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By A. Zaroual, S. El Qouatli, A. Bellochou, M. Boulghallat, A. Gamouh, R. Najih
& A. Chtaini

University Sultan Moulay Slimane, Morocco

Abstract- We report a sensitive electrochemical voltammetric method for analyzing p-Aminophenol, using a Natural phosphate (NP) modified carbon paste electrode NP-CPE, in Na_2SO_4 solution. Operational parameters have been optimized, and the stripping voltammetric performance has been studied using square wave voltammetry. The use of *Moringa oleifera* as natural chelating agent gave a significant improvement in the depollution of contaminated water sample.

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Electrochemical Study of the Capacity of *Moringa Oleifera* to Chelate p-Aminophenol

A. Zaroual ^α, S. El Qouatli ^σ, A. Bellochou ^ρ, M. Boulghallat ^ω, A. Gamouh [¥], R. Najih [§] & A. Chtaini ^χ

Abstract- We report a sensitive electrochemical voltammetric method for analyzing p-Aminophenol, using a Natural phosphate (NP) modified carbon paste electrode NP-CPE, in Na₂SO₄ solution. Operational parameters have been optimized, and the stripping voltammetric performance has been studied using square wave voltammetry. The use of *Moringa oleifera* as natural chelating agent gave a significant improvement in the depollution of contaminated water sample.

Keywords: electroanalysis; modified electrodes; p-aminophenol; *moringa oleifera*.

1. INTRODUCTION

Aminophenols are interesting electrochemical materials since, unlike aniline and other substituted anilines [1-2], they have two groups (-NH₂ and OH), which could be oxidized. Therefore, they could show electrochemical behavior resembling anilines and/or phenols [3-5]. An important factor would be the relative position of the amino and hydroxyl group in the aromatic ring. Accordingly, the reported electrochemical properties of the three positional isomers (ortho, meta and para) are strongly different. P-Aminophenol (p-AP) is a well-known compound which, in its simple form, or derivative [6], has been used as redox agent in photography. In neutral media, it is oxidized to complex oligomeric dyes that could be used in enzymatic assays [7]. Konopelnik et al. [8] have studied the oxidation of P-aminophenol (P-AP) in aqueous solution on SnO electrodes. According with these authors, only the amino group of m-aminophenol undergoes oxidation while the hydroxyl group remains unchanged. Common laboratory-based analytical methods for determining para-aminophenol compounds such as primarily gas and liquid chromatography (HPLC) [9-13], UV-vis spectrophotometry [14-15] and spectrofluorimetry [16] have been reported. The use of enzyme-linked immunosorbent assay (ELISA) has been studied [17]. However, some sample pretreatment involving separation, extraction and/or adsorption is generally necessary, and this can also be time-consuming and complex. Electrochemical methods, such as differential pulse polarography (DPP), anodic stripping voltammetry (ASV) and differential pulse

voltammetry (DPV), have been widely applied for the determination of pharmaceuticals, dyes, insecticides and pesticides [18-20]. In recent years, chemically modified electrodes (CMEs) were used for the voltammetric quantification of various organic and inorganic species after their open circuit accumulation [21-22]. Much of the work in this field was directed to exploit the chemical reactivity of the modifier towards a target analyte for electroanalytical purpose. Multitudes of modifying agents were used either as coatings on solid electrode surfaces or dispersed within a conductive matrix. It is noteworthy that this last approach is well suited when using electronically insulating modifiers requiring a direct contact to an electronically conducting substrate as used in connection with electrochemistry. The application of silicates and related mineral materials in electrochemistry is rather recent and was directed to combine their intrinsic properties to selected electrochemical reactions in order to improve the response of the electrode. Modified electrodes are being used frequently in the voltammetric determination of organic compounds because of their efficiency, the selectivity that can be obtained by varying the modifier and the sensitivity which is equivalent to that reached in anodic and cathodic stripping. In doing so, 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. Kauffmann [23] has reported that a carbon paste electrode (CPE) modified with lipids and proteins (enzymes) have potential application in environmental analysis. Recent works, reported in the literature, have shown several applications and electroanalytical methodologies employing glassy carbon electrode as working electrodes [24-25]. Luz and al. [25] constructed a glassy carbon electrode impregnated with a lithium tetracyanoethylene (LiTCNE) for the determination of para-aminophenol. The oxidation and reduction of this compound has been carried out on a modified glassy carbon electrode using cyclic and DPV [26-28]. This study proposed a new modified carbon paste electrode which has been prepared by the Natural Phosphate (NP) for para-aminophenol detection. It has shown a selective preconcentration and quantization of para-aminophenol by cyclic voltammetry (CV). This study has

Author ^{α ρ}: Laboratoire des Matériaux, Nanotechnologies et Environnement, Faculté des Sciences de Rabat, (MAROC).
e-mail: a.zaroual@yahoo.fr

Author ^{σ ω ¥ § χ}: Equipe d'Electrochimie Moléculaire et Matériaux Inorganiques, Faculté des Sciences et Techniques de Béni Mellal, Maroc. e-mails: s.elqouatli@yahoo.f, a.chtaini@usma.ma

led to the development of a new modified electrode for the determination of para-aminophenol with improved qualities such as simplicity of electrode preparation, wider linear range, and low detection limit (DL), high selectivity and very good stability of modifier. The procedure is based on the oxidation and reduction of para-aminophenol after it was preconcentrated on a carbon paste electrode modified with the clay, under open circuit conditions.

