study of response time

The time needed for the electrode to achieve a cell potential of 90% of the ultimate equilibrium values was known as the average response time. Response time has great importance for the characterization of the electrode when it used in the analytical application. The response time of the Cu(II)-MOF/CPEs (electrodes I and II) Cu(II)-MOF/SPEs (electrodes III and IV) were measured by the immersion of the Cu(II) electrodes using Cu(II) solution ranges from 1×10^{-6} to $1 \times 10^{-3} \text{ mol L}^{-1}$. The obtained results showed that in the whole concentration range the optimized electrodes reached the equilibrium response in a very short time of about 8, 7, 5 and 4 s for Cu(II)-MOF/CPEs (electrodes I and II) and Cu(II)-MOF/SPEs (electrodes III and IV), respectively (Figure 3). In general, the response time is more rapid when proceeding from diluted to concentrated solutions. Furthermore, the potential

readings remained constant for a prolonged period of time. Also, the electrode possessed a relatively short baseline recovery time once it is washed with distilled water.

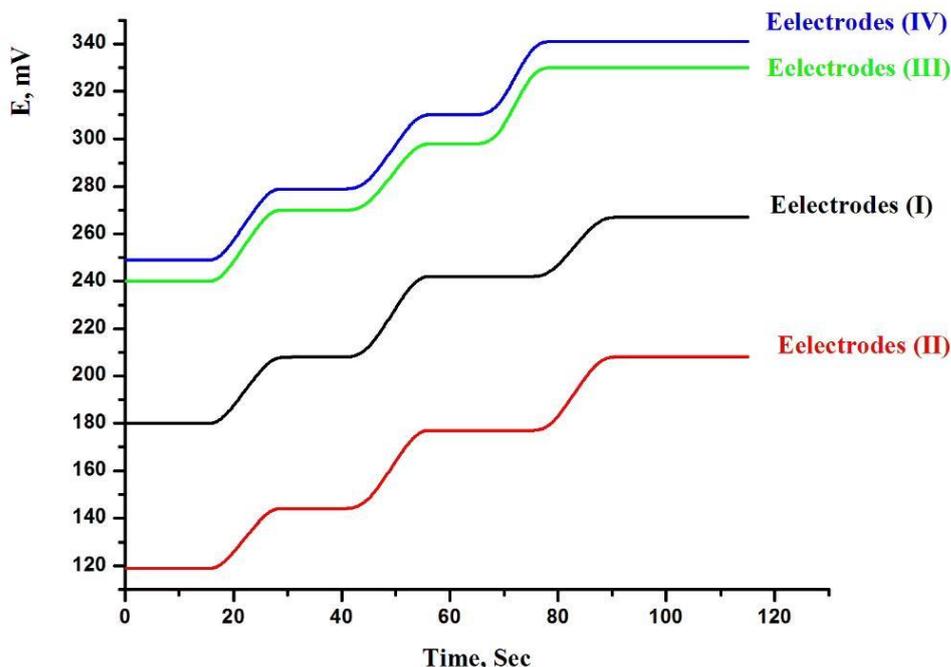


Figure 3. Dynamic response time of copper ion sensors (a) Cu(II)-MOF/CPEs (electrodes I and II) and (b) Cu(II)-MOF/SPEs (electrodes III and IV) at T = 25 °C, pH = 6.

3.4. Effect of pH

Series of pH values ranging from 1 to 10 were prepared using dilute acid (HCl) and alkali (NaOH) solutions. The past variety in pH arranged at consistent convergence of 10^{-3} and 10^{-5} mol L⁻¹ of Cu(II) solutions. At that point, the execution of both MCPE and MSPEs was measured and recorded. The came about information spoke to graphically as in Figure 4. Therefore the characteristic pH range for the modified sensors might be communicated as (3-8, 3-8.5, 3-8 and 2.5-8.5) for Cu(II)-MOF/CPEs (electrodes I and II) and Cu(II)-MOF/SPEs (electrodes III and IV), respectively. Likewise, the diagram demonstrates a sharp deviation far from the steady esteems upper and lower the ideal pH esteems. The watched float at higher pH esteems could be because of the arrangement of some hydroxyl buildings of Cu(II) particle in arrangement [41, 48-50].

