



## ELECTROCHEMICAL SENSOR BASED ON THE CARBON PASTE ELECTRODE MODIFIED WITH POLYMER FOR DETERMINATION OF COPPER IONS

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### ABSTRACT

In this work, we have studied the performance of carbon past electrodes (CPE) coated with  $\epsilon$  - caprolactone polymer composites was investigated as an electrochemical sensor in the determination of  $\text{Cu}^{2+}$  ions in a 0.1M NaCl solution. The presence of the polymer on the surface of the carbon paste electrode facilitates the analyte adsorption to the surface. It was found that the highest limit of quantification is obtained from the polymer-modified carbon paste electrode (polymer-CPE). The physical parameters that could influence the electrochemical response, such as the pH of the solution, the preconcentration time and the concentration of the solution containing the analyte, were studied. Under optimal conditions, all prepared electrodes showed a good linear response to  $\text{Cu}^{2+}$  in the concentration range of 0.627 mmol/L to 4.5 mmol/L.

**KEYWORDS:**  $\epsilon$  - caprolactone; Square wave voltammetry; EIS; Copper ions.

Heavy metals are classified in the list of toxic products that threaten human life. Among these heavy metals, copper is a widely distributed pollutant in natural water and is an essential micronutrient, part of several proteins involved in a variety of biological processes, required for growth, development and homeostasis, playing a central role in the biochemistry of every living organism. Low copper status has been associated with anaemia, bone demineralization, depigmentation of the skin and the hair, poor immune response and cardiovascular effects.<sup>[1]</sup>

The World Health Organization (WHO) has established the maximum concentration of copper ion tolerable in drinking water at 30 nM.<sup>[2]</sup>

Several methods have been employed for the determination of copper ions, among which, atomic absorption spectroscopy<sup>[3]</sup>, secondary ion mass spectrometry<sup>[4]</sup>, UV-vis spectroscopy<sup>[5]</sup>, potentiometric method<sup>[6]</sup>, inductively coupled plasma optical mass spectrometry<sup>[7]</sup> and adsorption.<sup>[8]</sup> Noting that these methods are highly selective, their use is limited because of the complexity of their implementation, the time of analysis, the need for the use of reagents, which makes their cost very high. Electrochemical methods have proved to be highly sensitive, fast, simple, and automated devices<sup>[9,10]</sup> Recently, several research projects using electrochemical methods have emerged, due to the appearance of new electrode materials<sup>[11,12]</sup> In the present study, we report the preparation methods of different electrodes of type polymer-CPE. The prepared electrodes are successfully proved to be a highly sensitive and selective for copper ion detection.

## 2. EXPERIMENTAL

### Instrumentation and software

Electrochemical measurements were carried out using a voltalab potentiostat (model PGSTAT 100, Eco Chemie B.V., Utrecht, The Netherlands) driven by the general purpose electrochemical systems data processing software (voltalab Master 4 Software) connected to Pentium III computer run under Windows 98. The conventional three electrode cell was used, including a reference electrode Ag-AgCl, KCl (3M), a platinum plate as the auxiliary electrode, and a polymer coated a carbon paste used as work electrodes. The pH of the solutions was measured using a Radiometer M210 pH-meter.

### Reagent

All reagents were of analytical grade, and were used without further purification. All solutions were prepared with doubly distilled water.

