



Determination of Cu^{2+} by N,N-dichromone-p-phenylenediamine modified carbon paste electrode

Datché TRAORE^{1,2}, A.S.M. ABDELAZIZ², Yapi S. BROU¹ and Albert TROKOUREY^{1*}

¹ *Laboratoire de Chimie Physique, Université Félix Houphouët Boigny (UFRSSMT),
22 BP582 Abidjan22, Côte d'Ivoire.*

² *Laboratoire d'Electrochimie et de Chimie Physique Mohammedia (FSTM),
Université Hassan II Mohammedia, B.P 150 Mohammedia, Maroc.*

*Corresponding author, E-mail: trokourey@gmail.com; Tel: +22540204798 / +22505043108

ABSTRACT

In this work, carbon paste electrode (CPE) is chemically modified with Schiff base N,N-dichromone - p-phenylenediamine (L_2) and used for the determination of copper(II) in water. The measurements are carried out using differential pulse voltammetry (DPV). The obtained results show that Cu (II) ions are chemically accumulated onto the surface of CPE/ L_2 in acidic medium at open circuit potential. Moreover, it is shown that the peak current increases linearly with the concentration of Cu (II) in the range of 0.1 to 10 nM and 0.096 nM can be obtained as detection limit with relative standard deviation of 2.1% for 10 successive determinations of 1 nM. These results suggest that CPE/ L_2 should be an excellent tool for the detection of Cu (II) ions at trace level in aqueous media.

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Keywords: Carbon paste electrode, L_2 Schiff base, copper (II) ions, differential pulse voltammetry (DPV), characterization.

INTRODUCTION

Copper is widely distributed in nature in its elemental state or in various minerals according to the environment. It is an essential element for human being and the environment. Reactivity and biological uptake of copper are strongly influenced by its free ion concentration (Jang et al., 2010; Ashrafi et al., 2012). Whole-body copper content in adult is between 50-120 mg (stern et al., 2007). Deficiency of copper can cause serious health problems (e.g., Menken's disease). Although Cu is a required element, it can be toxic at high concentration. The form taken by

the metal (ionic, complexed, precipitated) and hence its bioavailability, depends on environmental factors such as pH, redox potential, soil and sediment type, water hardness, and organic content. These factors vary in the environment thereby giving rise to possible conditions of copper deficiency or toxicity. The levels of biologically accessible copper in the natural environment are rising in localized geographic areas mainly as a result of human activities. To avoid an environmental problem, the Cu levels in environments and its biological availability should be monitoring (Rooney et al., 2006).

Moreover, the elimination of the metal in general and copper in particular, in given environment is onerous (Habibia et al., 2010).

For the determination of these trace metals, there are effective methods such as atomic absorption spectrometry (AAS) (Ghoneim, 2010), inductively coupled plasma-optical emission spectrometry (ICP-OES) (Qvarnstrom et al., 2000), graphite furnace atomic absorption (GFAAS) (Liang et al., 2003), capillary electrophoresis (Trindade et al., 2006), high performance liquid chromatography (HPLC) (Saïdat et al., 2010; Qun et al., 2003; Ramalhosa et al. 2001) and energy dispersive X-ray fluorescence (EDXRF) (Sudarshan et al., 2011). The main problems experienced with these techniques are their complexity cost of measurement, not suitable for on-site applications and much time is devoted for the analysis due to the preliminary preconcentration by chemical or physical procedures in most cases. To overcome this kind of problems, several methods including electrochemistry are used (Siswana et al., 2006). The electrochemical methods can minimize manual sample handling and exposure to potentially hazardous samples, and combines cost-effectiveness. The differential pulse voltammetry (DPV) with chemically modified electrode (CME), like other electrochemical techniques is advantageous for the detection of Cu (II): it possesses a high sensibility, does not require separation step and the limit of detection can go significantly beyond μM . Its great importance and interest are mainly due to its selectivity and ease of use (Arulmurugan et al., 2010, Sangamesh et al., 2010). Furthermore, chemically modified carbon paste electrodes (CM-CPE) have been widely investigated because of their convenient preparation by simple mixing a modifier with the paste. For instance CPE is a CME which is prepared and regenerated (Golcu et al., 2005) using graphite powder mixed with paraffin oil, nujol or silicon to renew and modify electrode

surfaces at a lower price. Modification with organic ligands can help in accumulation and possible detection of metals such as Cu (Sangamesh et al., 2010; Golcu et al., 2005; Ghiaci et al., 2009; Shabani et al., 2009).