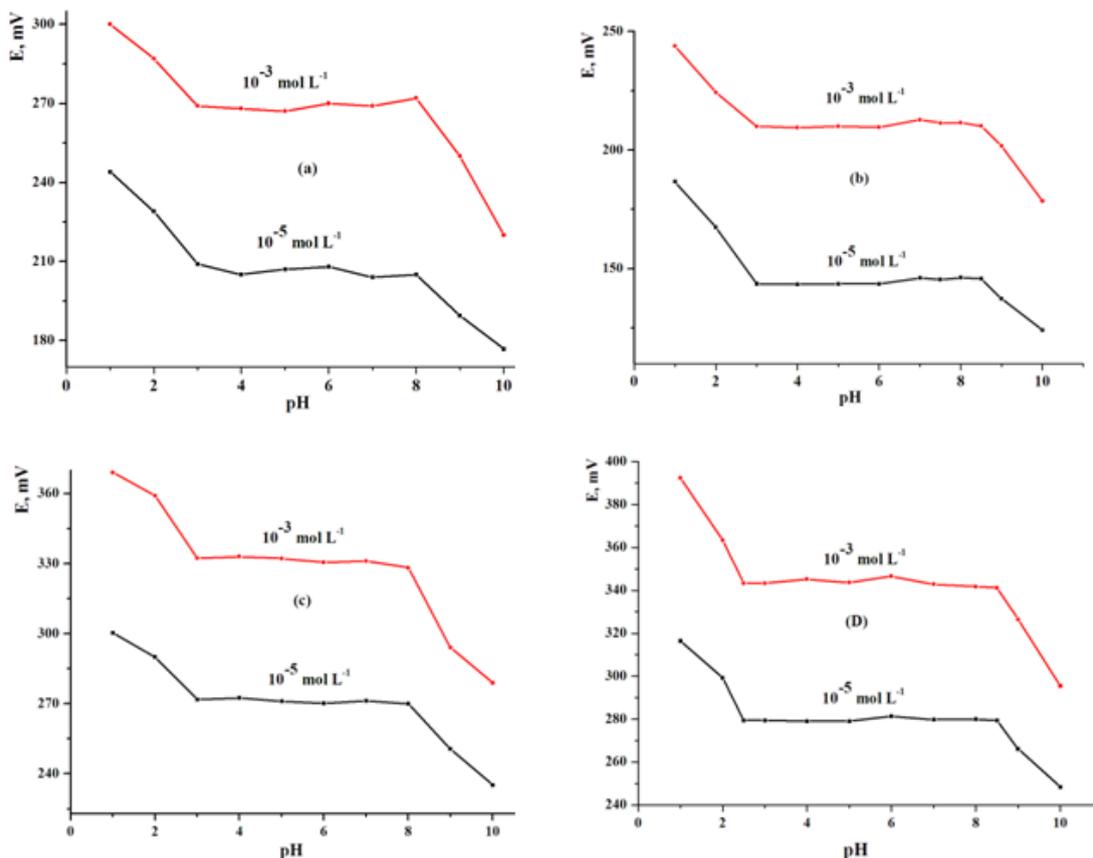


Figure 4. Impact of pH of the test solution on the sensitivity of (a) Cu(II)-MOF/CPEs (electrodes I and II) and (b) Cu(II)-MOF/SPEs (electrodes III and IV) at $T = 25 \text{ }^\circ\text{C}$.