### Electrodes preparation

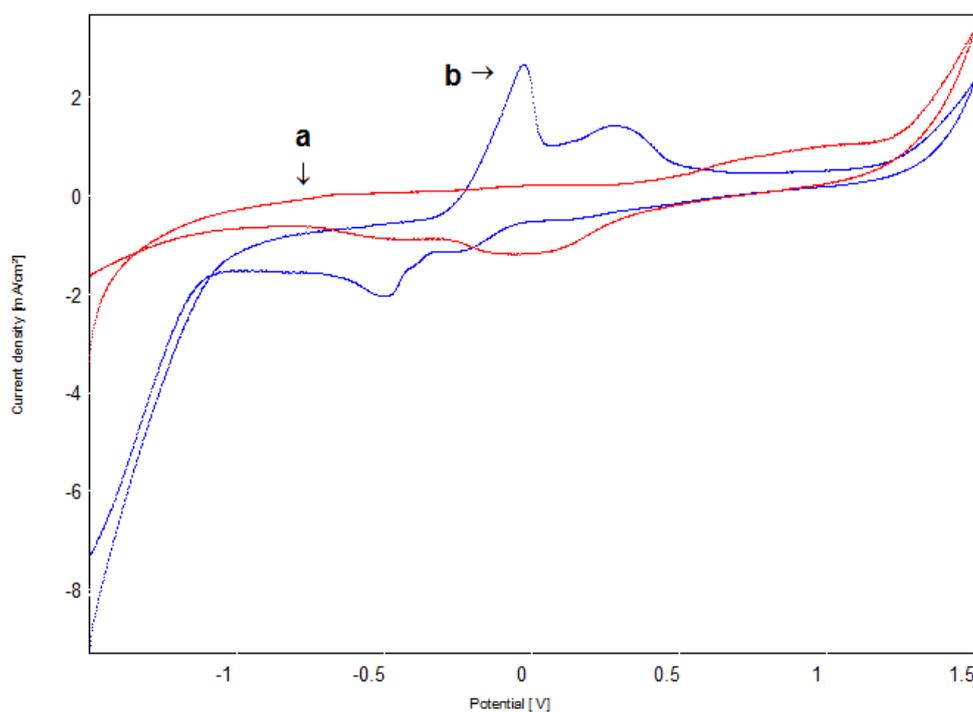
All electrodes were prepared according to the following procedure.<sup>[13]</sup> A past has been prepared by mixing the powders of graphite, with paraffin oil used as a binder and ethanol as solvent. The mixture was grinding in an agate mortar and then a portion of the resulting composite material was housed in PTFE cylinder. The geometric surface area of the working

electrode was  $0.1256\text{cm}^2$ . A bare of carbon inserted into the paste provided the electrical contact.

### 3. RESULTS AND DISCUSSION

#### 3-1- Carbon paste electrode

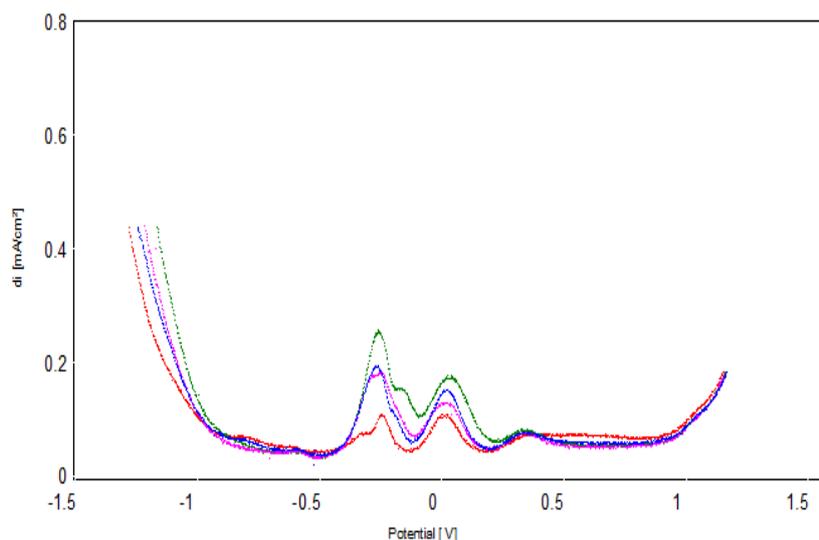
Preliminary experiments were carried out to study the behavior of the cyclic voltammograms recorded at carbon paste electrode (CPE), in electrolytic solution  $0.1\text{M NaCl}$ , in the absence (Fig. 1 curve a) and presence (Fig. 1 curve b) of  $\text{Cu}^{2+}$  ions. As shown in Fig. 2, the presence of  $\text{Cu}^{2+}$  ions in the solution is manifested by the appearance of a peak in the cathodic scanning direction at about  $-0.5\text{ V}$ , attributed to the reduction of  $\text{Cu}^{2+}$  ions, and two anodic peaks at  $0\text{ V}$  and  $0.5\text{ V}$  which could be attributed to the oxidation of copper ions.