In this work, we have fabricated a carbon paste electrode modified with L_2 (Scheme 1). The obtained modified electrode was applied for the detection of copper (II) in tap water. The substrate L_2 of this sensor used is a Schiff-base. The Schiff-base is commonly obtained by condensation of a carbonyl compound with primary amines and is regarded as privileged ligands (Wang et al., 2006) due to their capability to form complexes with different transition metals. It is shown that L_2 can act as catalysts for many different reactions (Wu et al., 2008; Mirkhani et al., 2008). Therefore, we aimed at initiating a rapid and simple method for the determination of Cu (II). The experimental conditions and analytical parameters such as preconcentration time, accumulation time, and accumulation potential were optimized and the detection limit was determined.

MATERIALS AND METHODS

Apparatus

Electrochemical experiments were carried out with an autolab PGSTAT 30 potentiostat (Ecochemie, Utrecht Netherlands) controlled by GPES 4.8 software. The three electrode system consisted of carbon paste or modified carbon paste electrode as working electrode (WE), the reference was an Ag/AgCl (3 mol/L KCl) electrode (RE) while platinum wire was used as the counter electrode (CE).

Reagents

All the reagents were of analytical reagent grade purchased from Merck (Darmstadt, Germany) unless otherwise stated and were used as received without further purification. Carbon paste was used for electrode preparation. L_2 was provided by

physical chemistry laboratory of University of Cairo Gyza, Egypt. Copper sulfate was obtained from Riedel-De Haen and the solution was prepared with distilled water obtained with water distiller SCHOTT D 82100-7 L/H (Labo & Co., France). Hydrochloric acid purchased from Sigma Aldrich was used throughout this work as supporting electrolyte. Standard copper (II) stock solution was prepared by dissolving CuSO_4 in distilled water. All experiments were carried out at room temperature ($\sim 25^\circ\text{C}$).

Preparation of electrodes

L_2 modified Carbon paste electrode CPE/ L_2 was prepared mixing thoroughly 1 g of graphite powder, 10 mg of L_2 and 0.3 mL of paraffin oil until uniformly wetted paste was obtained. The mixture was kept at room temperature ($\sim 25^\circ\text{C}$) for 24 h. The obtained paste was then inserted into the electrode cavity (2 mm deep with a diameter of 4 mm). A stainless steel wire provided the electrical contacts. The electrode surface is renewed by simple extrusion of a small amount of paste from the tip of the electrode. Before each use, the modified carbon paste electrode was rubbed with a piece of paper until a smooth surface was obtained (Mohammed et al., 2009; Sanaâ et al., 2003; Coulibaly et al., 2009). For the bare carbon paste electrode, a similar way is used without L_2 in the paste (simple mixing 1 g of graphite powder and 0.3 mL of paraffin oil). The paste was then inserted into the electrode cavity.

Copper determination

The surface of fresh electrode CPE/ L_2 was immersed in an aqueous solution containing CuSO_4 in 0.1 mol/L of HCl. The preconcentration of Cu^{2+} was carried out under open circuit conditions and stirring. After the preconcentration step, the electrode was withdrawn from the solution, rinsed with distilled water and placed in the measurement

cell containing a solution of 0.1 mol/L HCl. An initial potential of -0.6 V (vs Ag/AgCl) was applied for 30 s and then scanned from -0.1 to $+0.2\text{ V}$ using DPV technique. An anodic peak at $+0.032\text{ V}$ was observed. The parameters used were a potential step height of 10 mV, pulse amplitude of 50 mV and pulse duration of 50 ms (Sanaâ et al., 2003; Newton et al., 2005). The same procedure was used for the bare CPE.

Statistical method used

In this work, the obtained graphs are

the average calculated using
$$\bar{X} = \frac{1}{n} \sum_{i=1}^n X_i$$

(each essay is done three times), the standard deviation is obtained from

$$S = \sqrt{\frac{1}{n-1} \left(\sum_{i=1}^n (X_i - \bar{X})^2 \right)}$$
 and the relative

standard deviation is performed by

$$\text{RSD} = 100 \frac{S}{\bar{X}}$$

Limit of Detection (LoD)

LoD was evaluated by the equation: $\text{LoD} = 3S/\alpha$ where S is the standard deviation and α the analytical curve slope (Shrivastava, 2011; Refat et al., 2012).

