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# Study of carbon paste electrode modified with takawt plant for determination of Cu (II) by differential pulse voltammetry

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## Abstract

The aim of this study is to develop a sensor based on the carbon paste electrodes (CPEs) modified with takawt plant for determination of Cu(II). The measurements were carried out by differential pulse voltammetry (DPV). The Cu(II) ions were chemically deposited onto the surface of takawt natural plant in an acidic medium. The modified electrode exhibited a significantly increased sensitivity and selectivity of $Cu^{2+}$ compared with a bare carbon paste electrode. Copper was preconcentrated at open circuit on the modified electrode. Factors affecting the accumulation, and stripping steps were investigated and the optimum conditions were employed to develop an analytical procedure. A linear range was obtained in the concentration range 0.5-10 nmol/L with a correlation coefficient of 0.9997. The detection limit was 0.237 nmol/L and relative standard deviation for 10 successive determinations of 1 nmol/L was 1.42%. A study of interfering substance was also performed, and the method was applied to the direct determination of copper in real samples like tap water and industrial waste water.

*Keywords:* Carbon paste electrode, Takawt plant, Copper (II), Differential pulse voltammetry.

## 1. Introduction

In Morocco, a non-toxic herbal extract from the gallnut of athel-pine (Tamarix aphyla) is traditionally used to dye hair. This natural extract is locally known as "takawt" [1, 2]. Takawt contains paraphenylenediamine (pPD), which is an aromatic amine, this property will be used for detection of copper. Copper is a metal of prime environmental concern. Therefore, it is essential to develop sufficiently sensitive and reproductible analytical methods for precise determination of trace metals. Recently, several techniques, including flam atomic absorption spectrometry (FAAS) [3, 4], electrothermal atomic absorption spectrometry (ETAAS) [5, 6], inductively coupled plasma mass spectrometry (ICP-MS) [7, 8], atomic fluorescence spectrometry (AFS) [9] have been used for the determination of trace elements in different samples, but the wide utilization of these methods is limited by the expensive equipement [10]. At the same time, several voltammetric methods especially coupled with chemically modified electrodes (CME) have been developed. Electroanalytical techniques such as differential pulse voltammetry can be used for metals determination providing high sensitivity and precision with relatively low instrumental costs. Mi-Sook Won and his co-workers used a boron doped diamond electrode to determine Cd(II), Pb(II), Cu(II), and Hg(II) ions in Waste Water by Differential pulse anodic stripping voltammetry (DPASV) [11], Elena Gomez and his co-workers have detected copper in runoff waters using the same technique [12]. Selenium (IV) has also been detected in Pharmaceutical Products by DPV [13], Maria-Cristina Radulescu and his co-workers used a Glassy Carbon Electrode Modified with Synthesized N-(2-Aminoethyl)-4,4'-Bipyridine to determine Silver(I) by DPV[14] .

Since their first introduction in 1958 by Adams, carbon paste electrodes have been extensively employed in various electrochemical detection schemes due to their simple and fast preparation, simple surface renewing, biocompatibility, non-toxic character, and relatively low-background characteristics [15]. M. El Rhazi and co-workers used carbon paste electrode modified by poly (1,8-diaminonaphtalene) or paraphenylenediamine for the detection of lead and copper [16- 18]. The 2-aminothiazole organofunctionalized silica has been used as an agent modifier for the detection of copper [19]. M. Mazloum Ardakan and co-workers used carbon paste electrode modified by zeolite for the detection of copper [20]. In a country full of rich flora in a very important manner such as Morocco, the valorization of the sector of natural plants has become indispensable. So, initiatives and actions have been taken to give the added value to these plants and integrate them into a sustainable development and harmonious.

In this context, this work describes a sensor based on carbon paste electrode modified with takawt plant. This sensor will be applied to $Cu^{2+}$ determination directly in tap water and industrial wastewater samples by using differential pulse voltammetry.

## 2. Experimental

### *2. 1. Apparatus*

Electrochemical experiments were carried out with an autolab PGSTAT10 potentiostat (Eco Chemie, Utrecht Netherlands) controlled by GPES 4.8 software. The CV and DPV measurements were performed with a three electrode system, including the modified carbon paste electrodes as working electrode, a platinum plate as counter electrode, and Ag/AgCl (3 mol/L KCl) as reference electrode.