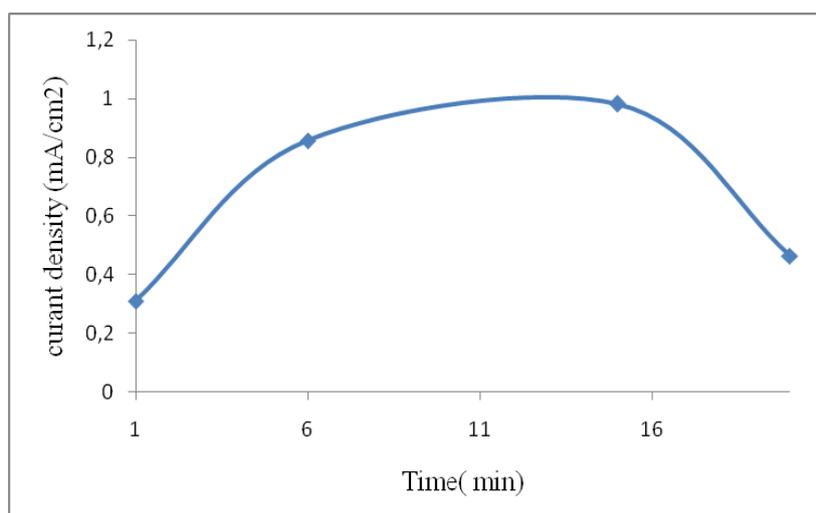
**Figure 1:** CV's recorded at, CPE, in  $0.1\text{M NaCl}$  solution, a- in absence of  $\text{Cu}^{2+}$ , b- after pre concentration in  $\text{Cu}^{2+}$  solution..

#### *Influences of accumulation time*

Fig. 2 shows the square wave voltammograms (SWV's) recorded at CPE, in  $0.1\text{ M NaCl}$  solution after accumulation in  $2.5\text{ mmol/L Cu}^{2+}$  ( $\text{pH}\sim 2$ ), for different times of pre-concentration. The peak current increases with the increasing in the preconcentration time between 0 and 11min above which it became nearly constant due to the surface saturation (Fig. 3). Hence, a 15 min preconcentration time was used in all subsequent experiments.



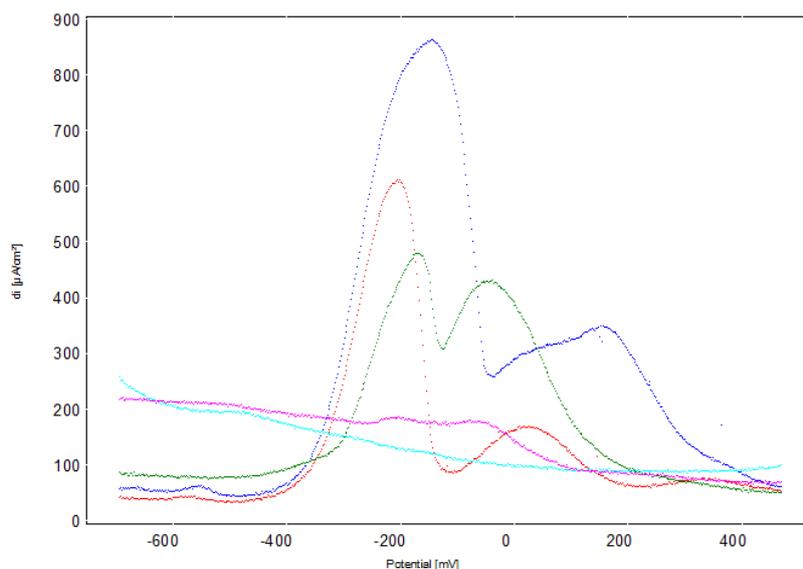
**Fig. 2:** Square wave voltammograms recorded at CPE in 0.1 M NaCl after pre concentration in Cu<sup>2+</sup> solution, at different time of accumulation.