In this work we prepared and characterized the phosphate Natural modified carbon paste electrode, which successfully exploits the favorable mechanical and electrochemical properties of carbon paste electrodes. Also, this study therefore focused on the determination of the effectiveness of the *Moringa oleifera* in the purification of water contaminated by 4-Aminophenol.

II. EXPERIMENTAL

a) Reagents

p-Aminophenol and sodium sulfate were of analytical grade and from Aldrich. A natural phosphate (NP) used in this work was obtained in the Khouribga region (Morocco). Stock solutions of p-Aminophenol were prepared by dissolving p-Aminophenol in deionized water. All preparations and dilution of solutions were made deionized water. Provisions were made for oxygen removal by bubbling the solution with azotes gas for about 5 min then the solution was blanketed with azotes gas while the experiment was in progress. For reproducible results, a fresh solution was made for each experiment. Carbon paste was supplied from (Carbon, Lorraine, ref. 9900, French).

b) Electrodes preparation

Firstly, the carbon-paste electrode was prepared according the following procedure [29]. The carbon-paste electrode was prepared by mixing the graphite powder with paraffin oil used as a binder.

The mixture was grinding in a mortar agate 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 cm². A bare of carbon vitreous inserted into carbon paste provided the electrical contact, and then the NP film is electrodeposited onto carbon paste electrode. The deposit of Phosphate natural on carbon paste electrode surfaces was processed at 20 V. The current was maintained by a galvanostat with a function generator.

c) Prepared electrode characterization

All the electrochemical experiments were performed in a standard one-compartment three-electrode cell. The reference electrode was SCE and the counter electrode was platinum. All electrode potentials were referred to this reference electrode. The working

electrode was NP modified carbon paste electrode (NP-CPE).

d) Apparatus

Electrochemical experiments were performed 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).

III. RESULTS AND DISCUSSION

a) Characterization of prepared electrodes surfaces

The surface structure of natural phosphate modified carbon paste surface was observed using scanning electron microscopy (Fig. 1). The film layer of NP was formed on the surface of carbon paste electrode; it was not disintegrated or detached from the surface when immersed in the electrolytic solution (0.1M Na₂SO₄). The morphology of the phosphate rock surface was observed by scanning electron microscopy (Figure 1). The treatment described previously gives compact particle fractions between 100 and 400 μm rich in phosphate. Rock phosphate treaty has the following chemical composition: CaO (54.12%), P₂O₅ (34.24%), F (3.37%), SiO₂ (2.42%), SO₃ (2.21%), CO₂ (1.13%), Na₂O (0.92 %), MgO (0.68%), Al₂O₃ (0.46%), Fe₂O₃ (0.36%), K₂O (0.04%) and order of several ppm metals.