The wavelength of takawt was verified by ultraviolet spectroscopy (UV) using an ati unicam UV2 model, UV/VIS spectrophotometer with super sipper sampling unit.

### *2. 2. Reagents*

All chemicals were of analytical reagent grade, except the modifier. Takawt plant (Tamarix aphylla) was obtained from the village of ighrem azogar 10 Km from province of agdaz, It is located in the Souss-Massa-Draa region, about 65 km south of Ouarzazate and 92 km north of Zagora. Copper sulphate was obtained from Riedel-de häen, Solution were prepared with distilled water. Standard copper (II) stock solution was prepared by dissolving $CuSO_4$ in water. All experiments were carried out at room temperature (25°C). Acidic solution served as the supporting electrolyte.

### *2. 3. Samples preparation*

Tape water sample were collected from our laboratory. Industrial reject of leather was obtained by the association of tannery at Casablanca. All samples were acidified with hydrochloric acid.

### *2. 4. Preparation of the electrodes*

The fabrication of CPE and modified CPE were as follows.

i) The carbon paste electrode was prepared by mixing 1 g of graphite powder (Fluka) and 0.3 mL of paraffin oil using a mortar and pestle until homogenous paste was obtained. The paste was then incorporated into the electrode cavity and polished on smooth paper.

ii) The modified carbon paste electrode (MCPE) was prepared in the same manner by thoroughly mixing weighed amounts of takawt (10 mg of takawt plant dissolved in a small volume of ethanol) with 1 g of graphite powder and 0.3 mL of paraffin oil until a uniformly wetted paste was obtained. The mixture was kept at room temperature for one day to let the solvent evaporate. After that, the paste was then packed into the electrode cavity (2mm) with Ø= 4 mm. The electrode surface could be renewed by simple extrusion of a small amount of paste from the tip of the electrode. Otherwise, before each use the electrode surface, it was rubbed with a piece of paper until a smooth surface was observed.

### *2. 5. Copper determination*

The surfaces of fresh MCPEs were immersed in aqueous solution containing a selected concentration of $CuSO_4$ in 0.1 M HCl. The preconcentration of $Cu^{2+}$ was carried out under open circuit. Following the preconcentration step, the rotation of the electrode was stopped and the solution was left to equilibrate for 10 s. An initial potential of –0.6 V was applied for an appropriate time and then scanned from –0.6 V to 0.4 V using differential pulse voltammetry. An anodic peak at 0.053 V (vs. ECS) was observed (fig. 3). The parameters used were a potential step height of 10 mV, pulse amplitude of 50 mV and duration of 50 ms. No deaeration of the solution was required.

## 3. Results and discussion

### *3.1. Characterization of modified electrode by UV and electrochemical methods*

Before any studies by electrochemical technique, we choose to check that the takawt contains a large amount of paraphenylenediamine (pPD). So, a certain weight of takawt was dissolved in acidic medium and placed in spectrophotometer and a scan of wavelength was performed between 200 nm to 600 nm.The ultraviolet spectra of takawt exhibit an intense peak at 281 nm corresponding to the free aromatic amino groups (fig not shown) as reported by H. Fujiwara and his co-workers. This result could be explained by the presence of the paraphenylenediamine compound present in takawt plant wich is confirmed by the results reported in literature [21].

Since the presence of pPD was confirmed by spectrophotometry, the cpe was modified by takawt plant (1%) as described in previous paragraph and placed in the electrochemical cell containing hydrochloric acid.

The cyclic voltammetry behavior of electrode before and after modification with takawt was studied using 0.1 M HCl, at a potential scan rate of 50 mVs$^{-1}$. Fig. 1. shows the CV curves obtained at carbon paste electrode and carbon paste electrode modified (curves b and a respectively). At CPE modified by takawt, a significant increase in anodic peak current compared with the unmodified electrode was observed.

To improve this signal, the response of modified electrode was examined by diffrentiel pulse voltammetry. Fig. 2. Shows the response of CPE modified with takawt in acidic media. A large anodic peak was observed at 0.65 V with a current of 25 µA. This response is attributed to pPD contained in takawt plant. Since in our previous studies, we proved that phenylenediamine can form complex with metal ion such as Hg(II), Pb (II) and Cu(II) [ 18], we will examine the response of copper in the presence of electrode modified with takawt.