RESULTS

The result of the characterization of the modified electrode is shown in Figures 1 and 2. The experiments were performed immersing the unmodified and modified CPE electrodes in 0.1 mol/L HCl at scan rate of 50 mV/s. The cyclic voltammograms of these different electrodes are shown in Figure 1. As exhibited, an oxidation peaks at 0.6 V and a reduction peak at 0.4 V are observed at CPE/ L_2 electrodes while at CPE bare electrode, no obvious peak is observed. Also, under 0.2 V and above 0.4 V, the current changes rapidly.

The determination of Cu^{2+} using a bare CPE and CPE/ L_2 electrodes was carried out in acidic solution (HCl, 0.1 mol/L) containing

10^{-5} mol/L of Cu^{2+} . From the DPV experiments displayed in Figure 2, an anodic peak at 0.032 V was recorded at both bare CPE and CPE/ L_2 . It can be observed that the peak at CPE is less apparent than that obtained at modified electrode CPE. This oxidation peak potential value is far different from the anodic peak obtained with CPE/ L_2 electrodes.

The optimization parameters are studied and the results are presented in Figure 3 to 7, the influence of other ions and the analytical application are displayed in Tables 2. In this investigation, the effect of different scan rates on CPE/ L_2 electrode response, in the presence of 1.10^{-6} mol/L of Cu (II) is studied varying the scan rate between 50-900 mV/s. Figure 3 shows the plot of peak current versus the square root of the scan rate. In this Figure, it is observed that the intensity of the peak current increases linearly with the increase of the square root of scan rate.

The effect of accumulation potential (P_{acc}) on the peak current of copper (II) was also investigated over the potential range of -0.1 V to -0.5 V (Figure 4). As displayed in Figure 4, at more negative accumulation potential, high peak current is obtained while a drop beyond -0.31 V is observed.

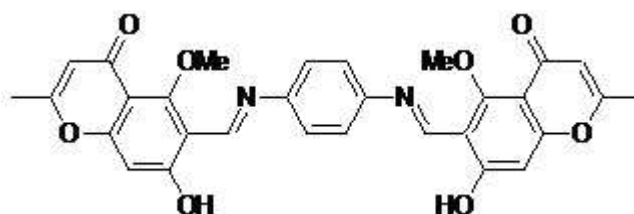
The influence of accumulation time (T_{acc}) on the copper peak current performed from 10 to 90 s is displayed in Figure 5. As shown in this Figure 5, the intensity of the peak current initially increases rapidly until 20 s and then decreases until 30 s and then becomes stable beyond.

Additionally, the preconcentration time is assessed. Figure 6 shows the effect of this preconcentration time on the peak current in 10 $\mu\text{mol/L}$ of copper (II) solution. Before ~4 min, the preconcentration time peak current increases and beyond, a significant decrease occurs.

In order to obtain a relationship between peak current and the concentration of Cu^{2+} , the DPV of different concentrations of copper were collected. The calibration plot is shown in Figure 7. It was found that the peak current was linearly proportional to the concentration of copper within the range of 0.1 nM to 10 nM.

The influence of other metal ions namely Zn^{2+} , Pb^{2+} , Fe^{2+} and Fe^{3+} , among cations which can compete with Cu at the binding sites of CPE/ L_2 surface were analyzed using the optimized conditions (preconcentration time of 180 s; accumulation potential of -0.3 V, accumulation time of 30 s, scan rate of 50 mV/s, potential height 10 mV and pulse amplitude 50 mV) for the determination of copper(II). As can be seen in Table 2, more than 80% of the peak current signal can be lost when the concentration of interference ion reaches 100-fold excess.

The applicability of the fabricated electrode CPE/ L_2 was assessed. As shown in Table 3, 89 to 125% was recovered after adding into the tap water samples, known amounts of Cu (II).