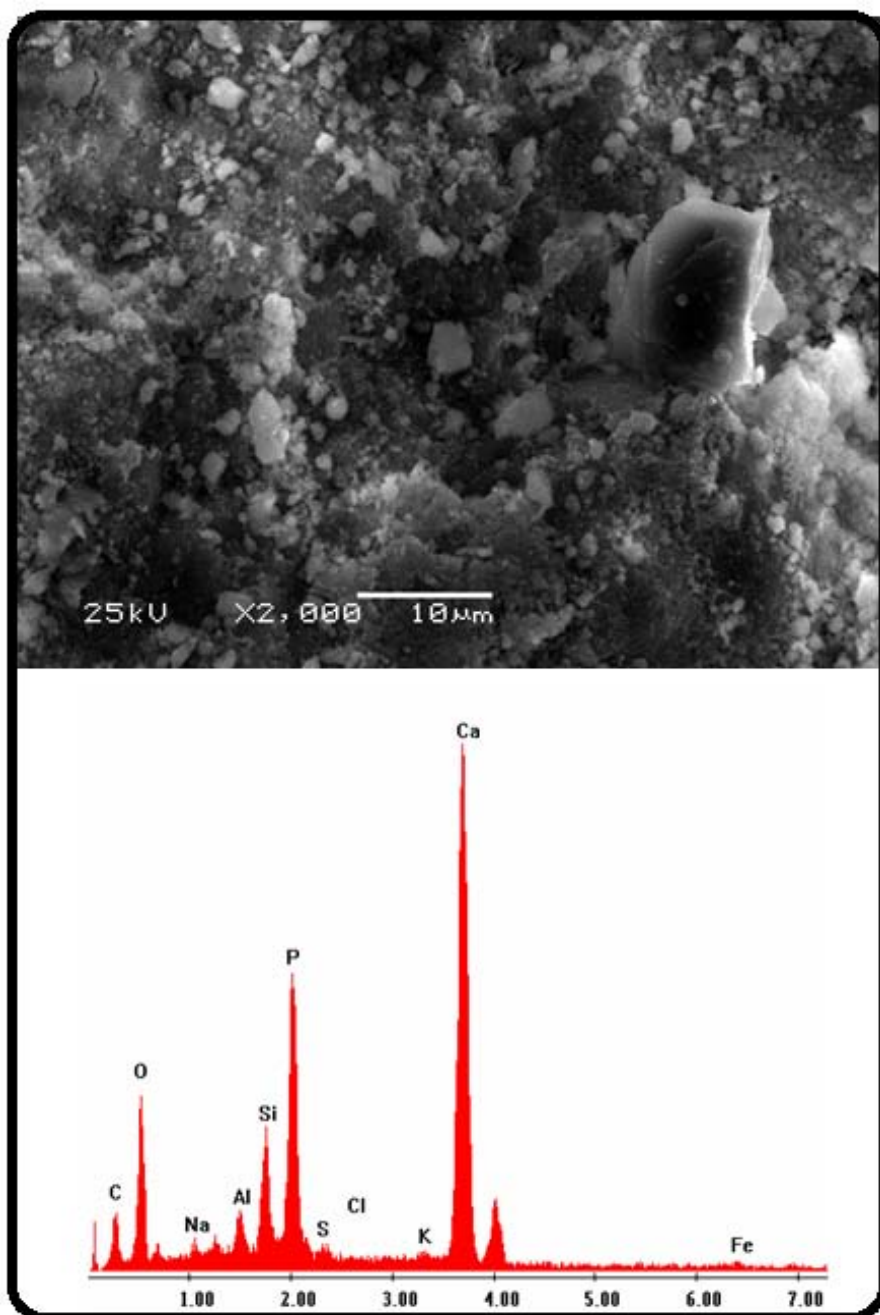


Figure 1: Scanning electron micrograph of NP-CPE

The cyclic voltammograms (CVs) of the NP modified carbon paste electrode and carbon paste electrode (CPE) were recorded in the supporting electrolyte (0.1 M Na_2SO_4) (Fig. 2).

We can see that the shape of the cyclic voltammogram was modified in the presence of NP at CPE surface, suggesting that the carbon paste electrode was effectively modified by natural phosphate.

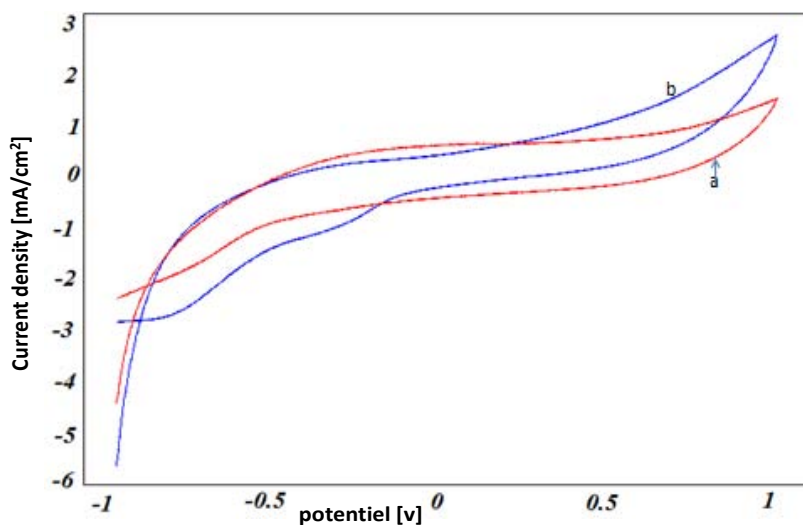


Figure 2 : Cyclic voltammograms recorded in electrolytic solution, at 100 mV/s, at a- carbon paste electrode, b- NP modified carbon paste electrode

b) *Electrochemical detection of studied metals*

The experimental conditions have been optimized and the response characteristics determined in a previous work [29]. The results obtained are:

- □ pH □ □
- □ Preconcentration time = 13 min.

In order to avoid the strong residual of reduction, the starting potential was fixed at -1V versus SCE. Fig. 3 shows a cyclic voltammograms performed between -1 V and 1 V for NP-CPE, in 0.1M Na₂SO₄ solution (curve a), and in 0.1M Na₂SO₄, after exposure NP-CPE to 0.510-3 mmol/L P-Aminophenol for 13 min, in a stirred solution (curve b). The reversible system

could be observed at NP-CPE, with cathodic potential value, of -0.3 V and anodic potential value of -0.1 V.

The square wave voltammetry (SWV) corresponding to the determination of P-Aminophenol, was recorded in the supporting electrolyte (curve a) and after, 13 min of accumulation in a solution containing P-Aminophenol (curve b).

The Square wave voltammograms are showed in Figures 4. A well-defined and enhanced peak is observed at NP-CPE, imprinted in P-Aminophenol solution. This peak is attributed to P-Aminophenol oxidation. The scheme 1 shows the proposed mechanism of this oxidation.

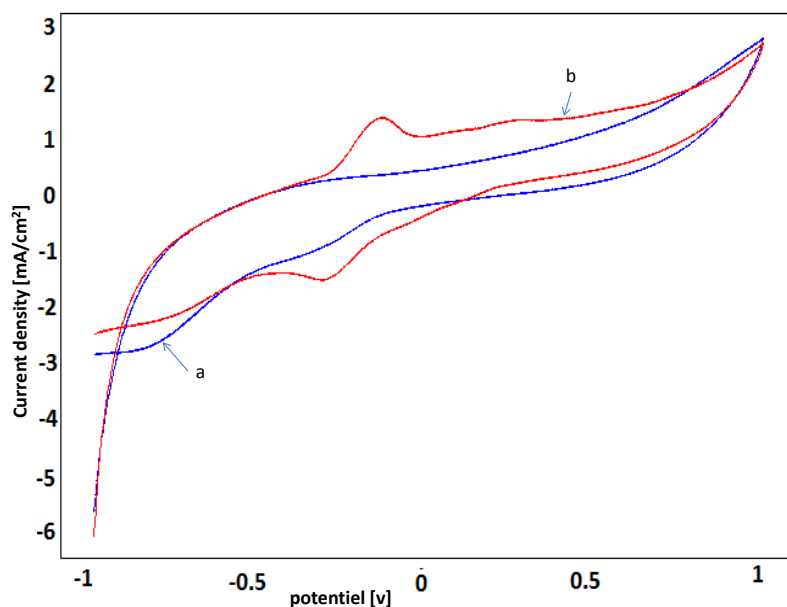


Figure 3 : Cyclic voltammograms recorded in electrolytic solution, at 100 mV/s, at NP modified carbon paste electrode, in 0.1 M Na₂SO₄ solution (a), and after exposing to P-Aminophenol solution