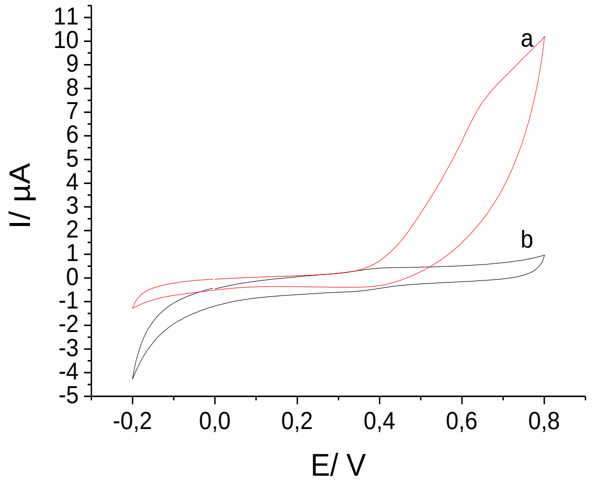

**Figure 1:** CVs of the bare CPE (b) and takawt modified CPE (a), in 0.1 M HCl at a scan rate of 50 mV s$^{-1}$.

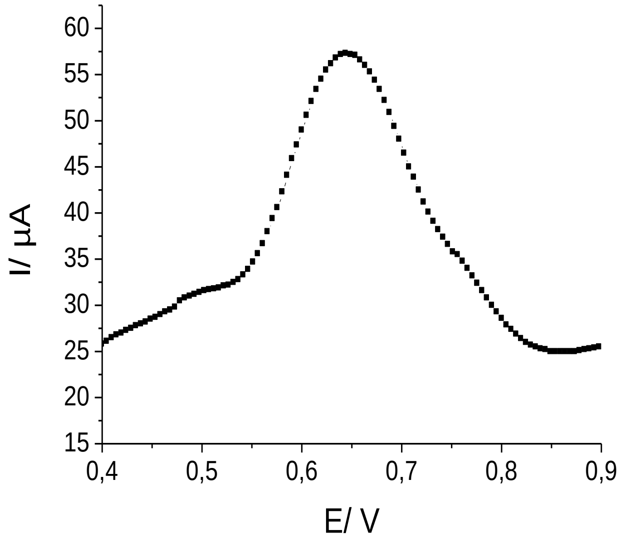

**Figure 2:** DPV of takawt modified electrode in 0.1 M HCl at a scan rate of 50 mV s$^{-1}$.

### *3. 2. Procedure for determining copper (II) using bare and modified CPE*

The determination of copper(II) using a bare CPE and CPE modified with takawt were carried out in an acidic solution (HCl 0.1 mol/L) containing 10 µmol/L of Cu(II) without any optimisation of the parameters.

Figure 3a shows an anodic peak of copper (II) at 0.053V with a peak current of 0.05 µA recorded at bare CPE. Figure 3b shows an oxidation peak well defined at the same potential with a current of 2 µA at CPE modified.

### *3. 2. Optimisation of the parameters for copper determination*

### *3. 2. 1. Effect of the accumulation potential*

The effect of accumulation potential on the peak current of copper(II) was studied over the potential range. Figure 4 shows the effect of the accumulation potential on the stripping peak current of 1 µmol/L of Cu(II). It was found that the maximum response for Cu(II) occurs with potential equal to -0.7 V. A potential of -0.6 V was chosen as the initial potential in our measurement in order to avoid possible interference with other metals especially lead which can form a stable complex with takawt.

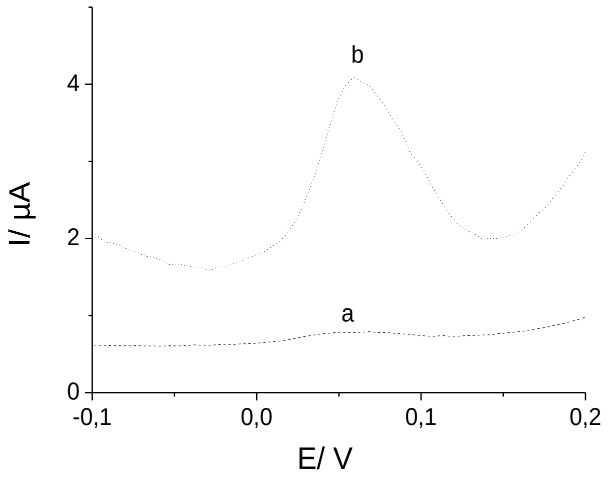

**Figure 3:** Differential pulse voltammograms after the deposition of 10 µmol/L Cu(II) in acidic medium HCl 0.1 mol/L at modified CPE(b) and at bare CPE(a) .