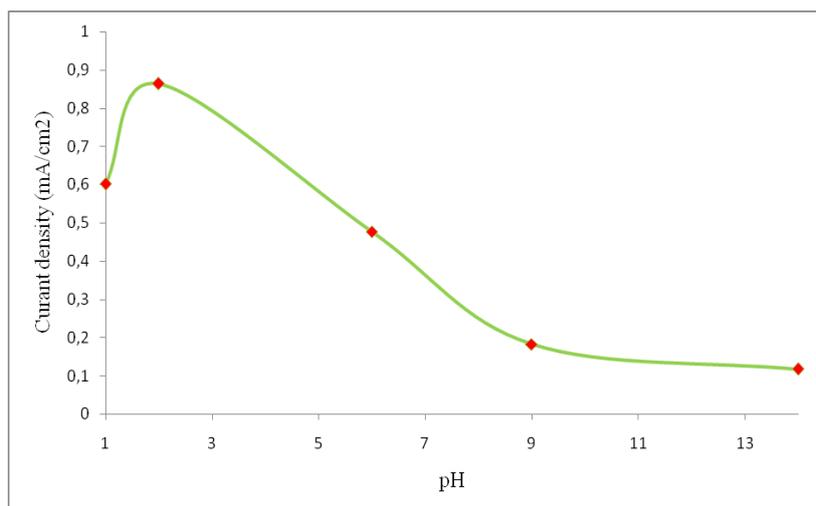
**Fig. 3:** Effect of the accumulation time on peak currents.

### *Influences of pH*

The influence of pH on the SWV peak currents of Cu<sup>2+</sup> was studied in the pH range of 1.0 to 13 (Fig. 4). The peak current density gives a maximum peak at pH ~ 2. A decrease in the current is observed when the solution pH is higher than 2.0. Thus, the optimum pH for further studies was fixed in 2.0 (Fig. 5). The decrease in peak currents at higher pH values can be explained by the fact that the accumulation of Cu<sup>2+</sup> ions on the surface of the electrode is conditioned by the presence of an excess of protons, while at basic pH the presence of hydroxide ions leads to the formation of Cu(OH)<sub>2</sub> species which limit the accumulation of Cu<sup>2+</sup> ions.



**Fig. 4:** Square wave voltammograms recorded at CPE in 0.1 M NaCl after pre concentration in  $\text{Cu}^{2+}$  solution, at different pH.

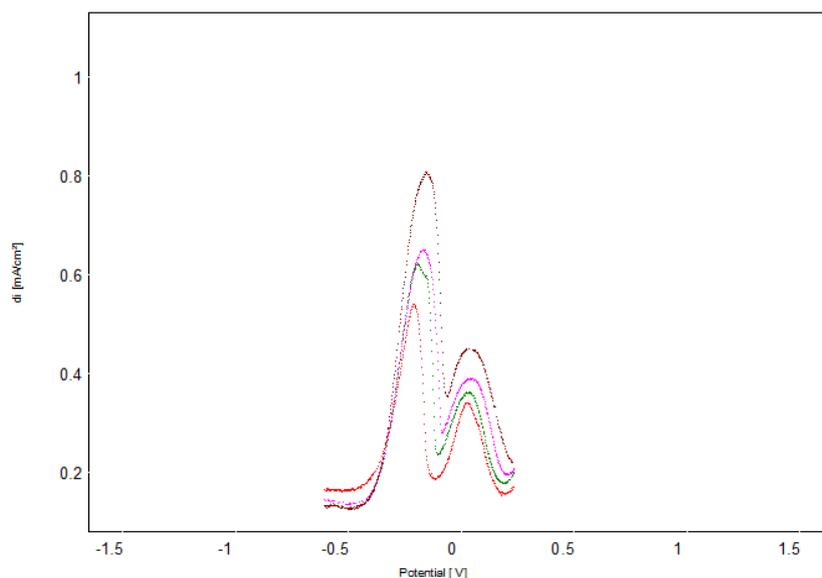


**Fig. 5:** pH dependence of the peak current on square wave voltammetric response for 2.5 mmol/L  $\text{Cu}^{2+}$  for 15 min at CPE.

### *Calibration graph*

In order to obtain an analytical curve for the developed sensor, we carried out square wave voltammograms for reduction of Cu(II) at different concentrations in 0.1M NaCl after the optimization of the experimental parameters (Fig. 6). Under optimized conditions the proposed sensor showed a typical linear response ranging from 0.6 mmol/L to 3.8 mmol/L, which can be expressed according to the following equation:

$$iP \text{ (mA)} = 0.04 \times [\text{Cu}^{2+}] \text{ (mmol/L)} + 0.3, R^2 = 0.99$$