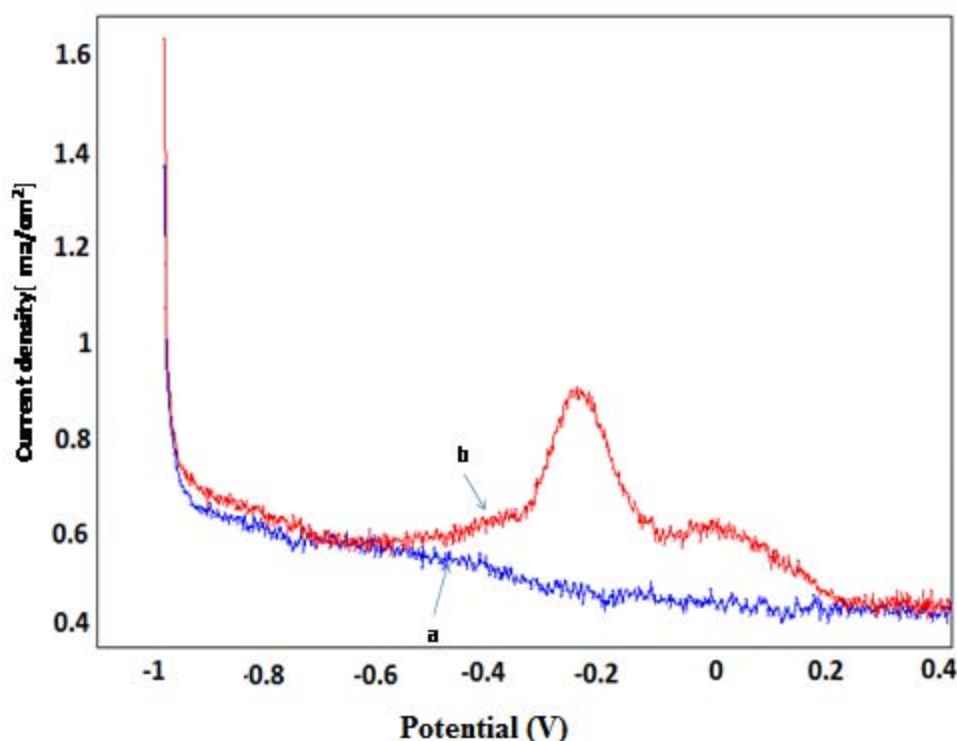
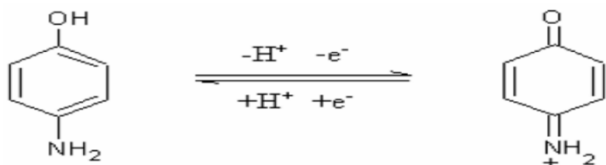


Figure 4 : Square wave voltammograms obtained for PN-pectively, in supporting solution (curve a), and after exposing electrode to P-Aminophenol solution (curve b)



Scheme 1: mechanism of electrochemical redox reaction of p-aminophenol at NP-CPE

c) Chelating effect of *Moringa oleifera*

Moringa oleifera is the best known species of the Moringaceae family. Moringaceae is a family of plants belonging to the order Brassicales. It is represented by fourteen species and a single genus (*Moringa*), being considered an angiosperm plant. It is a shrub or small tree which is fast growing, reaching 12 meters in height. It has an open crown and usually a single trunk. It grows mainly in the semi-arid tropics and subtropics. Since its preferred habitat is dry sandy soil, it tolerates poor soils, such as those in coastal areas [31].

Firstly, the *Moringa oleifera* was prepared according the following procedure [30]. *Moringa oleifera* seeds collected for the analysis were shelled off and sun dried to maintain constant weight. The sun-dried seeds were grinded into powdered form using machine. The powdered was added to the solutions containing heavy metals. After 15 min of contact with *moringa oleifera*, the solutions were purified and analysis in electrochemical sensor.

The SQWV's recorded at prepared electrode, in supporting solution containing p-aminophenol (curve a) and after addition of the *moringa oleifera* (curve b), are shown in Figure 7. The peak current decreased considerably after *moringa* treatment. This current density reduction is due to a sharp decline in p-aminophenol concentrations, which suggests that *moringa* has a strong complexing power of p-aminophenol (Figs. 7 and 8). We not that the solution pH was varied after *moringa* treatment. It was decreased from 7.2 to 6.5.