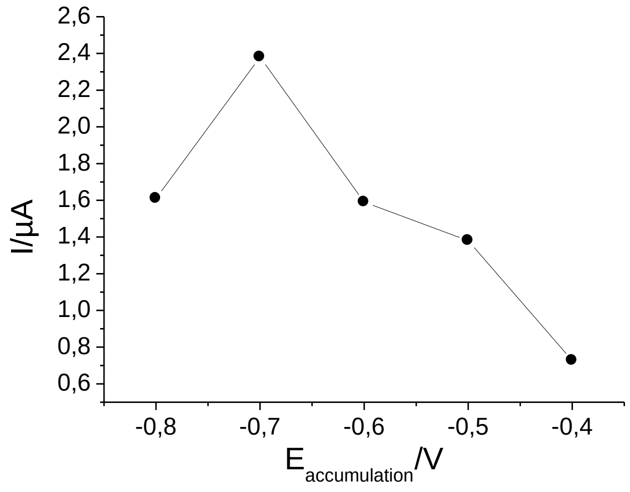

**Figure 4:** Effect of accumulation potential applied on the peak current of 1 µmol/L Cu(II) after 5 mn of preconcentration.

*3. 2. 2. Effect of the accumulation time*

The effect of accumulation time on the peak current of copper was examined. Figure 5 shows the effect of accumulation time on the peak current. The peak current increase with the increasing of accumulation time up to 30 s and then decrease until 40 s and becomes stable. The better response of peak current was 30 s. So, for further experiments, an accumulation time of 30 s will be used to reduce time of analysis.

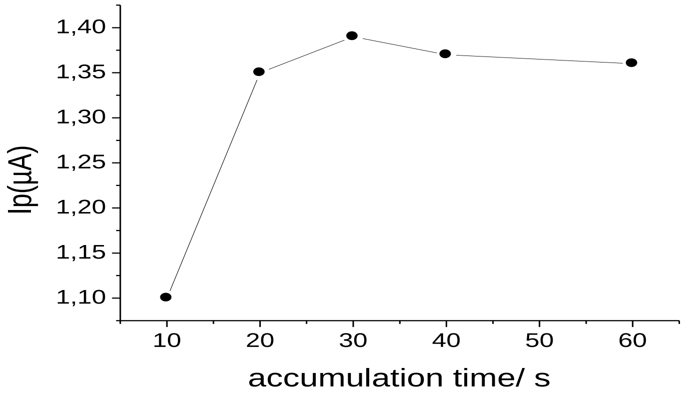

**Figure 5:** Effect of accumulation time on the peak current of 1 µmol/L of copper after 5 mn of preconcentration.

*3. 2. 3. Effect of the preconcentration time*

Figure 6 shows the effect of the preconcentration time on the peak current of 1 µmol/L copper. The peak current decrease up to 8 mn when preconcentration time increase. This diminution of the response can be explained by the saturation of the binding site after the 3 mn. The maximum response for copper is obtained at 5 mn so 5 mn is used for the further experiments.

*3. 3. Calibration plot*

Under the experimental conditions selected during the optimisation studies (initial potential –0.6 V, accumulation time 30 s and preconcentration time 5 mn), a calibration graph for the determination of Cu(II) was constructed for a concentration range 0.5–10 nmol/L. A linear range was obtained in the concentration range 0.5-10 nmol/L with a correlation coefficient of 0.9997 (Fig. 7). The detection limit was 0.237 nmol/L and relative standard deviation for 10 successive determinations of 1 nmol/L was 1.42%.