Scheme 1: Structure of L_2 (N,N- dichromone- p- phenylenediamine)

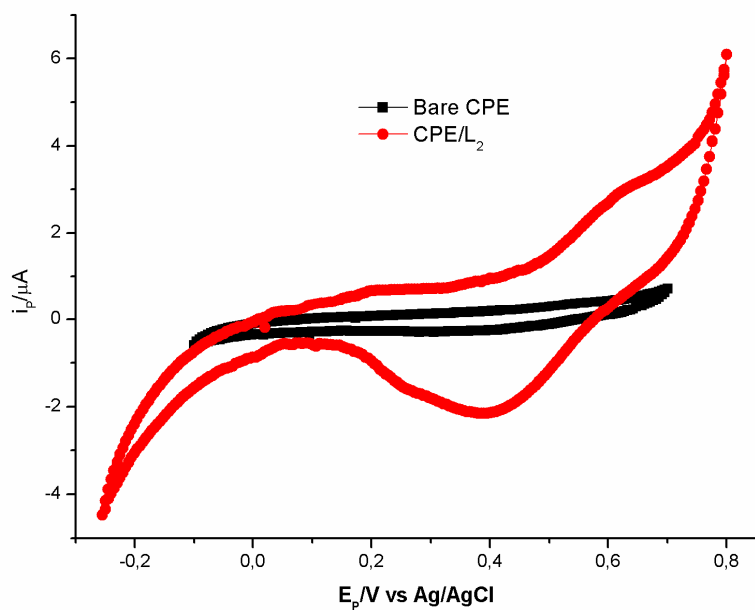


Figure 1: CV voltammograms of bare CPE and CPE modified at 50 mV/s.

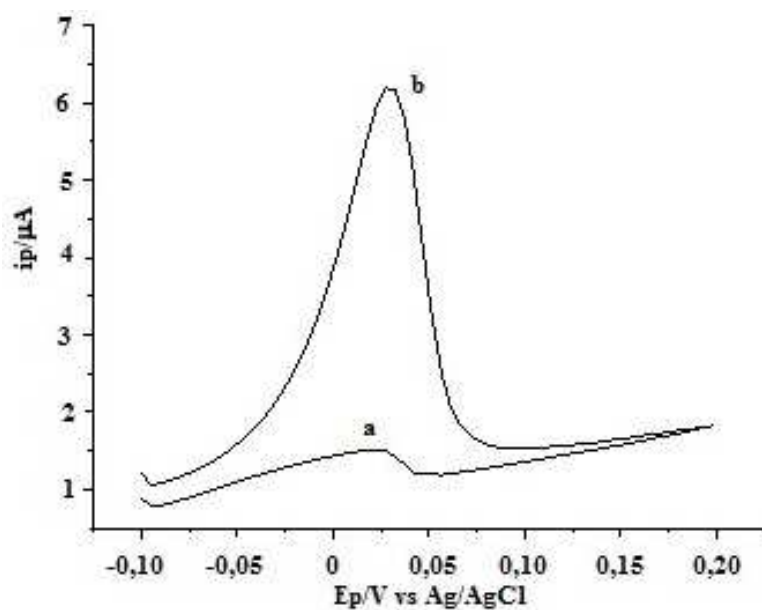


Figure 2: Difference pulse voltammograms after the deposition of 10^{-5} mol/L Cu (II) solution in 0.1 M HCl at bare CPE (a) and at modified CPE (b). conditions: accumulation potential at -0.3 V; Accumulation time 30 s, scan rate 50 mV/s, potential step height of 10 mV, pulse amplitude 50 mV.

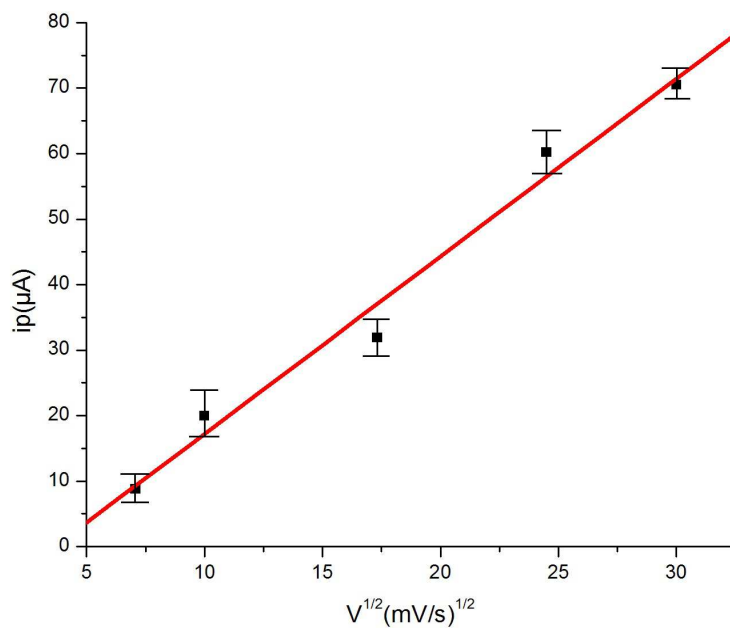


Figure 3: Relationship between peak current and square root of scan rate at CPE/L₂ electrode in a solution of Cu (II) (10^{-6} mol/L).