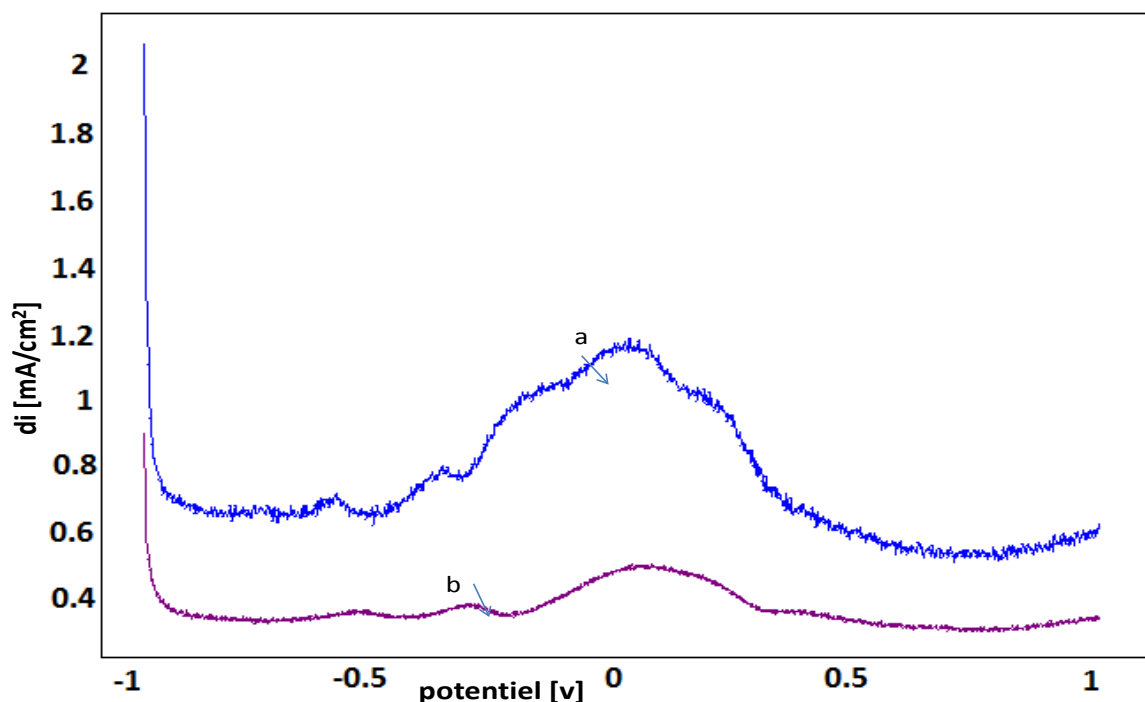


Figure 7 : Square wave voltammograms obtained for NP-respectively, in supporting solution, after exposing electrode to p-aminophenol contaminated solution. (a) - before moringa treatment, b-after moringa treatment