3.5. Effect of Temperature

This impact was concentrated to decide the working temperature extend for the examined electrodes and henceforth deciding the isothermal coefficient for both Cu(II)-MOF/CPEs and Cu(II)-MOF/SPEs. To accomplish that adjustment charts of the acquired information speaking to the electrode potential (E_{elec}) versus $p[\text{Cu(II)}]$ were built at various temperatures ($10 - 60 \text{ }^\circ\text{C}$). The standard terminal potential (E°) was resolved as the captures of the past alignment diagrams at $p[\text{Cu(II)}] = 0$ and used to get the isothermal temperature coefficient (dE°/dT) when plotted against $(t-25)$ as shown in Figure 5. Where (t) was the working test temperature. Figure 5 gives a straight line according to Antropov's equation [51].

$$E = E^\circ(25) + (dE/dt)(t-25) \quad \text{Eq. (1)}$$

In this equation the standard electrode potential at $25 \text{ }^\circ\text{C}$ is symbolized as $E^\circ(25)$. The obtained straight line's slopes were taken as the coefficient of isothermal temperature and its values were 0.000398 , 0.000352 , 0.000202 and $0.000102 \text{ V/}^\circ\text{C}$ for Cu(II)-MOF/CPEs (electrodes I and II) and Cu(II)-MOF/SPEs (electrodes III and IV), respectively and this value considered fairly enough to be good thermal stability for the studied electrodes.

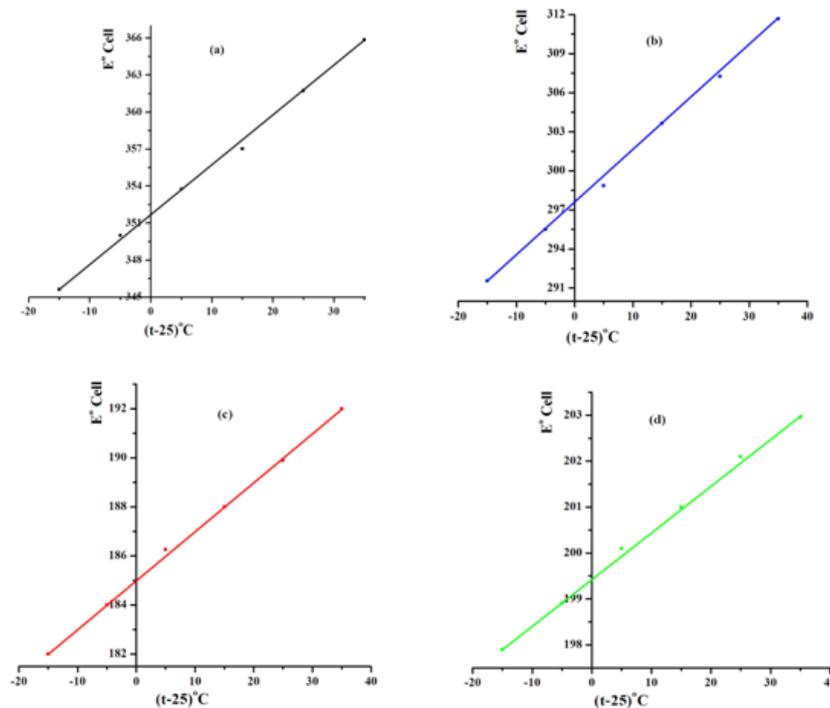


Figure 5. Influence of temperature on output of (a) Cu(II)-MOF/CPEs (electrodes I and II) and (b) Cu(II)-MOF/SPEs (electrodes III and IV) at pH = 6.

3.6. Characterization of electrode selectivity

The selectivity of the potentiometric sensors is a standout amongst the most imperative execution parameter that decides the utility of the sensor. It can be determined by calculating the selectivity coefficient $K^{\text{Pot}}_{A,B}$. It examines the relative electrode behavior of the primary ion in the existence of other ions in the solution. The selectivity coefficients $K^{\text{Pot}}_{A,B}$ were generated by taking the matched potential method (MPM) [52]. The selectivity coefficient A, B is calculated by the equation:

$$K^{\text{MPM}}_{\text{Cu},B} = \Delta A / a_B, \quad \text{Eq. (2)}$$

where, $\Delta A = a'_A - a_A$, a_A is the initial primary ion activity and a'_A the activity of A in the presence of the interfering ion, a_B . The values of (a_A) and (a'_A) for Cu(II) were taken as 1.0×10^{-4} and 5.0×10^{-4} mol/L and the proposed electrodes used are electrodes (I, II, III and IV) and their data were listed in Table (2). The low values of $K^{\text{Pot}}_{A,B}$ can also be due to the fact that an increase in the ionic strength decreases the ionic activity coefficient and thus the behavior of the primary ion (Cu(II) ion). This decrease in the behavior of the primary ion alone results in a decrease in the potential that counteracts, to some degree, the increase in the potential due to interference ions.

Table 2. Potentiometric selectivity coefficients of some interfering ions using Cu(II)-MOF/CPEs (electrodes I and II) and Cu(II)-MOF/SPEs (electrodes III and IV).

Interfering ions (B)	MPM $-\log K_{A,B}$			
	Cu(II)-MOF/CPEs		Cu(II)-MOF/SPEs	
	I	II	III	IV
Li ⁺	4.96	5.02	5.13	5.20
NH ₄ ⁺	5.04	5.08	5.11	5.21
Na ⁺	4.88	4.92	4.96	4.99
K ⁺	5.12	5.16	5.27	5.29
Zn ²⁺	4.38	4.41	4.45	4.48
Cd ²⁺	4.04	4.18	4.25	4.41
Mn ²⁺	4.09	4.14	4.26	4.28
Mg ²⁺	4.57	4.59	4.61	4.63
Co ²⁺	3.99	3.97	4.07	4.12
Ca ²⁺	3.74	3.77	3.86	3.88
Sr ²⁺	3.46	3.48	3.50	3.52
Ba ²⁺	5.06	5.07	5.18	5.18
Ni ²⁺	4.68	4.66	4.70	4.72
Pb ²⁺	4.79	4.84	4.86	4.88
Fe ²⁺	2.39	2.28	2.40	2.42
Fe ³⁺	1.99	2.01	2.06	2.08
Al ³⁺	3.87	3.88	3.90	3.93
Ce ³⁺	2.66	2.65	2.68	2.71
Th ⁴⁺	4.08	4.11	4.16	4.18
Cl ⁻	3.56	3.57	3.60	3.62
I ⁻	3.25	3.27	3.28	3.30

3.7. Life Time

The average lifetime of the developed electrodes was studied. The potential measurements were recorded every day over a period of time to determine the lifetime of the electrodes.