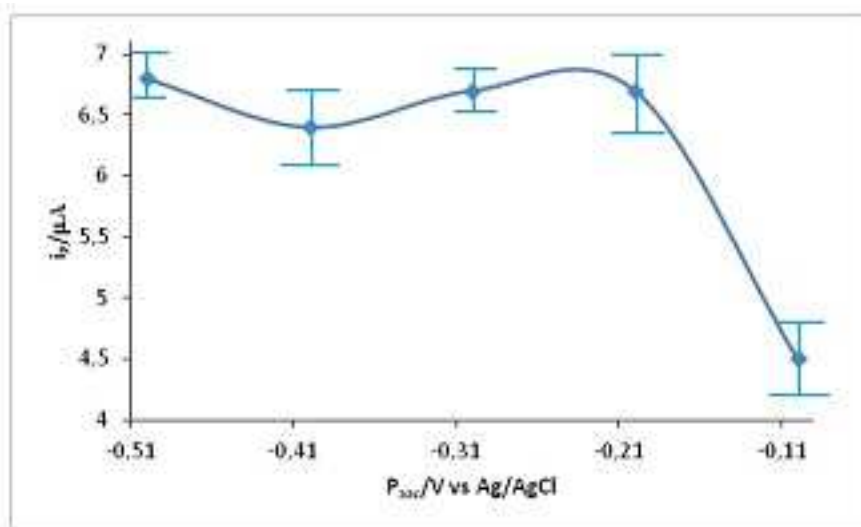


Figure 4: Effect of accumulation potential applied on the peak current of $10 \mu\text{mol/L}$ Cu (II). Accumulation potential -0.3 V, accumulation time 30 s, scan rate 50 mV/s, potential step height 10 mV, pulse amplitude 50 mV.

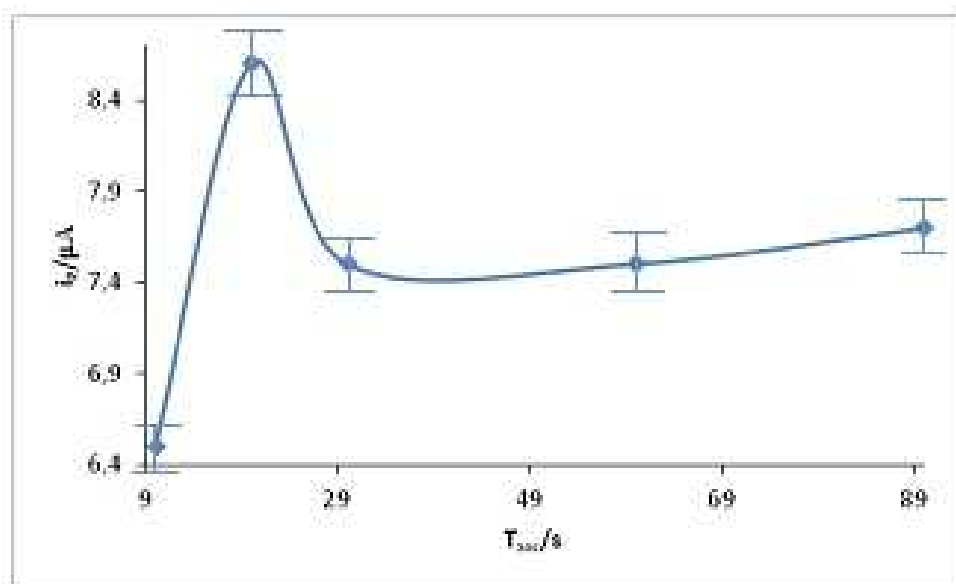


Figure 5: Effect of accumulation time on the peak current in 10 $\mu\text{mol/L}$ of copper. Accumulation potential: -0.3 V, accumulation time: 30 s, scan rate: 50 mV/s, potential step height: 10 mV, pulse amplitude: 50 mV.