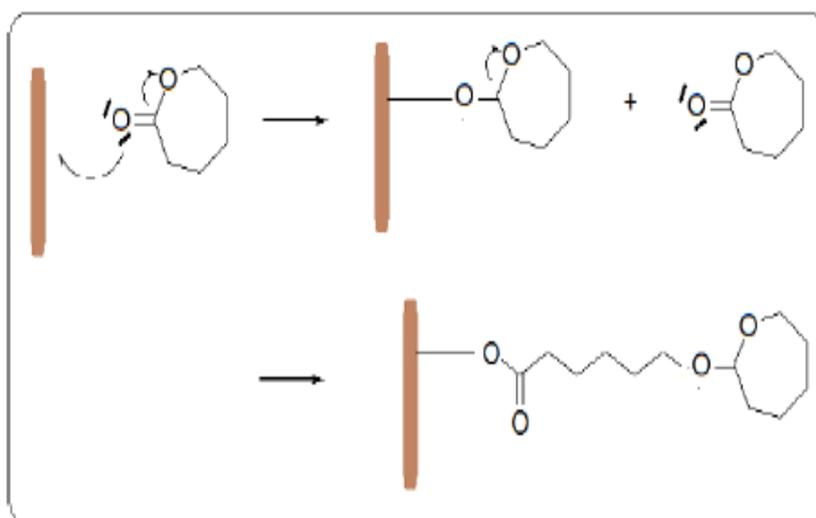


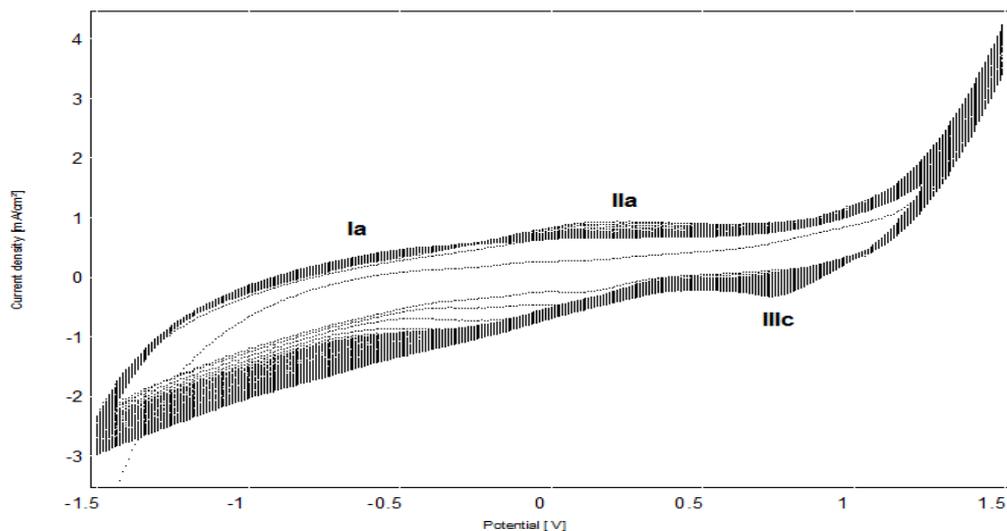
**Fig. 6:** Square wave voltammograms at CPE after pre concentration in  $\text{Cu}^{2+}$  solution at different concentrations, accumulation time: 15 min and pH: 2.

### 3-1- Polymer coated carbon paste electrode

Figure 7 shows the consecutive cyclic voltammograms (CVs) of graphite carbon electrode in 0.1 M NaCl solution containing 2 mM  $\epsilon$ -caprolactone. The CV exhibits three peaks, the first one (Ia), in the anodic scan, at about -0.5 V attributed to monomers oxidation, the second one at 0.5 V, corresponds to the evolution of the polymer, the third peak appears in the direction of cathodic scan may correspond to the polymer reduction.