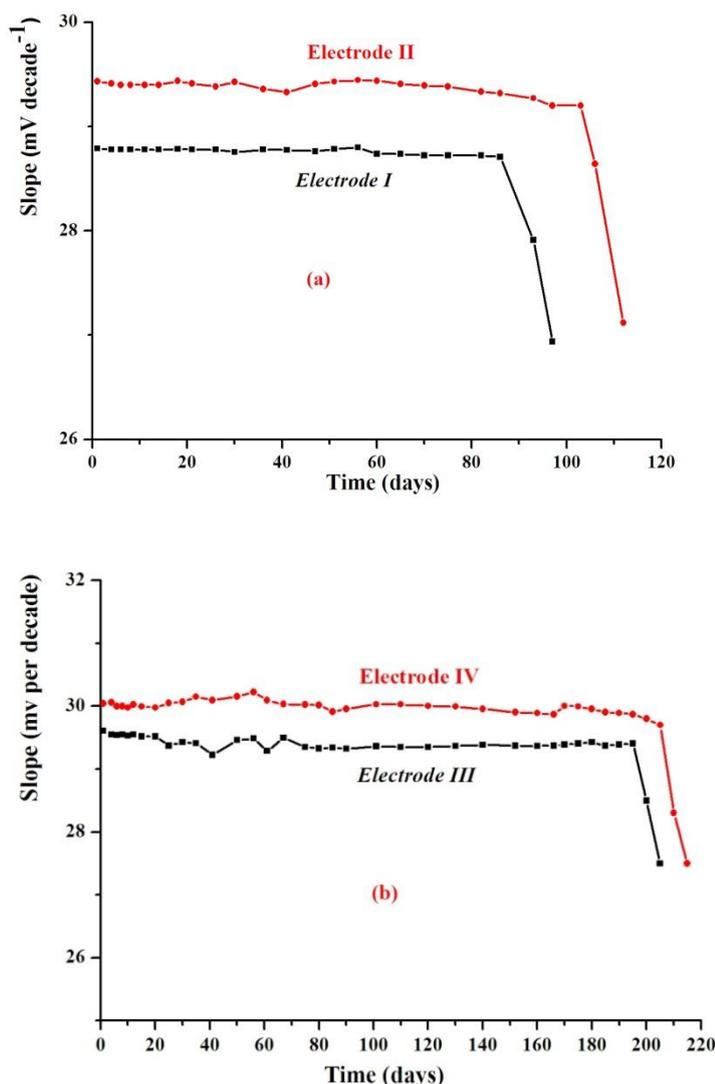


Figure 6. The lifetime of (a) MCPES Cu(II)-MOF/CPEs (electrodes I and II) and (b) Cu(II)-MOF/SPEs (electrodes III and IV) at $T = 25\text{ }^{\circ}\text{C}$, $\text{pH} = 6$.

As can be seen from Figure 6, preceding 86, 103, 195 and 205 days, no significant change in the execution of the electrode was noticed. There was a slight slow decline in the slants (28.81 ± 0.31 to 26.93 ± 1.36 and 29.43 ± 0.74 to 27.11 ± 1.29 mV decade^{-1}) for Cu(II)-MOF/CPEs (electrodes I and II) and (29.61 ± 0.20 to 28.10 ± 0.55 and 30.04 ± 0.22 to 28.99 ± 0.47 mV decade^{-1}) for Cu(II)-MOF/SPEs (electrodes III and IV), respectively. This behavior interpreted the lifetime of the proposed Cu(II) electrodes was around 86, 103, 195 and 205 days for electrodes (I, II, III and IV), respectively.

3.8. Real sample analysis and analytical performance using both Cu(II)-MOF/CPEs and Cu(II)-MOF/SPEs

The proposed sensor has also been successfully used in various water samples for direct monitoring of the Cu(II) ion. The Cu(II) ion concentration of the sample was calculated by the standard addition method using the proposed electrode. Using the proposed electrode and inductively

coupled plasma atomic emission spectrometric (ICP-AES) process, the Cu(II) ion content in various water samples. A strong agreement provides a comparison of the findings obtained in this analysis to those obtained by ICP-AES. The proposed Updated Cu(II)-MOF/CPEs and Cu(II)-MOF/SPEs electrodes tend to be a quick and easy analytical method for determining the Cu(II) ion in real samples. Data on the contents of Cu(II) in different samples determined by the sensors proposed electrodes (I, II, III and IV) as shown in Table (3).

Table 3. Potentiometric determination of Cu(II) in real spiked water samples using Cu(II)-MOF/CPEs (electrodes I and II) and Cu(II)-MOF/SPEs (electrodes III and IV).

Sample No.	[Cu(II)] mg mL ⁻¹					RSD(%)				
	ICP-AES	I	II	III	IV	ICP-AES	I	II	III	IV
1	0.489	0.491	0.493	0.495	0.498	1.041	1.001	0.997	0.993	0.863
2	0.691	0.694	0.696	0.698	0.699	0.746	0.771	0.698	0.662	0.660
3	0.990	0.994	0.995	0.997	0.998	1.221	1.198	1.121	1.023	0.994
4	0.987	0.989	0.991	0.993	0.995	1.346	1.327	1.311	1.274	1.225
5	1.486	1.489	1.485	1.491	1.493	1.577	1.468	1.442	1.373	1.361

SD values for water samples (ICP-AES = 0.375- 0.997), (I = 0.336- 0.983) (II = 0.320-0.962), (III = 0.236- 0.905) and (IV = 0.199- 0.847).