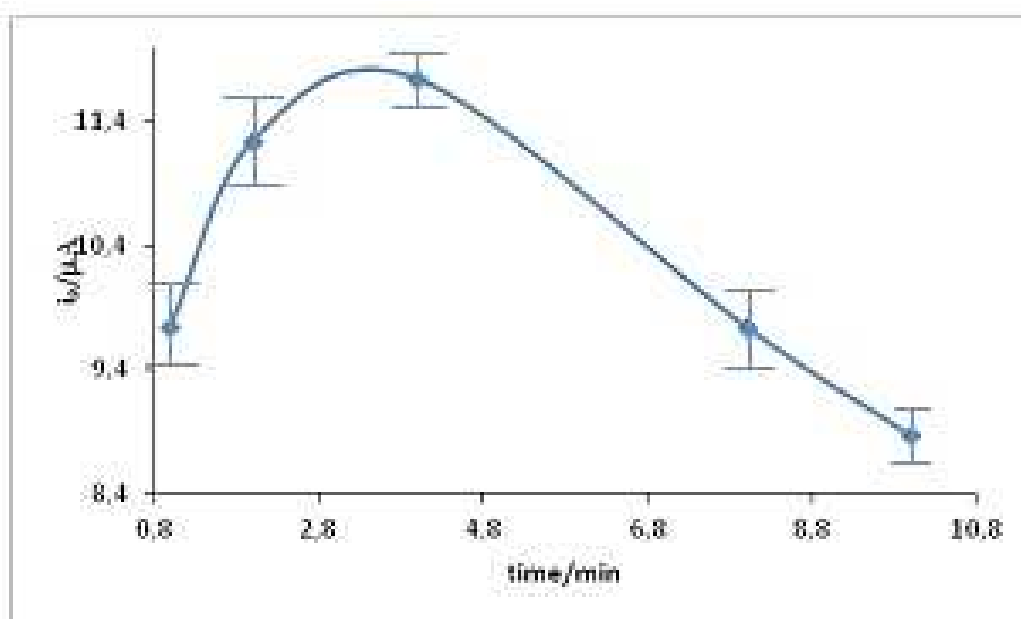


Figure 6: Effect of preconcentration time on the peak current in 10 $\mu\text{mol/L}$ of copper solution. Accumulation potential: -0.3 V, accumulation time: 30 s, scan rate: 50 mV/s, potential step height: 10 mV, pulse amplitude: 50 mV.

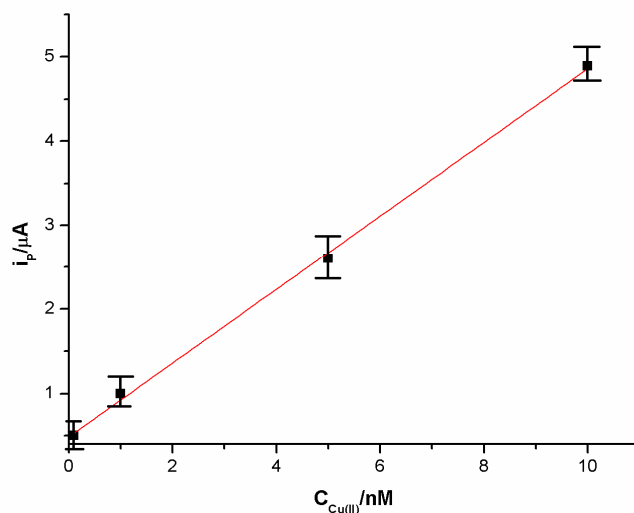


Figure 7: Calibration curve ($i_p(\mu A)/C_{Cu(II)} \text{ mol/L}$) for different concentrations (10^{-10} , 10^{-9} , 5.10^{-9} , 10^{-8} M) of Cu(II) in 0.1 mol/L HCl. $P_{acc}=-0.3$ V, $T_{acc}=20$ s, preconcentration time = 4 min, equilibrium time 10 s, potential scan: -0.25 V to 0.1 V.

Table 1: Comparison of the present work with other chemically modified electrodes as Cu^{2+} sensor

Electrode	modifier	Electrochemical method	Detection Limit (M)	Reference
Carbon paste	Salen Schiff Base	ASV ^(a)	1.8×10^{-10}	Ghiaci et al., 2009
Carbon paste	Sam of mercapto Compounds on gold	potentiometric	3.5×10^{-9}	Mashhadizadeh et al., 2008
Carbon paste	L_2	DPV ^(b)	9.6×10^{-11}	Current work

(a) Anodic Stripping Voltammetry, (b) Differential Pulse Voltammetry

Table 2: Influence of other metal ions on the determination of 10^{-8} mol/L of Cu (II).

