

## Electrochemical Study of the Capacity of *Moringa oleifera* to Chelate Heavy Metals

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### Abstract

We report a sensitive electrochemical voltammetric method for analyzing heavy metals, such, Pd<sup>2+</sup> and Cd<sup>2+</sup> using a modified carbon paste electrodes. 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; Heavy metals; *Moringa oleifera*

### Introduction

Heavy metals have become of particular interest in recent decades within the framework of environmental investigation. This has without doubt been due to the fact that highly sensitive analytical procedures are available for determining and detecting metal content with high precision. Lead, for example, is a toxic heavy metal that appears in the environment mainly due to industrial processes, it is a microelement naturally present in trace amounts in all biological materials, it has no physiological function in the organism. Lead is absorbed by plants through roots where most of the lead is also accumulated. Lead enters the organism with food and air. In children it affects most the central nervous system [1]. Therefore sensitive methods must be established for the trace amounts of lead quantification in human's body fluids, water samples, plants and animals. Some of the methods used for the determination of lead are Atomic Absorption Spectrometry (AAS) [2,3], Atomic Emission Spectrometry (AES) [4] and Mass Spectrometry (MS).

These methods, although highly sensitive, require relatively large volumes of sample for analysis, complicated operation, costly maintenance, expensive apparatus and low electrical power requirement [5]. Electrochemical methods are well known as very powerful techniques for determination of diverse range of metallic and biological targets in environmental, biological and industrial samples.

Modified electrodes are also attracting interest [6,7]. Recent works, reported in the literature, have shown several applications and electro analytical methodologies employing micro-electrodes as working electrodes [8-12]. Mercury based electrodes such as, mercury film electrodes and hanging mercury drop electrodes, has been traditionally used in stripping techniques because of their advantages such as high sensitivity, reproducibility, purity of the surface, high hydrogen over potential, and possibility of the amalgam formation and they have been recognized as the most sensitive electrodes for determination of heavy metals [13]. It has been shown that bismuth film electrodes maintain all the advantages of mercury electrodes and, at the same time, are environmentally friendly as the toxicity of bismuth and its salts is negligible. In addition to their lower toxicity, bismuth film electrodes resulted in compared to the performance of mercury electrodes were less sensitive to dissolved oxygen and had a wide potential window for analysis. However, the determination of copper using bismuth film electrodes has been relatively ignored due to the similar stripping

potentials of copper and bismuth with only a few reports in the open literature [11,12].

Many researchers detected heavy metal ions at modified carbon paste electrode [12], but no researchers using deposited carbon paste onto steel as electrode for the detection of Pb (II) were reported. In this work we prepared and characterized the copper 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 heavy metals.

### Experimental

#### Reagents

Potassium nitrate was dissolved into Bidistilled Deionized Water (BDW) to form 1 mg.L<sup>-1</sup> stock solutions. Working standards for calibration were prepared by diluting the primary stock solution with BDW. Carbon paste was supplied from (Carbon, Lorraine, ref. 9900, French). All chemicals were of analytical grade and used without further purification.

#### Electrodes preparation

Firstly, the carbon-paste electrode was prepared according the following procedure [13]. 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 cm<sup>2</sup>. A bare of carbon vitreous inserted into carbon paste provided the electrical contact, and then the copper film is electro deposited onto carbon paste

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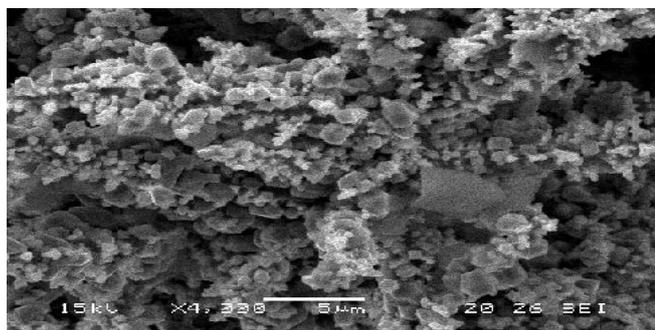


Figure 1: Scanning electron micrograph of Cu-CPE.

