

## Electroanalytical Determination of Iron and Copper with Organic Film Modified Natural Phosphate Paste Electrode

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### Abstract

We report a sensitive electrochemical voltammetric method for analysing Iron (II) and copper (II) using an organic molecule (2-Chloroquinoline-3-Carbaldehyde), noted later (MO), as modifier of Natural Phosphate paste Electrode (MO-NPE). The analytical performance of the MO-CPE sensor that is designed for the detection of metals was studied. Organic compound plays an important role in the complexation of metal ions because of their good and high response to these ions. The modified electrode MO-CPE was used for the voltammetric determination, respectively, of iron and copper ions (square wave voltammetry). Na<sub>2</sub>SO<sub>4</sub> solution 0.1 mol/l was used as the support electrolyte. Using optimal parameters, calibration graph is linear for 5 min of pre-concentration time with the correct detection limit about  $1 \times 10^{-8}$  mol/L. These results indicate that the developed method is simple, with high stability and sensitivity for the determination of low concentration of Fe (II) and Cu (II).

**Keywords:** Modified electrode; Natural phosphate; Cyclic voltammetry; Square wave voltammetry

### Introduction

The pollution of sites and soils by heavy metals represents a significant risk for the environment, mainly due to their harmfulness, as well as to health because of the various pathologies that these elements may cause. Exposure to heavy metals takes two forms: inhalation of particles, and ingestion, direct (of dust) or through contaminated food. A protected environment free from toxic threats, water and healthy food are issues of growing importance in our society. To meet these legitimate requirements, complex scientific research is implemented and their efficiencies are intimately linked to the quality of the analytical tools available to them. It is known that iron and copper are metals of biological importance, involved in many phenomena of transport of oxygen in the blood and electron transfer. In general strongly complexed with transport or storage proteins such as transferrin, ferritin, hemosiderin and enzymes such as cytochromes, peroxidases, superoxide dismutase, catalases, they could exist in "free" form weakly complexed in the state traces and then participate in "oxidative stress" by producing toxic oxygen radicals. In recent years electrochemical sensors has been widely applied High sensitivity, rapidity of response, simplicity, low cost, miniaturized and automated devices. Carbon paste electrodes chemically modified are endowed with many good qualities, such as ease of handling and applicability to anodic oxidations. Different modifiers for carbon paste have been reported in the last years for electrochemical stripping analysis of heavy metals [1].

Several analytical methods are usually accomplished by means of Atomic Adsorption Spectrometry (AAS), Atomic Emission Spectrometry (AES) and Mass Spectrometry (MS). However, these techniques have some disadvantages, such as complicated operation, high cost of maintenance, expensive apparatus, and require well-controlled experimental conditions. Electroanalytical methods and sensors employing these methods provide excellent, efficient and

sensitive ways to determination of heavy metals in a variety of matrices. In doing so, clay, zeolite and silica-modified electrodes were prepared, characterized and applied (sometimes tentatively) in various fields including for example electroanalysis and sensors, electrocatalysis, photochemistry, thin-film technology, fuel cells, molecular recognition. Accumulation of the target metals from solution onto/into the working electrode of an electrochemical cell and subsequent stripping of the deposited metals offer some of the most sensitive strategies for the determination of very low concentrations of metals. Various electroanalytical techniques have been also applied to the determination of cadmium and copper. Highly Boron-Doped Diamond (BDD) films were used for simultaneous electrochemical measurement of micromolar-level concentrations of Pb and Cd, and for the examination of their interactions. The organofunctionalized amorphous silica with 2-benzothiazolethiol was used in the preparation of carbon paste electrodes for the determination of cadmium with a good detection limit of  $1.0 \times 10^{-7}$  mol/L. Mercury is often the best electrode material for the trace analysis of metals. This is due to the fact that many metals of interest have fast electrode kinetics at mercury and form amalgams. However, the toxicity of mercury has lead to a growing interest in the search for new electrode materials (carbon, gold, and platinum), which offer a similar or better performance for various electroanalytical applications. The aspartic acid (ASP)-modified clinoptilolite electrode was used for removal of Cu(II) from aqueous solutions, the removal of Cu(II) ions increased during 300 min contact time. Many effort had been done to fabrication of amperometric biosensors for determination of heavy metals with various modified carbon graphite electrode. Naturel phosphate is most often used as a substrate for its relatively high electric conductivity but also for its morphological structure which has a sheet shape. The natural phosphate modified carbon paste electrode has been shown to be very effective to determination of Cu(II).