Cation	Concentration of interferent ion ($\mu\text{mol/L}$)	Recovery (%)
Zn^{2+}	1	-41.1
Pb^{2+}	1	-26.24
Fe^{3+}	1	-16.58
Fe^{2+}	1	-46.23
Hg^{2+}	1	+28.88

Table 3: Application of CPE/L₂ for the determination of Cu (II) in tap water samples.

sample	[Cu(II)]* added (nmol/L)	[Cu(II)]* found (nmol/L)	Recovery (%)
Tap water	1	1,25	125
	5	4,93	98,6
	10	8,92	89,2

* Copper (II) concentration.

DISCUSSION

Electrochemical characterization of bare CPE and CPE/L₂ electrodes in acidic media (HCl) is showed in Figure 1. As exhibited, an oxidation peaks at 0.6 V and a reduction peak at 0.4 V are observed with CPE/L₂ electrodes while at CPE bare electrode, no obvious peak is observed. As no obvious peak is observed at bare CPE, the oxidation peaks at 0.6 V and the reduction peak at 0.4 V may be the typical oxidation and reduction peaks of the L₂. This result suggests that CPE/L₂ electrode could have a high capacitive charge. However, the rapid change in current observed may indicate that L₂ can improve the properties of the carbon paste electrode. On the other hand, the potential release at the cathode and that at the anode gas were reduced due to the electrocatalytic properties of the modified electrode. Indeed, at very negative potential, water is oxidized to form hydrogen gaseous and at very positive potential, it is reduced to form oxygen gaseous. The observed phenomena are mainly due to the good catalytic properties of the modified electrode (Ghiaci et al., 2009). To avoid the interference of L₂ peaks during the copper determination, the range from -0.1 to 0.2 V is used for the remaining experiments.

Moreover, the measurements involving Cu²⁺ using DPV technique show a high peak current at 0.032 V (Figure 2). This peak is different from those observed in the case of cyclic voltammetry performed in Figure 1 without Cu²⁺. The appearance of this peak at bare CPE and CPE/L₂ electrodes may indicate that both CPE and CPE/L₂ electrodes can be used for the detection of Cu²⁺. However, the

high peak at CPE/L₂ electrode compared with that at bare CPE suggests that the presence of L₂ may increase the catalytic properties of the CPE electrode (Fodjo et al., 2011). This interaction between Cu²⁺ and the CPE/L₂ electrode may be done through the formation of relative stable complex between copper and L₂ at the CPE/L₂ electrode. The process which occurs at CPE/L₂ electrode may be sustained by the mechanism (1-3) below as suggested in the literature (Janegitz et al., 2009; Rizea et al., 2007; Coulibaly et al., 2009).

Preconcentration step: Cu²⁺+L₂→Cu²⁺-L₂ (1)Deposition step: Cu²⁺-L₂+2e⁻→Cu⁽⁰⁾+L₂ (2)Stripping step: Cu⁽⁰⁾→Cu²⁺+2e⁻ (3)

The effect of different scan rates on CPE/L₂ electrode response, in the presence of 1.10⁻⁴ mol/L of Cu (II) is also investigated varying the scan rate between 50-900 mV/s (Figure 3). In the results assigned in this figure, it can be observed that the peak current intensity increases linearly with the increase of the square root of scan rate. This linear relationship between the peak current and the square root of the scan rate indicates that the redox process occurring at the modified electrode is controlled by diffusion (Fodjo et al., 2011). As the well defined voltammogram was obtained at a scan rate of 50 mV/s, so the scan rate 50 mV/s was used for the studies.

For further optimization of experiment conditions, the effect of accumulation potential (Pacc) on the peak current of copper (II) was studied over the potential range of -0.1V to -0.5V. As displayed in Figure 4, at more negative accumulation potential, high peak current is obtained while a drop beyond -0.31 V is observed. This high peak current

obtained insinuates that Cu (II) is more reduced when the accumulation potential is highly negative. However, it can be seen in this Figure 4 that the peak current increased up to -0.31 V and became nearly constant. This suggests a good response for Cu (II) at potential around -0.31 V. The phenomenon observed when the Paac increase negatively may be due to the saturation on the electrode surface (Janegitz et al., 2009; Dalibor et al., 2011). Therefore -0.31V was chosen throughout the experiments.