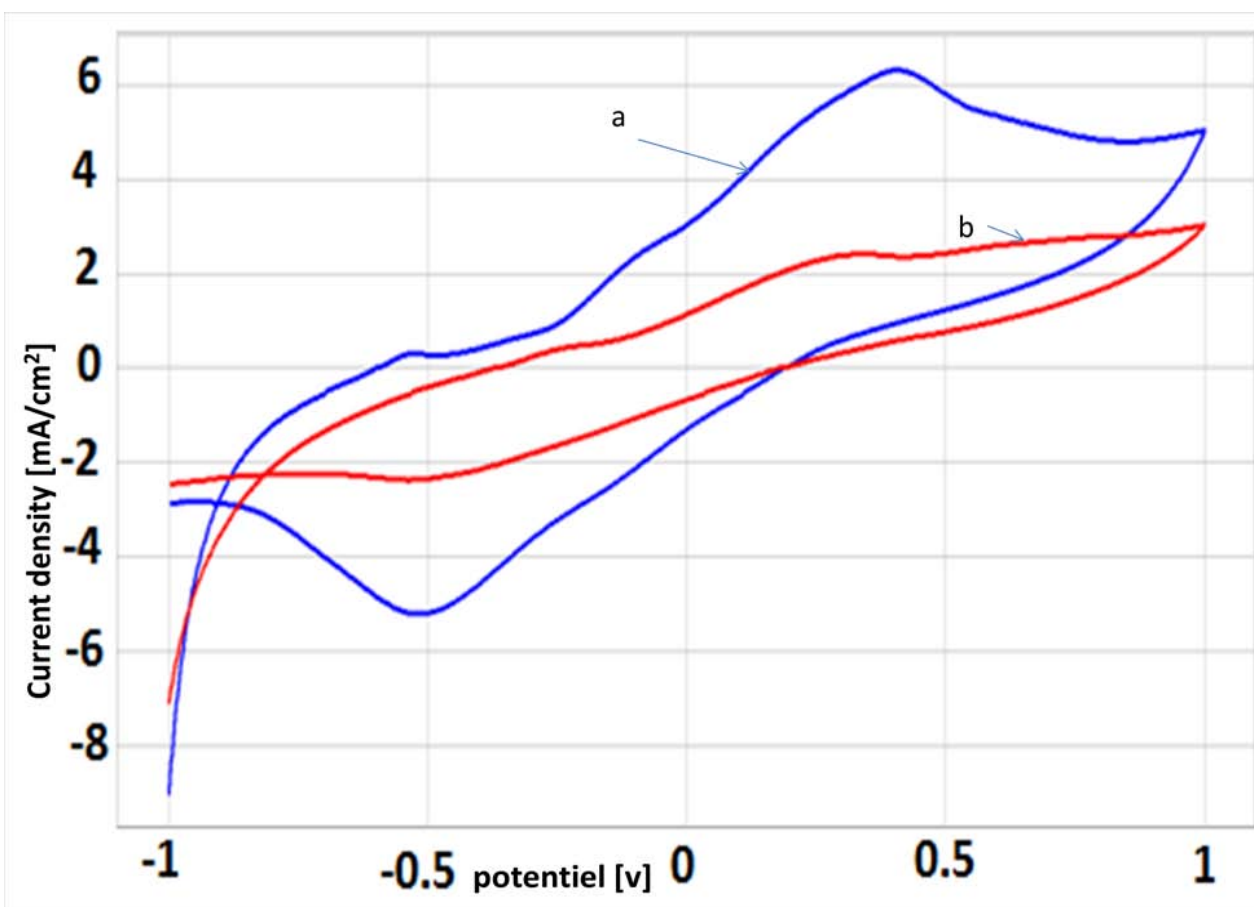


Figure 8 : Cyclic voltammograms obtained for NP-respectively, in supporting solution, after exposing electrode to p-aminophenol contaminated solution. (a) - before moringa treatment, b - after moringa treatment

d) Optimization of experimental conditions

i. The *Moringa oleifera* concentration effect on *p*-aminophenol

In order to obtain an analytical curve for the developed sensor, we carried out cyclic voltammograms and Square wave voltammograms to show the *Moringa oleifera* effect on *p*-aminophenol at different concentrations, in 0.1M Na₂SO₄ (pH 7), the sweep rate was fixed at 100 mVs⁻¹.

Figure 7 and 8 shows the CV and SQW curves recorded, for different concentrations of *moringa oleifera*

(MO), at NP-CPE was increased from 2 ml/200 ml (electrolytical solutions) to 13 ml/200 ml (electrolytical solution). Both the anodic and cathodic peak current increases linearly with the concentration of *moringa oleifera* and the plot of current versus concentration obeys Randles-Sevcik equation, which implies that the electrode process is adsorption controlled reaction. It was also observed that the cathodic peak potential shift towards negative values and anodic peak potential shift towards positive side. This kind of shift in *E_p* in the cathodic and anodic.

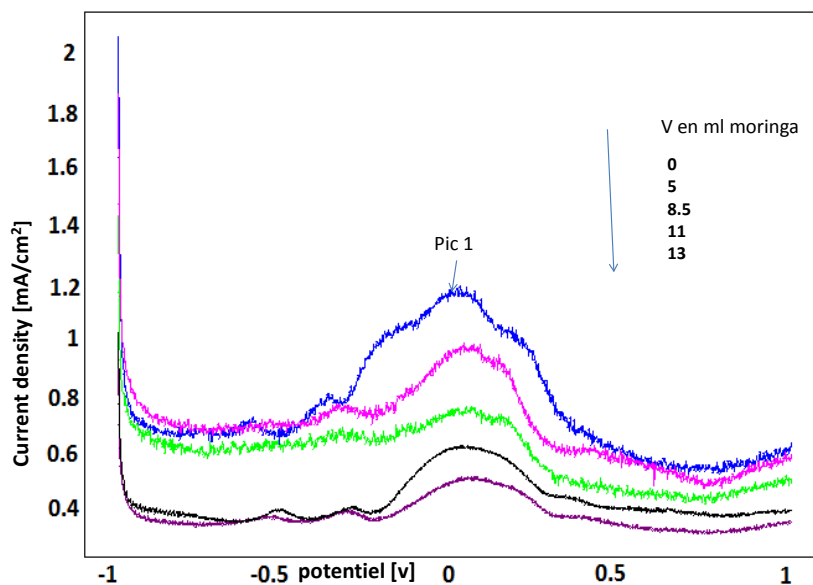


Figure 7 : Cyclic Voltammogram of different concentration of MO (0 ml to 13ml) in (0.5 mM) aminophénol at NP-CPE in 0.1 M Na₂SO₄, Scan rate 100 mV/s