In our previous papers, we proposed some methods to determine Fe(II) and Cu(II) using organic compound modified natural phosphate paste electrode (MO-NPE). The aim of this work is to use this electrode in conjunction with Square Wave Voltammetry (SWV) method for the determination of iron and copper. The MO-CPE successfully exploits the favorable mechanical and electrochemical properties of natural phosphate paste electrodes.

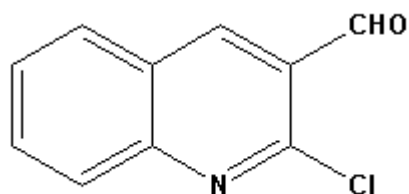
## Experimental Section

### Instrumentation and software

**Apparatus:** The electrochemical experiments were conducted by a potentiostat voltalab(model PGSTAT 100, Eco Chemie B.V., Utrecht, The Netherlands) driven by the software (Voltalab master 4 Software). All the electrochemical experiments were performed in a standard one-compartment three-electrode cell. The natural phosphate paste electrode modified by the molecule (Mo-NPE) has been used as a working electrode, the electrode Ag/AgCl as reference electrode, and platinum as counter electrode. The modified carbon paste electrode was immersed in a cell containing 20 mL of iron, at pH  $\approx$  7.5, sample to get a chemical accumulation. Meanwhile, the solution was rotated at open circuit. After a desired preconcentration time, the electrode was removed from the preconcentration cell, rinsed with double distilled water and placed in the measurement cell containing the supporting electrolyte (1.0 mol/ L Na<sub>2</sub>SO<sub>4</sub>). The solution was deaerated with nitrogen for 10 min. The square wave voltammetry and cyclic voltammetry measurements were carried out in a range of potential between -1.5 V and 1.5 V and the scan rate was 100 mVs<sup>-1</sup>. All measurements were made at room temperature.

**Reagents and solutions:** All chemicals were of the highest quality. Graphite powder (spectroscopic grade RWB, Ringsdoff-werke GmbH, Bonn-Bad Godesberg, Germany) was obtained from Aldrich and was used without further purification. The natural phosphate was extracted from natural deposit of the Moroccan city "Khouribga" and calcined at 1000°C. FeSO<sub>4</sub>, and Na<sub>2</sub>SO<sub>4</sub> were obtained from Merk Chemicals, deionized water used to prepare all solutions. The organic molecule was synthesized in our laboratory.

**Preparation of the electrochemical sensor:** The working electrode was prepared by mixing appropriate weight of organic compound (2-Chloroquinoline-3-Carbaldehyde) with a Natural Phosphate (NP) powder to give an appropriate ratio. The whole cell modified NP was subsequently packed firmly into the electrode cavity (0.1256 cm<sup>2</sup>) and polished to a smooth shiny finish by gently rubbing over an ordinary weighing paper. Electrical contact was established with a bar of carbon. The resulting electrode is hereby denoted as MO-NPE. The natural phosphate electrode (NE) alone was prepared in a similar way. The organic molecule used as modifier is presented in Figure 1.