The influence of the accumulation time (Tacc) on the copper peak current was also performed in the time ranging from 10 to 90 s in order to optimize the experiments conditions (Figure 5). As shown, the intensity of the peak current initially increases rapidly until 20 s, decreases from 20 to 30 s and then becomes stable beyond. The high value obtained at 20 s indicates that the maximum accumulation time is obtained at 20 s so this value is chosen as optimal accumulation time. It should be noted that short preconcentration period yield well-defined peaks for mg.L⁻¹ level and proves also the efficiency of the electrode to concentrate the analyte. The accumulation time (Tacc) value obtained is in concordance with the literature. Moreover, the decrease in peak current observed beyond 20 s is due to a large amount of matter which could accumulate on the surface of the electrode. At long time, a break of this accumulation can arise showing a decrease in peak current (Ghiaci et al., 2009). In addition of these above parameters, the preconcentration time is also evaluated in 10 µmol/L of copper (II) solution (Figure 6). As can be seen, before 4 min, the preconcentration time peak current increases and beyond, a significant decrease occurs. This increase in peak current with preconcentration time indicates the rise of complex Cu (II) ions on the surface of the electrode while the decrease beyond may indicate the drop of the accumulation of Cu (II) on the electrode surface (Mojica et al.,

2005). As the maximum is reached after 4 min, 4 min is chosen as optimal preconcentration time for further experiments.

In order to obtain a relationship between the peak current and the concentration of Cu²⁺, the DPV of different concentrations of copper are collected. Under the selected experimental conditions: Paac = -0.3 V, Tacc = 20 s, preconcentration time 4 min, the calibration plot of the peak current versus the concentration of Cu²⁺ ranging from 0.1 to 10 nmol/L in 0.1 mol/L HCl is exhibited in Figure 7. It was observed that the peak current was linearly proportional to the concentration of copper within the range of 0.1 nM to 10 nM. The value of 0.999 is obtained as coefficient of correlation. Moreover, using Equation (4), 0.096 nM is obtained as limit of detection. Based on standard addition method, the relative standard deviation for 10 successive determinations of 1 nM is 2.1%. Compared with the literature (Table 1), these results are in the same order as those of Ghiaci (2009).

$$LoD = \frac{3S}{\alpha} \quad (4)$$

where LoD is limit of detection, S the standard deviation and α the curve slope (Figure 6).

As some ions could affect the determination of copper (II), the interference effects of Zn²⁺, Pb²⁺, Fe²⁺ and Fe³⁺ were also assessed adding 10⁻⁶ mol/L of interference ion to a solution containing 10⁻⁸ mol/L copper. The concentration was determined using the calibration plot obtained in Figure 7 and the results exhibited in Table 2 are determined using Equation (5). According to these results, 100-fold excess of the studied ions could significantly reduce the electrode response of copper determination by competing with copper ions on binding sites (Coulibaly et al., 2009).

$$I \% = \frac{I_1 - I_2}{I_1} \cdot 100 \quad (5)$$

where I_1 , I_2 are signal of copper with and without interference ion respectively.

For its application, the proposed method was applied to the determination of copper (II) in tap water preparation. The standard addition method was applied for the determinations of Cu^{2+} . In the tap water from the laboratory, were dissolved a different known amounts of copper with pH adjusted at ~1.4. The recovery of Cu (II) (Table 3) was 89.2% ~125% which seems to be interesting. This suggests that the fabricated electrode can be used in real sample.

Conclusion

In this work, it has proven that carbon paste electrode based on the Schiff base ligand modifier can be used for the detection of copper ion. The use of Schiff base ligand modified electrode for copper analysis in the concentration of 10^{-5} mol/L in tap water is evident. These results indicate that the Schiff base ligand modifier can increase the electrocatalytic properties of electrode for the detection of copper ions in particular and cations in general at trace level concentration. Besides the simplicity of preparation, it is found that this electrode is highly sensitive. These electrocatalytic properties and sensitivity suggest that this obtained electrode provide a reference for future studies on detection of heavy metals and organic materials in wastewater from food industries or in soil.

ACKNOWLEDGEMENTS

Authors would like to thank Prof. El Rhazi for allowing the achievement of this research in her laboratory.

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