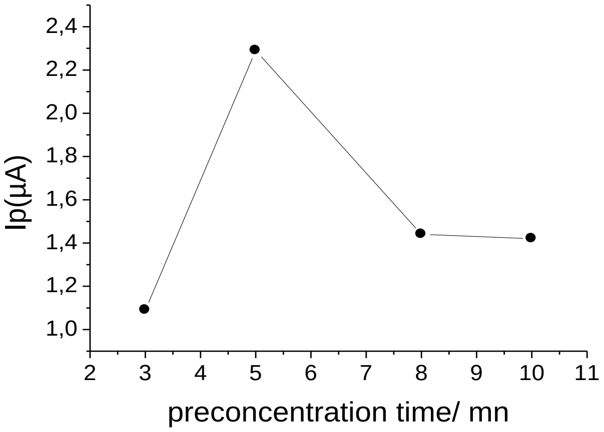

**Figure 6**: Effect of preconcentration time on the peak current of 1 µmol/L copper

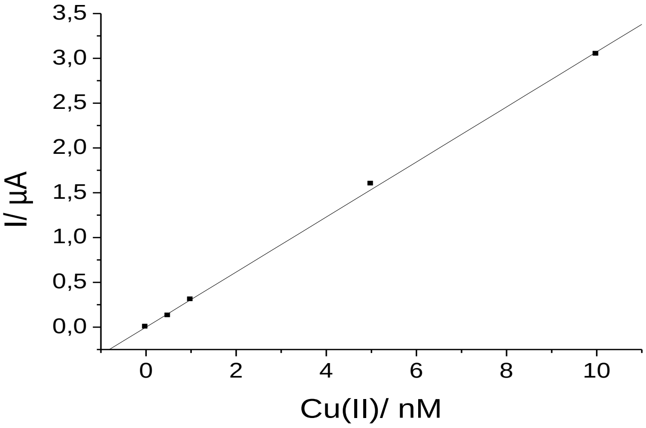

**Figure 7:** Calibration curve for $Cu^{2+}$ in 0.1 mol/L HCl, initial potential - 0.6 V, accumulation time 30 s, preconcentration time 5 mn, equilibrium time 10 s, potential scan - 0.6 V to 0.4 V.

*3. 4. Interferences*

The influence of other metal ions, which can compete for complexation at binding sites on the takawt, were tested using the same procedure as that optimized for copper determination. The interference of Pb(II), Zn(II), Hg(II) and Fe(II) with the current stripping peak was investigated by adding increasing amounts of these metals to a solution containing 1 µmol/L of copper.

In table 1, the results obtained show that 100- fold excess of these ions over Cu(II) in the analyte solution, the interfering ions reduced the electrode response to copper by competing with copper ions for binding sites. To avoid possible interference with others metals, the choice of deposition potential is very important.

**Table 1:** Interference of others metal ions with the determination of 1 µmol/L of Cu(II)

| Cation | Interferent concentration, µmol/L | (Change in peak current), % |
|---|---|---|
| $Zn^{2+}$ | 1 | + 28 |
| $Pb^{2+}$ | 1 | + 28 |
| $Fe^{2+}$ | 1 | + 36 |
| $Hg^{2+}$ | 1 | - 24 |

*3. 5. Analytical applications*

The developed method was applied to the determination of Cu(II) in tap water and industrial wastewater samples. The different samples were collected, adjusted to pH< 2 and measured without any further treatment. The standard addition method was applied for the determinations of copper ions. Also, in order to evaluate the validity of the proposed method for the determination of $Cu^{2+}$, recovery studies were carried out on samples to which known amount of $Cu^{2+}$ was added. The Cu(II) recovery studies showed values in range from 98% to 108%. Consequently, that is a good accuracy for Cu(II) determinations in the samples matrix studies. The results were summarized in Table 2.

**Table 2:** Recovery analysis of Cu(II) in tap water and industrial wastewater samples.

| Sample | Added, nmol/L | Found, nmol/L | Recovery (%) |
|---|---|---|---|
| Tap water | 0.5 | 0.49 | 98 |
| | 1 | 0.99 | 99 |
| | 5 | 4.91 | 98.2 |
| industrial wastewater | 0.5 | 0.54 | 108 |
| | 1 | 1.06 | 106 |
| | 5 | 5 | 100 |

## 4. Conclusion

The carbon paste electrode (CPEs) modified with takawt showed a sensitive, precise and accurate response for Cu(II) determinations in tap water and industrial wastewater samples. The developed electrode can be easily prepared and the detection limits of 0.237 nmol/L were achieved under the optimized conditions.

Further work is currently underway in order to investigate optimization of the method for the determination of other metal species of environmental interest.

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