**2-chloroquinoline-3-carbaldehyde**

**Figure 1:** Structure of the organic molecule (MO) used as modifier.

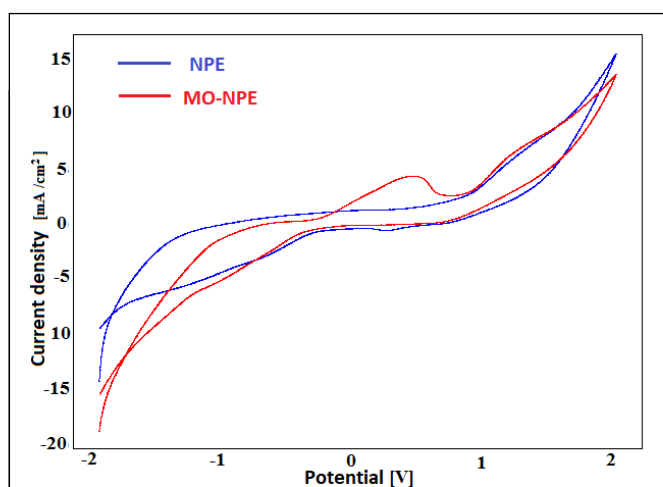
## Results and Discussion

### Modified electrodes (MO-NPE) characterization

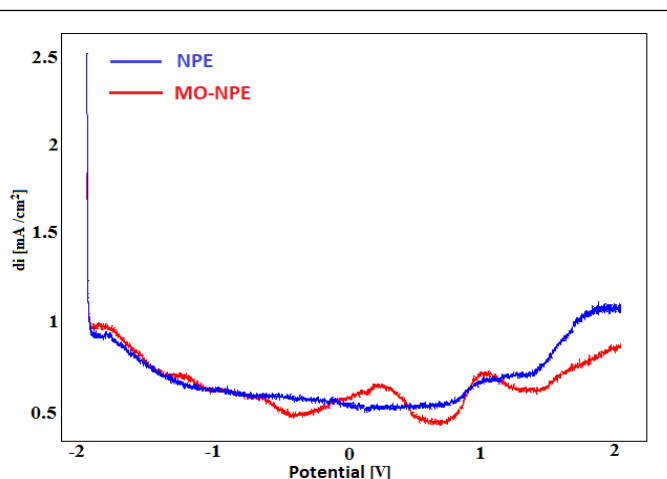
As shown in Figure 2, the cyclic voltammograms recorded respectively for NPE and MO-NPE electrodes in Na<sub>2</sub>SO<sub>4</sub> (0.1 M) solution.

The presence of the organic compound in the matrix shows two oxidation peaks, the first one at about 0.3 V and the second at 1.2 V, and a reduction peak at -1V.

The different peaks observed are sufficiently far apart, which shows that they are not the same redox systems. This result is confirmed by the square wave voltammetry (SWV) (Figure 3).



**Figure 2:** Cyclic voltammograms obtained by MO-NPE and NPE at 100 mV/s in 0.1M Na<sub>2</sub>SO<sub>4</sub> solution.



**Figure 3:** Square wave voltammograms obtained for MO-NPE modified by molecule and NPE in 0.1M Na<sub>2</sub>SO<sub>4</sub> Solution.

### Effect of organic compound (MO) loading

Figure 4 shows CVs recorded at NPE modified with organic molecule at different mass, the increase in the mass percentage of the organic molecule in the mineral matrix is reflected, in cyclic

voltammetry, by the increase of the current densities of the oxidation and reduction peaks. This increase reaches its maximum at 5.66% by mass of the molecule in the NPE, and then begins to decrease, due to the insulating nature of the developed organic film (Figures 4 and 5).

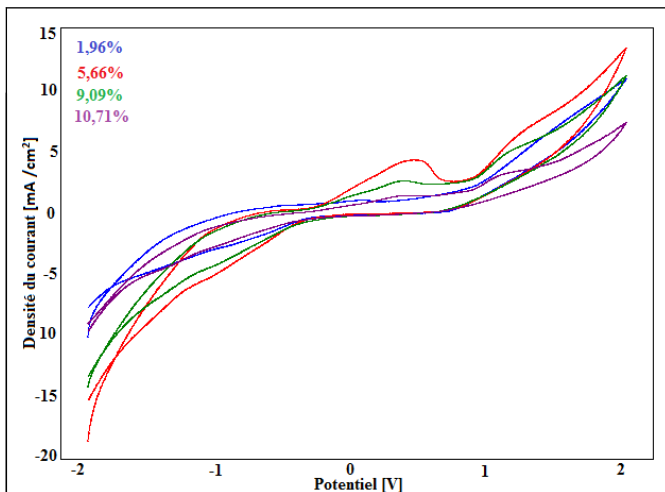


Figure 4: Cyclic voltammograms obtained by NPEs at 100 mV/s for different % of the mass of molecule in 0.1M Na<sub>2</sub>SO<sub>4</sub> solution.