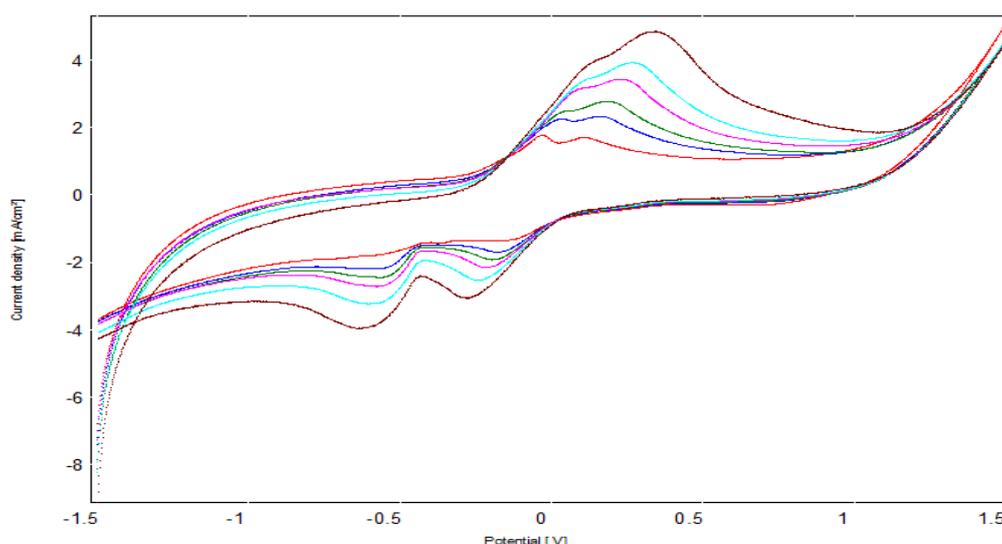
The proposed mechanism of polymerization is as follows<sup>[14]</sup>:





**Fig. 7: Cyclic voltammograms for electrochemical polymerization of 2 mmol monomer in 0.1 M NaCl, at CPE.**

The cyclic voltammograms (CVs) recorded on the polymer-CPE electrode, pre-concentrated in solutions containing different concentrations of  $\text{Cu}^{2+}$  ions, are shown in Figure 8. All CVs show four peaks each, two in the anodic scanning direction to about 0.1 V and 0.5 V, corresponding respectively, to the oxidation of copper metal followed by the release of  $\text{Cu}^{2+}$  ions in the solution, and the oxidation of copper which remains adsorbed on the electrode surface. In the cathodic direction, two peaks of reduction of  $\text{Cu}^{2+}$  ions, the first at -0.1 V and the second towards -0.5V. The peaks are symmetrical, suggesting that the reactions are reversible.

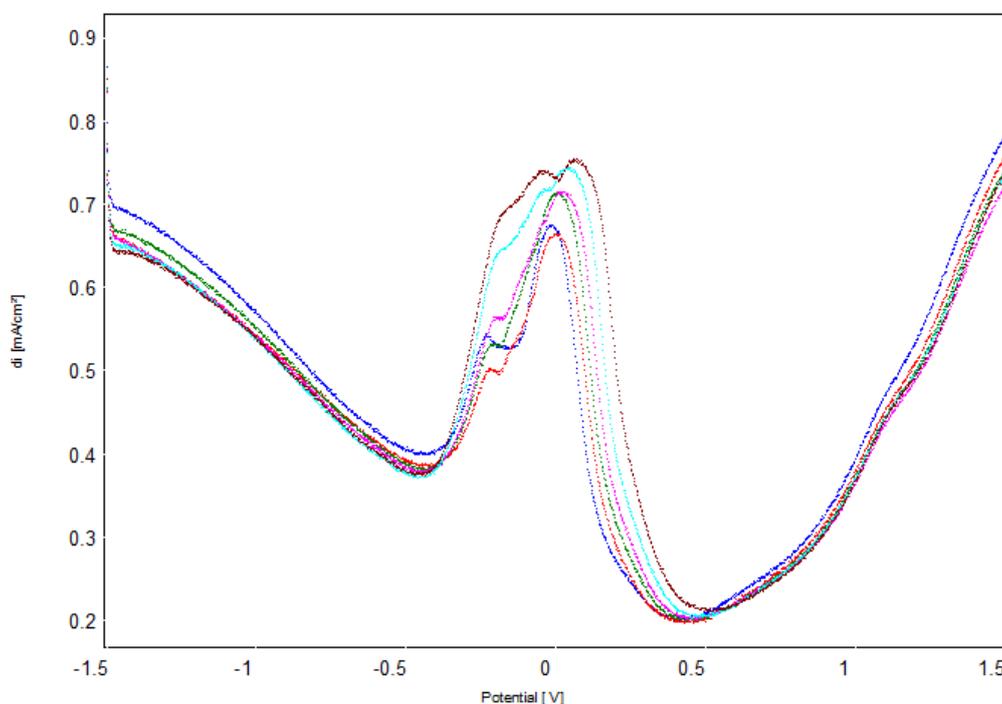


**Fig. 8: Cyclic voltammograms recorded at polymer-CPE, in 0.1 M NaCl solution after pre concentration in  $\text{Cu}^{2+}$  solutions at different concentrations.**