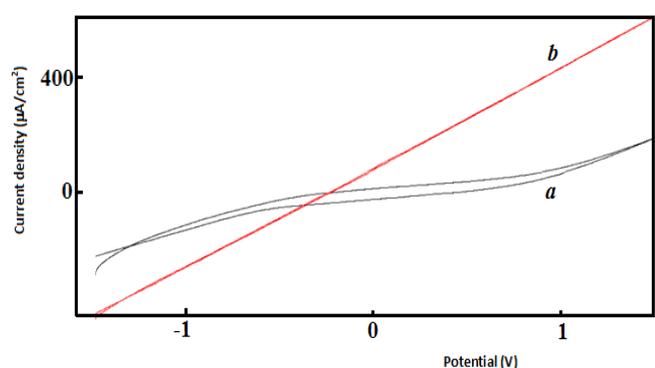


Figure 2: Cyclic voltammograms recorded in electrolytic solution at 100 mV/s at a- carbon paste electrode, b- copper modified carbon paste electrode.

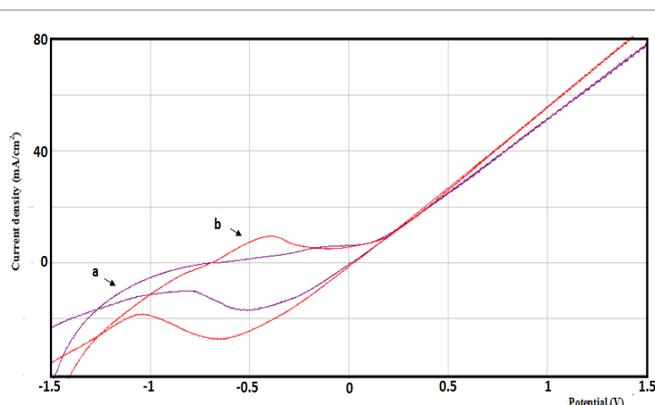


Figure 3: Cyclic voltammograms recorded in electrolytic solution, at 100 mV/s, at copper modified carbon paste electrode, in 0.1 M  $\text{Na}_2\text{SO}_4$  solution (a), and after exposing to cadmium solution.

electrode. The deposit of copper on carbon paste electrode surfaces was processed at 20 V. The current was maintained by a galvanostat with a function generator.

### 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 copper modified Carbon Paste Electrode (Cu-CPE).

### 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 (Volta lab master 4 software).

### Results and Discussion

#### Characterization of prepared electrodes surfaces

The surface structure of copper modified carbon paste surface was observed using scanning electron microscopy (Figure 1). The film layer of copper was formed on the surface of carbon paste electrode; it was not disintegrated or detached from the surface when immersed in the electrolytic solution ( $0.1\text{M Na}_2\text{SO}_4$ ).

The Cyclic Voltammograms (CVs) of the copper modified Carbon Paste Electrode (Cu-CPE) and Carbon Paste Electrode (CPE) were recorded in the supporting electrolyte ( $0.1\text{M Na}_2\text{SO}_4$ ) (Figure 2). We can see that the shape of the cyclic voltammogram was modified in the presence of copper at CPE surface, suggesting that the carbon paste electrode was effectively modified by copper.

#### Electrochemical detection of studied metals

The experimental conditions have been optimized and the response characteristics determined in a previous work [13]. The results obtained are:

- $\text{pH} \approx 7.2$
- Preconcentration time = 15 min.

In order to avoid the strong residual of reduction, the starting potential was fixed at  $-1.5\text{V}$  versus SCE. Figure 3 shows a cyclic voltammograms performed between  $-1.5\text{V}$  and  $1.5\text{V}$  for Cu-CPE, in  $0.1\text{M Na}_2\text{SO}_4$  solution (curve a), and in  $0.1\text{M Na}_2\text{SO}_4$  after exposure Cu-CPE to  $1.0 \cdot 10^{-6}\text{ mol/L Cd}^{2+}$  for 15 min, in a stirred solution (curve b). The reversible system could be observed at Cu-CPE, with cathodic potential value, of  $-0.6\text{V}$  and anodic potential value of  $-0.4\text{V}$ .