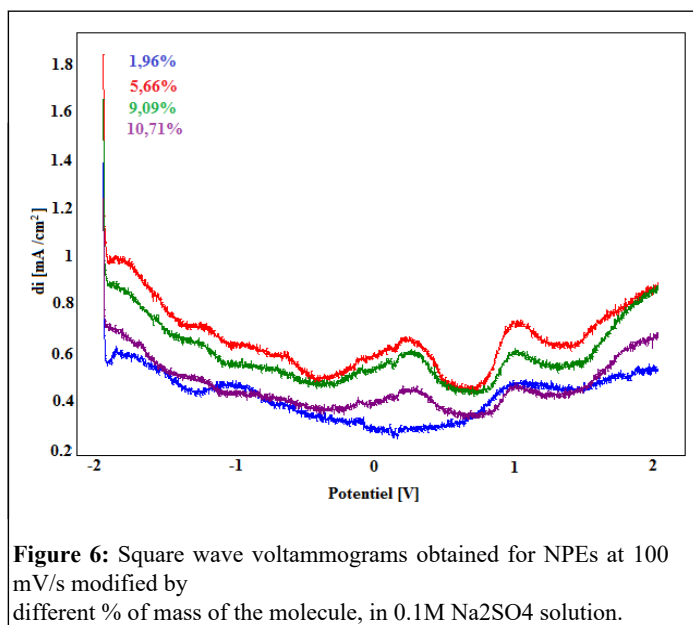


Figure 6: Square wave voltammograms obtained for NPEs at 100 mV/s modified by different % of mass of the molecule, in 0.1M Na<sub>2</sub>SO<sub>4</sub> solution.

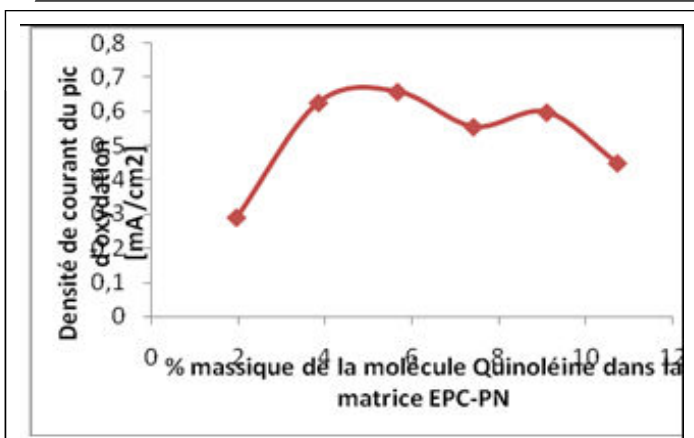


Figure 5: Influence of the mass percentage of the organic molecule on the behavior of the NPE in Na<sub>2</sub>SO<sub>4</sub> (0.1M).

Figure 6 illustrates the evolution of the SQWs, recorded for the elaborated electrode, according to the mass percentages of the organic molecule. There are two oxidation peaks: the first one towards 0.3V and the second at about 1.2V and a peak of reduction towards approximately -1V.

### Chelation of Fe<sup>2+</sup> ions

We chose to chelate ferrous and cupric ions with the organic modified electrode at 5.66% by.

Fe<sup>2+</sup> ions are added progressively to the electrochemical measuring cell, whose working electrode molecule with 5.66% by weight.