The square wave voltammetric determination of a series of standards solutions of  $\text{Cu}^{2+}$  was performed under the optimized working conditions. The results show that reduction peak current have a linear relationship with a concentration of  $\text{Cu}^{2+}$  in the range from 0.627 mM to 3.76 mM (Figures 9 and 10). The linear correlation coefficient is 0.941. According to Miller and Miller<sup>[15]</sup> the standard deviation of the mean current (S.D.) measured for seven voltammograms of the blank solution in pure electrolytes was calculated from:

$$SD = \frac{1}{(n-2)} \sum_{j=0}^n (i_j - I_j)^2$$

Where  $i_j$  is the experimental value of the experiment number  $j$  and  $I_j$  is the corresponding recalculated value, at the same concentration using the regression line equation.

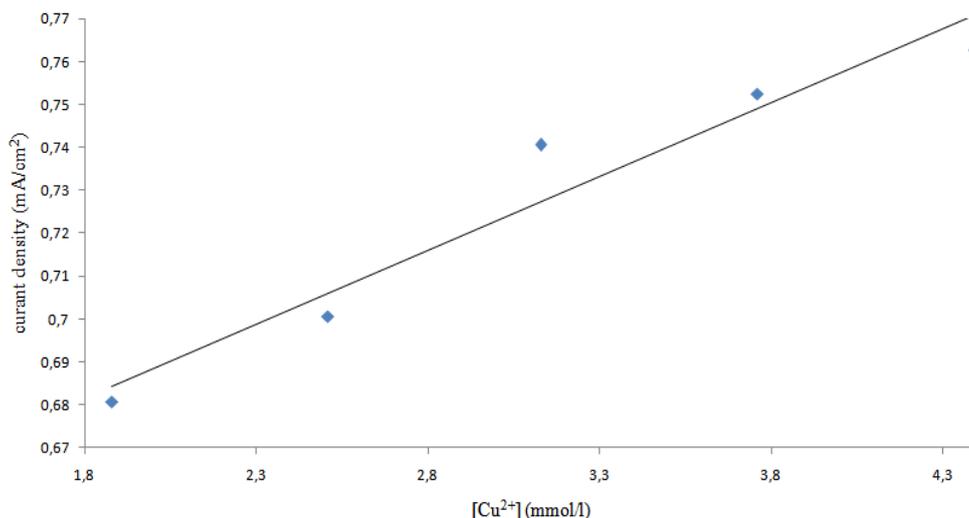


**Fig. 9: Square wave voltammograms recorded at CPE after pre concentration in  $\text{Cu}^{2+}$  solution at different concentrations, accumulation time: 15 min and pH: 2.**

The calculated S.D. was used in the determination of the detection limit (DL,  $3 \times \text{S.D.}/\text{slope}$ ) and the quantification limit (QL,  $10 \times \text{S.D.}/\text{slope}$ ). From these values, the detection and quantification limits were  $2.77 \cdot 10^{-5}$  and  $8.33 \cdot 10^{-3}$  mmol/L.

The linear regression analysis gave:

$$I_p = 0.034 [\text{Cu}^{2+}] + 0.619$$



**Fig. 10: Calibration curve deduced from square wave voltammetry measurements.**

The morphological study of the various electrodes elaborated was investigated by optical microscopy. As shown in Fig. 11, the polymer developed on the CPE surface forms a continuous film over the entire surface and shows a more or less transparent appearance. After analysis of  $\text{Cu}^{2+}$  ions, the morphology of the surface changes, due to  $\text{Cu}^{2+}$  ions remaining adsorbed on the electrode.



**Fig. 11: Optical microscopy.**

## CONCLUSION

In this study, we proposed an electrochemical sensor for the determination of  $\text{Cu}^{2+}$  based on a polymer modified carbon paste electrode. Polymer-CPE exhibits higher activity towards  $\text{Cu}(\text{II})$ . The presence of the polymer on the carbon paste electrode surface makes it possible to facilitate the adsorption of the  $\text{Cu}^{2+}$  ions, which leads to an improvement in the sensitivity of the electrode. The main purpose of covering the electrode with a polymer was to protect its surface against dissolution.

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