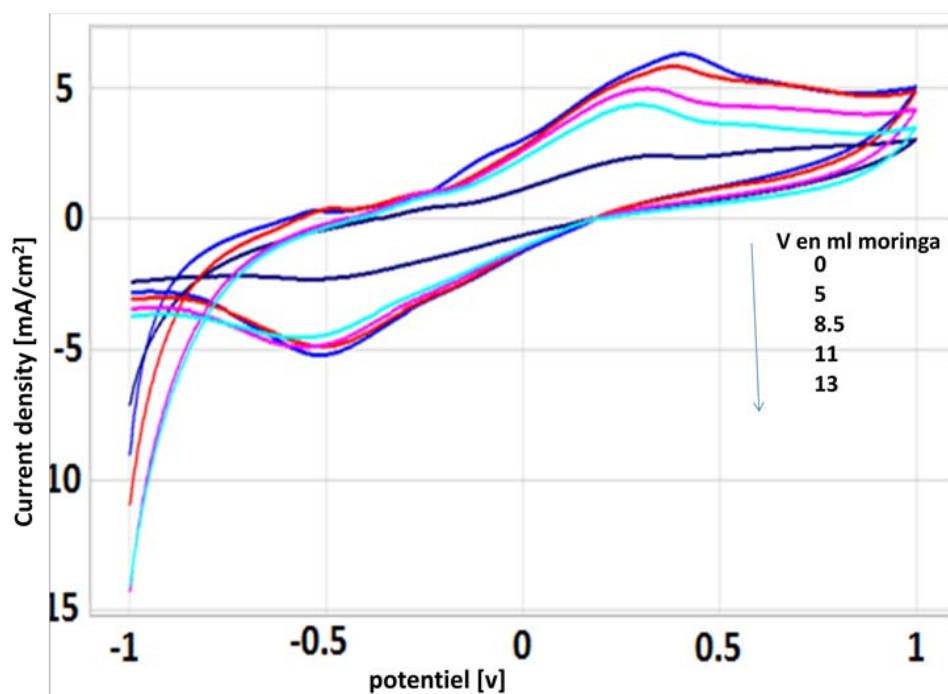


Figure 8 : Square wave voltammograms of different concentration of MO (0 ml to 13ml) in (0.5 mM) aminophenol at NP-CPE in 0.1 M Na₂SO₄, Scan rate 100 mV/s

The effect of the MO concentration of MO is investigated (Figure 9), this significantly affects the oxidation peak current of p- aminophenol. The peak current decrease greatly with MO concentration.

Similarly, the effectiveness of the Moringaenol to chelate p- aminophenol increases considerably with the MO concentration. (Fig. 10)

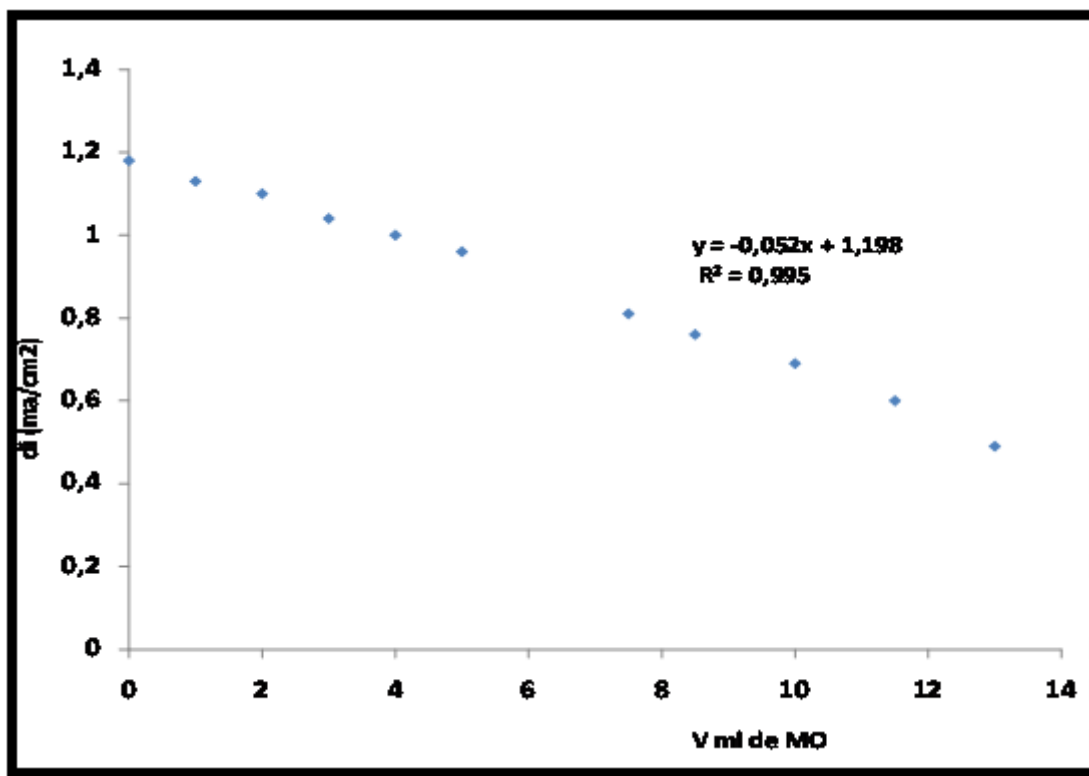


Figure 9 : Peak area of land depending on the concentration of added MO on Peak 1