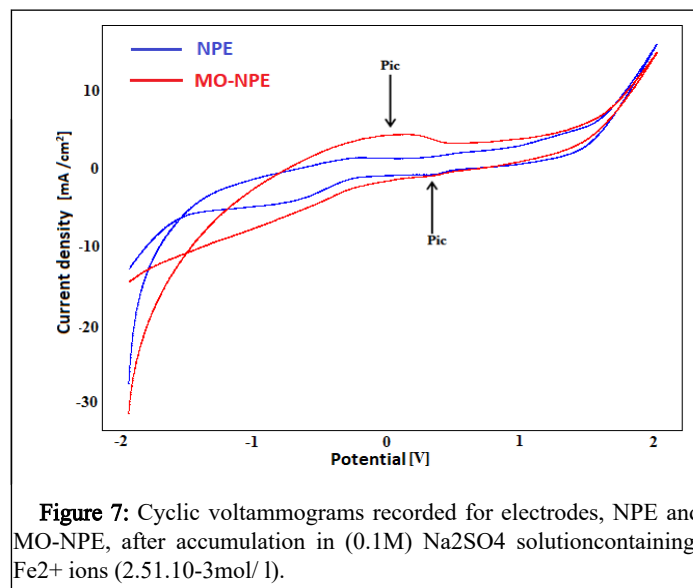
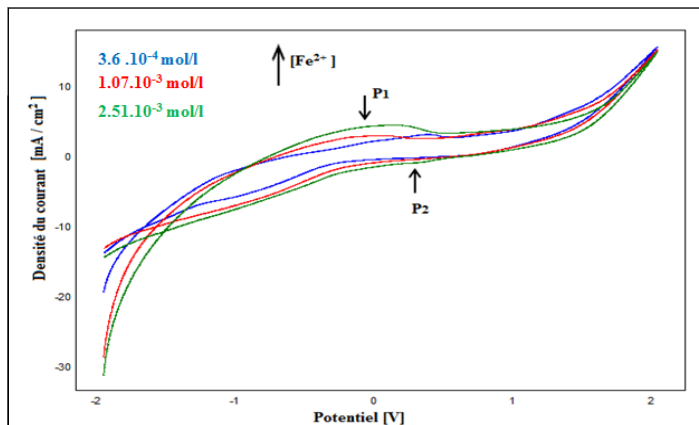


Figure 7: Cyclic voltammograms recorded for electrodes, NPE and MO-NPE, after accumulation in (0.1M) Na<sub>2</sub>SO<sub>4</sub> solution containing Fe<sup>2+</sup> ions (2.51.10<sup>-3</sup>mol/l).

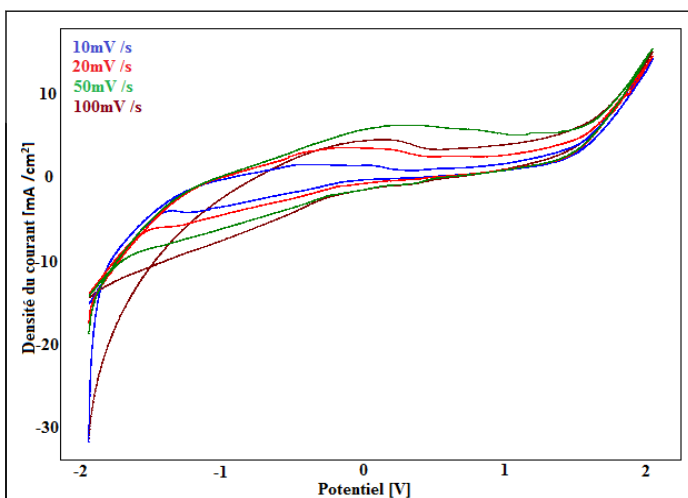
The Figure 7 shows the cyclic voltammograms. During the cathodic potential sweep, a reduction peak is formed at around 0.5V which corresponds to the reduction of the iron and its incorporation into the organic matrix.