3.9. Comparative study

Table 4. Comparing some of the Cu(II)-MOF/CPEs (electrodes I and II) and Cu(II)-MOF/SPEs (electrodes III and IV) characteristics with some of the previously reported Cu(II)-ISEs.

References	Slope (mV decade ⁻¹)	Response time (s)	pH	Life time (days)	Linear range (mol L ⁻¹)	DL (mol L ⁻¹)
Proposed I	28.81	8	3.0-8.0	86	$1.0 \times 10^{-6} - 1.0 \times 10^{-2}$	1.0×10^{-6}
Proposed II	29.43	7	3.0-8.5	103	$1.0 \times 10^{-6} - 1.0 \times 10^{-2}$	1.0×10^{-6}
Proposed III	29.61	5	3.0-8.0	195	$4.9 \times 10^{-7} - 1.0 \times 10^{-2}$	4.9×10^{-7}
Proposed IV	30.04	4	2.5-8.5	205	$4.9 \times 10^{-7} - 1.0 \times 10^{-2}$	4.9×10^{-7}
[46]	29.1	20	4 – 8	120	$1 \times 10^{-5} - 1.0 \times 10^{-1}$	2.8×10^{-6}
[53]	30.00	≤20	4-5	90	$1.0 \times 10^{-5} - 1.0 \times 10^{-1}$	4.0×10^{-6}
[54]	29.40	8	2.8 - 7.9	120	$6.3 \times 10^{-6} - 1.0 \times 10^{-1}$	6.3×10^{-6}
[55]	20.0	>20	2.0 - 5.4	-	$1.0 \times 10^{-3} - 1.0 \times 10^{-1}$	3.0×10^{-4}
[56]	26.20	2–18	-	-	$1.0 \times 10^{-5} - 1.0 \times 10^{-2}$	2.5×10^{-6}
[57]	30.30	<15	4.5 – 7	< 30	$1.0 \times 10^{-6} - 1.0 \times 10^{-1}$	7.5×10^{-7}
[57]	25.90	<15	4.5 – 7	< 30	$3.1 \times 10^{-6} - 1.0 \times 10^{-2}$	2.1×10^{-6}

The characterization of the proposed Cu(II)-MOF/CPEs (electrodes I and II) and Cu(II)-MOF/SPEs (electrodes III and IV) are compared together and with that of the corresponding values of some previously reported Cu(II) ion-selective electrodes [46, 53-57]. Such comparison includes pH, linear range, slope, detection limit and response time.

It is notable that the characteristic parameters are observably improved comparing to the previously reported electrodes and the data reported in Table (4) show this comparative study.

4. CONCLUSION

Cu(II)-MOF/CPEs (electrodes I and II) and Cu(II)-MOF/SPEs (electrodes III and IV) based on the Cu(II)-MOF ionophore and plasticizer (DOS and o-NPOE) was developed. Its linear range, slope and limit of detection were $1.0 \times 10^{-6} - 1.0 \times 10^{-2}$ and $4.9 \times 10^{-7} - 1.0 \times 10^{-2}$ mol L⁻¹, 28.81 ± 0.31 , 29.43 ± 0.74 , 29.61 ± 0.20 and 30.04 ± 0.22 mV decade⁻¹, 1.0×10^{-6} and 4.9×10^{-7} mol L⁻¹ for Cu(II)-MOF/CPEs (electrodes I and II) and Cu(II)-MOF/SPEs (electrodes III and IV), respectively. The effect of pH on the potential response indicated that a larger influence of pH occurred when the pH of the solution was in the range of 3.0 – 8.0, 3.0 – 8.5, 3.0 – 8.0 and 2.5 – 8.5 for electrodes (I, II, III, IV), respectively. The proposed electrodes were successfully applied to the determination of Cu(II) ion in different water samples. The analytical method proposed proved to be a simple, rapid and accurate method.

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