The Square Wave Voltammetry (SWV) corresponding to the determination of  $\text{Cd}^{2+}$ , was recorded in the supporting electrolyte (curve a) and after, 15 min of accumulation in a solution containing Cd (II) (curve b). The voltammograms are showed in Figure 4. A well-defined and enhanced peak is observed at Cu-CPE, imprinted in cadmium solution. This peak is attributed to cadmium oxidation.

The performance of the Cu-CPE is tested to, on the preconcentration

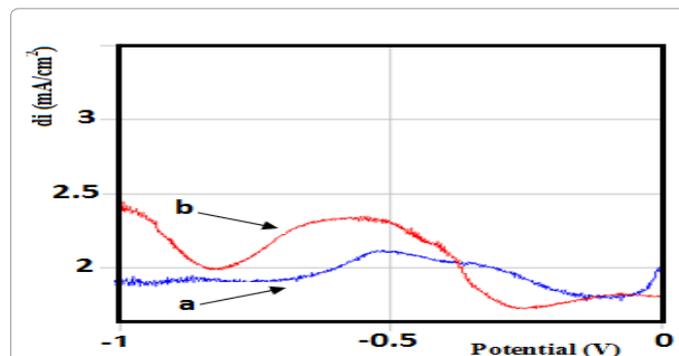
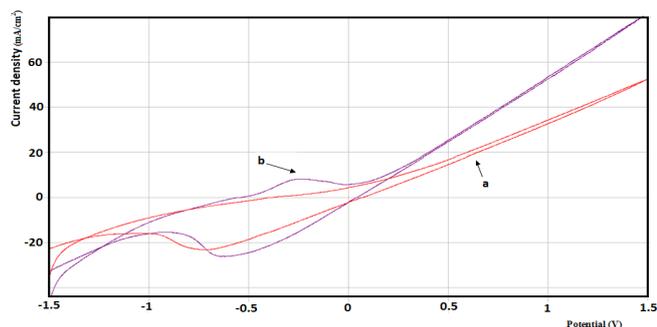
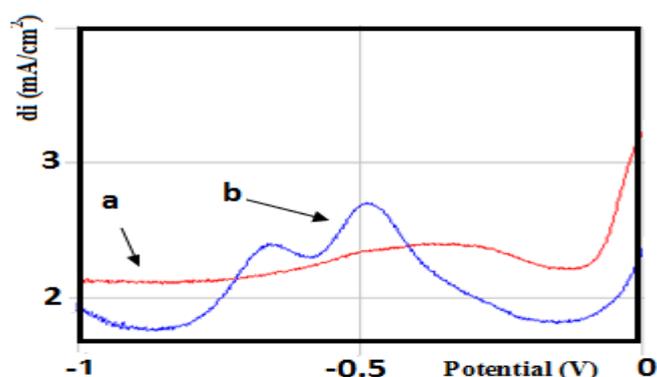


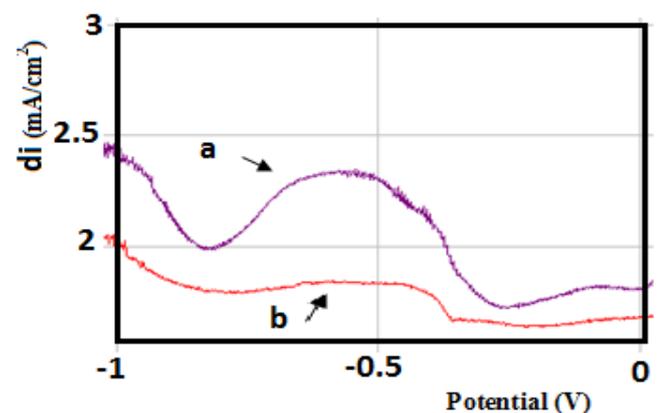
Figure 4: Square wave voltammograms obtained for Cu-pectively, in supporting solution (a), and after exposing electrode to cadmium solution.