In the direction of anodic scanning, the modified electrode has a broad peak towards 0V which corresponds to the oxidation of iron complexes in the organic matrix. The fact of not having a well-defined oxidation peak is a sign of the formation of a complex between the organic film and the ionic iron.

The addition of Fe<sup>2+</sup> ions in the solution results in the increase of the current densities of the two peaks, anodic and cathodic (Figures 8 and 9).



**Figure 8:** Cyclic voltammograms recorded for the modified electrode, after accumulation in the solution containing Fe<sup>2+</sup> ions.

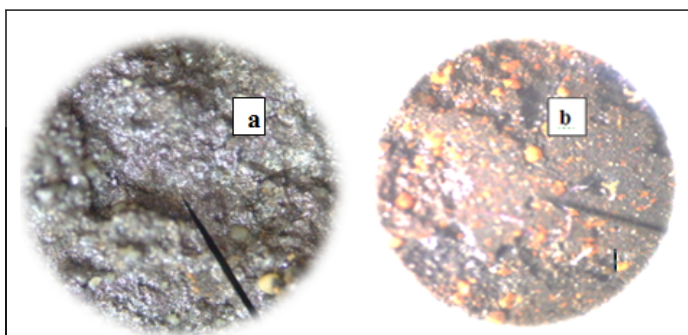


**Figure 10:** Cyclic voltammograms recorded for MO-NPE in (0.1M) Na<sub>2</sub>SO<sub>4</sub> solution containing Fe<sup>2+</sup> ions (2.10<sup>-3</sup> mol/l) at different scanning rates.

The peak current density is linear for relatively low scan rates. After, the curve changes slope, which shows that the reaction is almost fast. Under optimal conditions, the variation of the intensity of the anodic peak as a function of the concentration of iron, contained in the solution of the measuring cell. A calibration straight line has been plotted for the concentrations Fe<sup>2+</sup> ions between 3.59.10<sup>-4</sup> and 2.51.10<sup>-3</sup> mol / l. The linear regression coefficient is R<sup>2</sup>=0.9922.

### Electrode surfaces seen at light microscopy

Figure 11 illustrates the images of the electrode surfaces viewed under an optical microscope

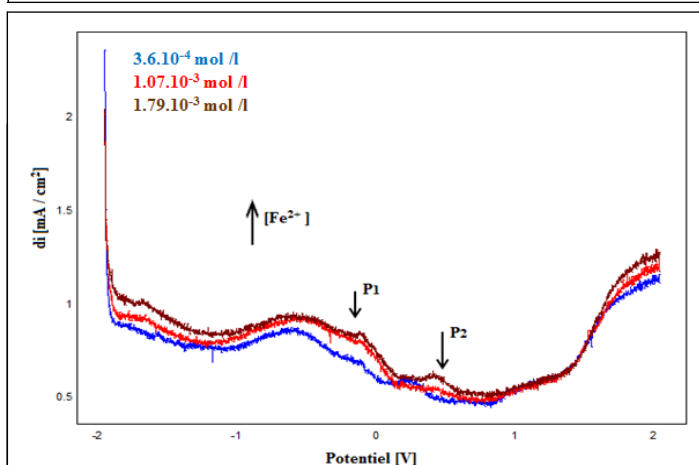


**Figure 11:** Images obtained by optical microscopy with a magnification of 4/ 0.10 a) NPE; b) MO-NPE after accumulation in the solution containing Fe<sup>2+</sup> (2.51 × 10<sup>-3</sup> mol/l).

The morphology of the surface has changed in the modified electrode, we observe clusters of crystals, and they correspond to the formation of complexes on the whole surface.