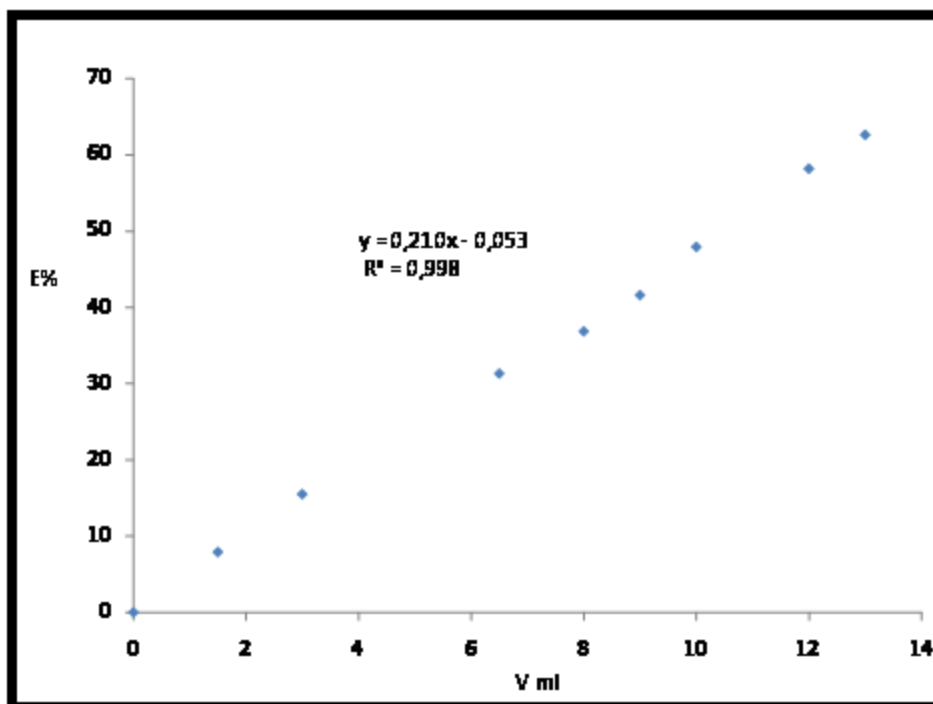
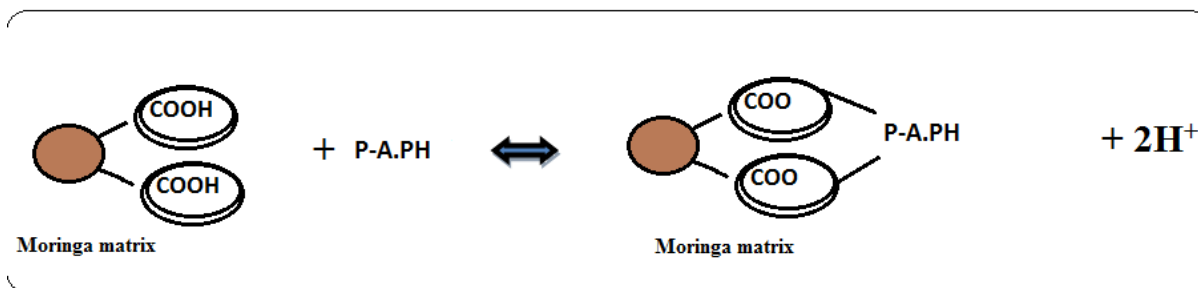


Figure 10 : The MO efficiency on 0.5 mM [p-aph] vs MO concentration

Based on the pH variation of the solution after treatment with MO, we proposed the following mechanism:



P-A.PH (p-aminophenol)

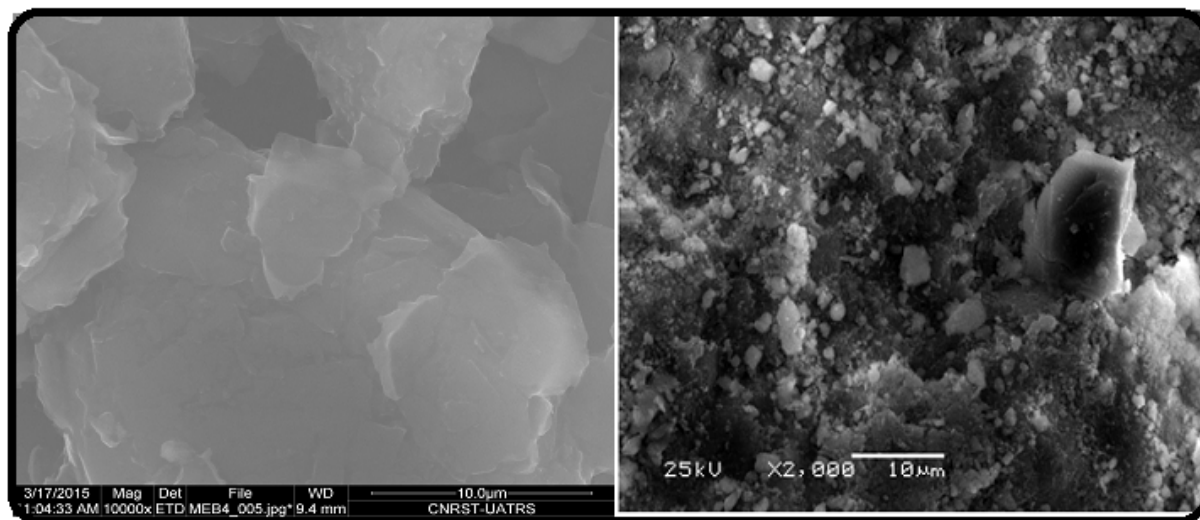


Figure 11: MEB images of NP modified carbon paste electrode, a-before and b- after MO treatment

In Figure 11, we present the SEM images, taken to the surface of the modified electrode; we can see that after MO treatment, the surface morphology changed dramatically with the advent of large compact crystals, leaving suggest that MO-p-aminophenol complex is adsorbed on the electrode by forming a continuous film.

IV. CONCLUSION

In conclusion, it was possible demonstrating the potentiality of the proposed electrode (NP-CPE) for determining P-aminophenol. Such a sensor is characterized by a higher sensitivity and reproducibility.

The *Moringa oleifera* seeds have the ability to retain p-aminophenol. The metal is sequestered by chemical sites naturally present in the moringa matrix. The chelating process is rapid and takes place under normal temperature and pressure. *Moringa oleifera* is an environmentally-friendly natural complexing most suitable for the treatment of water containing undesirable p-aminophenol concentrations. The removal efficiencies were 60 % for P-aminophenol. It is an eco-friendly technology that is economically more advantageous than other treatment alternatives.

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