**Figure 5:** Cyclic voltammograms recorded in electrolytic solution, at 100 mV/s, at copper modified carbon paste electrode, in 0.1 M Na<sub>2</sub>SO<sub>4</sub> solution (a), and after exposing to lead solution.



**Figure 6:** Square wave voltammograms obtained for Cu-respectively, in supporting solution (a), and after exposing electrode to lead solution.



**Figure 7:** Square wave voltammograms obtained for Cu-respectively, in supporting solution, after exposing electrode to Cd<sup>2+</sup> contaminated solution. (a) – before moringa treatment, b – after moringa treatment.

of Pb<sup>2+</sup> from aqueous solution. As can be seen from Figures 5 and 6, two peaks appears, respectively, in SQW and cyclic voltammograms, the first one attributed to Pb<sup>2+</sup> reduction, at -0.6 V, the second at -0.7 V corresponding to the oxidation of Pb<sup>2+</sup>.

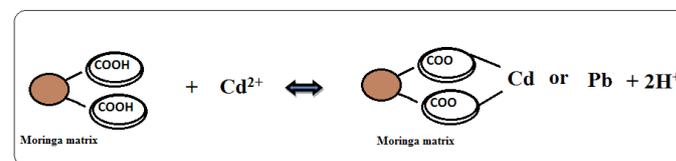
### Chelating effect of *Moringa oleifera*

*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 [14].

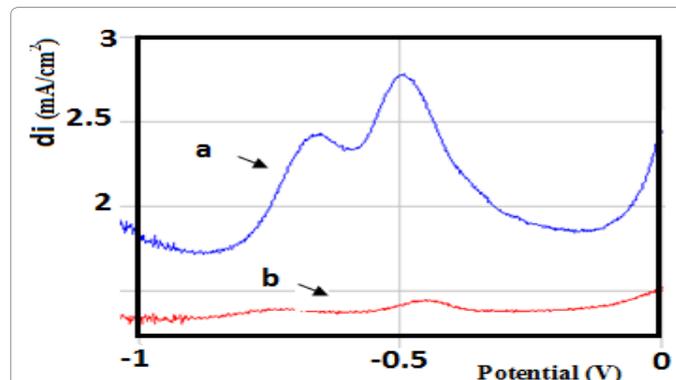
Firstly, the *Moringa oleifera* was prepared according the following procedure [15]. *Moringa oleifera* seeds collected for the analysis were shelled off and sun-dried to maintain constant weight. The sun-dried seeds were grinded into powdered form using machine. The powdered was added to the solutions 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 carbon paste electrode modified with copper film, in supporting solution containing Cd<sup>2+</sup> (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 Cd<sup>2+</sup> and Pb<sup>2+</sup> concentrations, which suggests that Moringa has a strong complexing power of heavy metals (Figures 7 and 8). We not that the solution pH was varied after Moringa treatment. It was decreased from 7.2 to 6.5. The decrease in pH of the treated solution, suggests to us that the Moringa exchanged two protons against the metal ion. The proposed mechanism is as follows:



### Conclusion

In conclusion, it was possible demonstrating the potentiality of the proposed electrodes for determining heavy metals. Such a sensor is characterized by a higher sensitivity and reproducibility. The *Moringa oleifera* seeds have the ability to retain metals. 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



**Figure 8:** Square wave voltammograms obtained for Cu-respectively, in supporting solution, after exposing electrode to Pb<sup>2+</sup> contaminated solution. (a) – before moringa treatment, (b) – after moringa treatment.

most suitable for the treatment of water containing undesirable heavy metal concentrations. The removal efficiencies were 70% for  $Pb^{2+}$  and 60 for  $Cd^{2+}$ . It is an eco-friendly technology that is economically more advantageous than other treatment alternatives.

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