### Chelation of Cu<sup>2+</sup> ions

**Procedure:** We proceeded in the same way as for Fe<sup>2+</sup> ions.

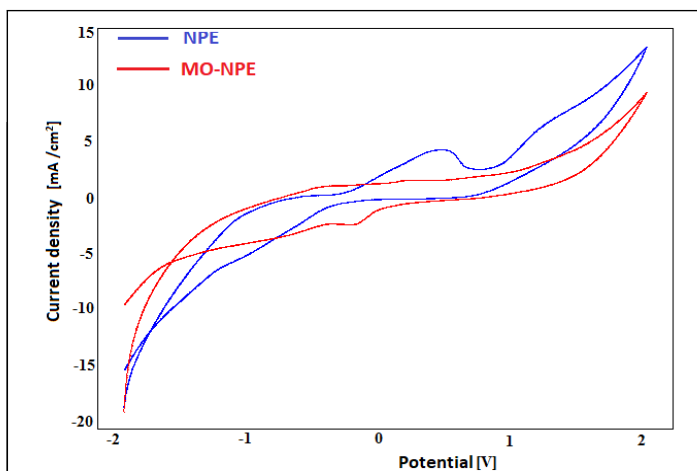


**Figure 9:** Square wave voltammograms recorded for the modified electrode, after accumulation in the solution containing Fe<sup>2+</sup> ions (3.6 · 10<sup>-4</sup>, 1.07 · 10<sup>-3</sup> and 1.79 · 10<sup>-3</sup> mol / l)

### Effect of the scan rate

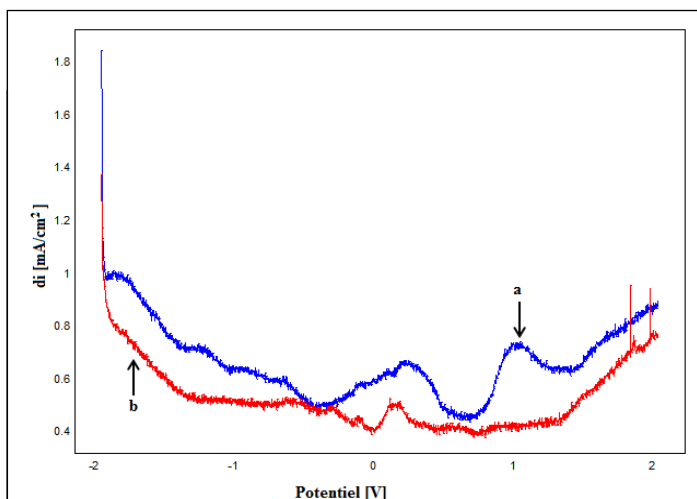
The influence of the scanning rate was studied in order to get an idea about the mechanism of the reaction; the results are showed in Figures 10 and 11.

### Effect of copper concentration



**Figure 12:** Cyclic voltammograms recorded for electrodes MO-NPE and MO-NPE accumulated 5 min at copper (II) ( $4.38 \cdot 10^{-3}$  mol/L) solution, in (0.1 M) Na<sub>2</sub>SO<sub>4</sub> solution at 100 mV/s.

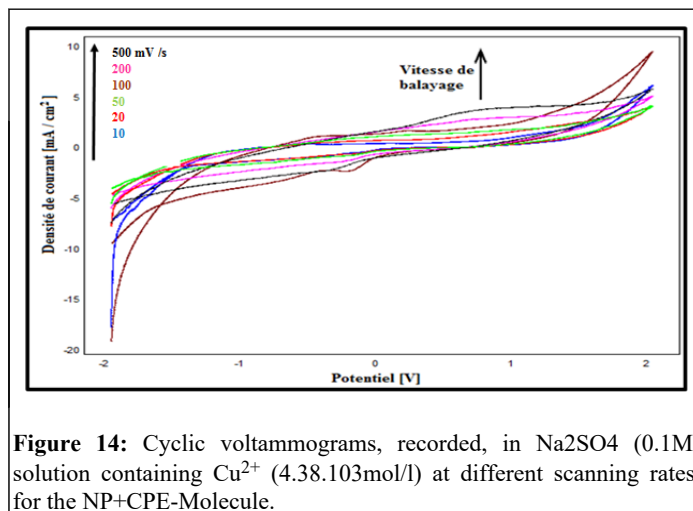
We find that the presence of Cu<sup>2+</sup> ions in the solution removes the oxidation peak of the organic molecule, which suggests that the latter chelated the Cu<sup>2+</sup> ions, which led to its stabilization. On the other hand, in the direction of the cathodic scanning, we notice the appearance of a peak of reduction towards -0.1 V; it corresponds to the reduction of copper in the organic matrix. This result is confirmed by SQW which shows the disappearance of the oxidation peak at 1.2 V (Figure 13).



**Figure 13:** square wave voltammograms recorded for electrodes. b-NPE and a-MO-NPE, in (0.1 M) Na<sub>2</sub>SO<sub>4</sub> solution at 100 mV/s

### Influence of scanning rate

In the studying of the scanning rate effect, we observed the appearance of an oxidation peak around 0.8 V (Figure 14).



**Figure 14:** Cyclic voltammograms, recorded, in Na<sub>2</sub>SO<sub>4</sub> (0.1 M) solution containing Cu<sup>2+</sup> ( $4.38 \cdot 10^{-3}$  mol/l) at different scanning rates, for the NP+CPE-Molecule.

The influence of the scanning rate was studied in a final step for the electrode emerging in the 0.1 M Na<sub>2</sub>SO<sub>4</sub> solution enriched by Cu<sup>2+</sup> ions (Figure 14). The intensity of the oxidation peak varies linearly with the sweep rate at the potential at 0.8 V. This linearity has left us thinking that the oxidation reaction is managed by the electron transfer phenomenon.

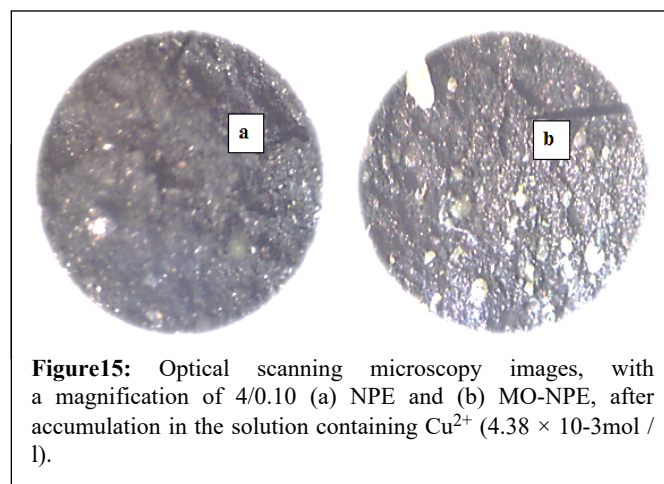
### Calibration curve of copper

The calibration curve was plotted under the optimized conditions, previously described, using the square-wave voltametry. The current intensity of the anode peak on Mo-NPE is proportional to the concentration of Cu<sup>2+</sup> in the concentration range of 10 to 70 mg/100 ml.

Under the optimal conditions, the variation of the anodic peak intensity as a function of the copper concentration contained in the measuring cell. A calibration straight line has been plotted for the concentrations between 10 and 70 mg/100 ml. The linear regression coefficient is  $R^2=0.8794$ .

### Electrode surfaces seen at light microscopy

We observe that the morphology of the surface has changed in the modified electrode, and clusters of crystals cover its surface, they correspond to the formation of complexes on the whole surface (Figure 15).



**Figure 15:** Optical scanning microscopy images, with a magnification of 4/0.10 (a) NPE and (b) MO-NPE, after accumulation in the solution containing Cu<sup>2+</sup> ( $4.38 \times 10^{-3}$  mol/l).

## Conclusion

The Natural Phosphate Paste Electrode (NPE) was successfully modified with organic molecule. Electrochemical characteristics specific to this sensor, such as stability, reproducibility, limit of detection and quantification have been determined. The limit of detection of the metals studied is  $1.15982 \cdot 10^{-6}$  mol/l and  $5.56876 \cdot 10^{-5}$  mol/l respectively for iron and copper. The accumulation of Fe (II) and Cu (II) in the modified electrodes takes place by diffusion in the paste and chelation at the sites of the organic matrix.

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