



Carbon Paste Electrode Modified by 2-Benzimidazolethiol Used for the Electrochemical Detection of Lead in Water and Orange Juice Samples

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Abstract A carbon paste electrode modified with 2-Benzimidazolethiole (MO-CPE) was evaluated as an electrochemical sensor for Pb(II) in buffer solution. The electrode was prepared by immobilisation the organic molecule on the carbon paste electrode surface and its complex formation with Pb(II) was studied by square wave voltammetry and cyclic Voltammetry. Interferences by some metals were investigated. Pb²⁺, Hg²⁺ and Cu²⁺ apparently affected the peak currents separate. The carbon paste electrode modified with organic molecule (MO) was applied to the determination of Pb(II) in orange juice and tap water samples. The results indicate that this electrode is sensitive and effective for the determination of Pb(II).

Keywords biosensor; cyclic voltammetry; lead; square wave voltammetry; modified electrode; 2-Benzimidazolethiole

Introduction

Heavy metals are the natural metallic elements whose density exceeds 5g / cm³ [1]. They have high toxicity [2], the most commonly considered poisons for humans are lead (Pb), mercury (Hg), arsenic (As), cadmium (Cd), others such as copper (Cu), zinc (Zn), chromium (Cr) yet necessary to the body in small quantities, but become toxic at larger doses [3,4]. As a consequence their presence in the water, which is a vital resource for life and for human activities, requires the realization of an underwater warning and control device, fast and effective. To do this, biosensors are considered advantageous instruments compared to other existing means that appear heavy and tedious, Indeed, they combine ease and simplicity of use with reliability and speed of measurements. In addition, they have a low manufacturing cost.

One of the essential objectives of electrochemists is the control of the reactivity of the electrode-solution interface. The application of a potential makes it possible to vary the energy level of the interface but generally without control of selectivity. In order to impose and control the properties of the interface, many researchers in several disciplines have modified the surface of electrodes by all kinds of organic or organometallic compounds [5-9].

The carbon paste electrodes (CPEs) are cheaper and are suitable for preparing the electrode material with desired composition and pre-determined properties [10,11]. The electrochemical response of CPE mainly depends on the properties of the modifying species. The modification of the carbon paste electrode can be done by different ways like grinding in an agate mortar [12,13] electro polymerization [14,15] and immobilization method [16].

Experimental

Reagents and chemicals

All the chemicals used in this work, are of high quality. Graphite powder (spectroscopic grade RWB, Ringsdorff-Werke GmbH, Bonn-Bad Godesberg, Germany) was obtained from Aldrich and was used without further purification. HgCl_2 , CuSO_4 and PbSO_4 were obtained from Merck chemicals. Deionised water was used to prepare all solution.

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).

All the electrochemical experiments were performed in a standard one-compartment three-electrode cell. The modified paste electrode (MO-CPE) as the working electrode, a saturated calomel electrode (SCE) serving as reference electrode, and platinum as an auxiliary electrode.

Electrode Preparation

The paste constituting the indicator electrode consists of a mixture of graphite powder and binder (paraffin) [17]. The carbon paste is then shaped into the cavity of an electrode body and then polished to obtain a flat surface. The modified carbon paste electrode (CPE) is obtained by immobilizing the 2-Benzimidazolethiole compounds by soaking the preformed carbon paste electrode in a solution containing the organic molecular solution [18].

Optimization of Experimental Conditions

Electrochemical Behavior

A carbon paste electrode modified with organic molecule (MO-CPE) was carefully washed with distilled water, heated at room temperature and transferred to electrochemical cell containing 0.1 M buffer solution electrolyte pH 7, the contact time of the CPE with MO is 24 hours [18].

Cyclic voltammograms (CV's), recorded simultaneously for the modified carbon paste electrode by the organic molecule (MO-CPE) [19] and the carbon paste electrode (CPE) in an electrolytic medium are illustrated by Fig.1. The shape of the voltammogram has changed considerably in the presence of the organic molecule on the carbon surface, which confirms the modification of the base electrode according to the following proposed reaction:

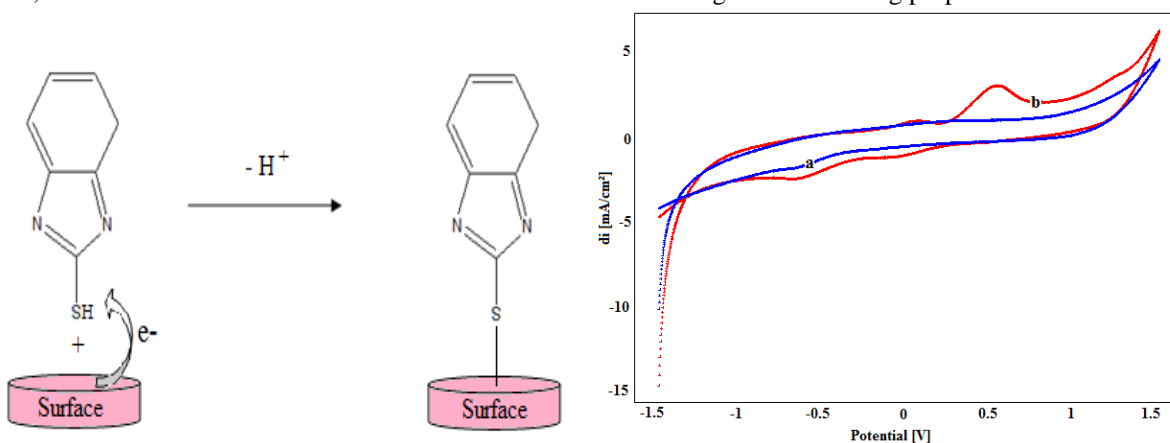


Figure 1: Cyclic voltammograms recorded in buffer solution (pH 7), CPE (a) and MO-CPE (b), scan rate 100 mV/s.

Chelation of lead (II) ions

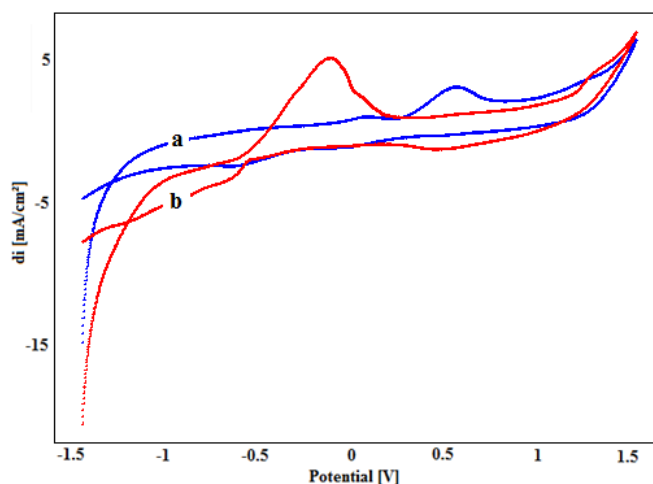


Figure 2: Cyclic voltammograms recorded at the MO-CPE, in a buffer solution, before (curve a) and after (curve b) the accumulation of Pb^{2+} .

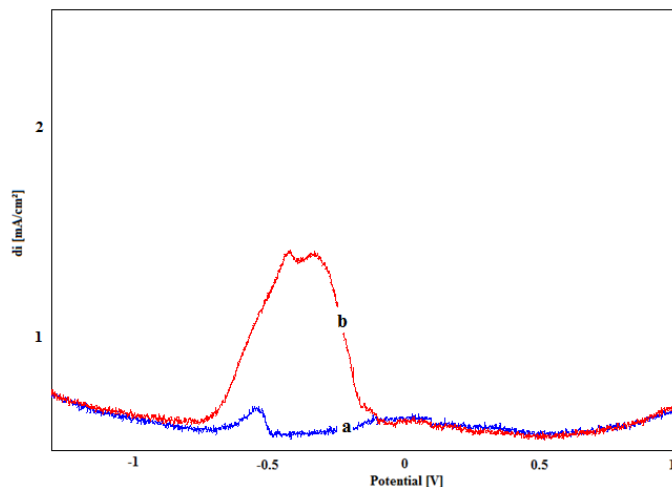


Figure 3: SQW voltammograms recorded at the MO-CPE, in a buffer solution, before (curve a) and after (curve b) the accumulation of Pb^{2+} , at 100 mV/s and pH 7

The electrochemical behavior of lead on MO-CPE was studied by cyclic voltammetry in a 0.1 M solution of trisHCl. The results are shown in Figure 2. After preconcentration in a solution containing 0.602 mmol/l of lead (II). In the sense of cathodic scan, the voltammogram has negative current densities, corresponding to the reduction reaction of accumulated Pb^{2+} ions at the surface of the electrode during the preconcentration step, according to reaction (1). In the direction of anodic scanning, the voltammogram shows a peak around 0.1V, which corresponds to the oxidation of lead on the surface of the electrode according to reaction (2). This result is confirmed by SQV which shows the appearance of two overlapping peaks of oxidation and reduction of Pb^{2+} ions (Fig. 3).



Influence of Accumulation Time

The influence of preconcentration time was examined, in a solution containing Pb^{2+} (3.3 mmol.L⁻¹). The current density of the anode peak increases with the preconcentration time, in particular, between 0 and 40 min. Beyond 5 minutes, the current density becomes almost constant due to the probable saturation of the surface of the modified



electrode (Fig. 4). Subsequently the preconcentration time of the lead, adopted in the previous manipulations is 5 minutes.

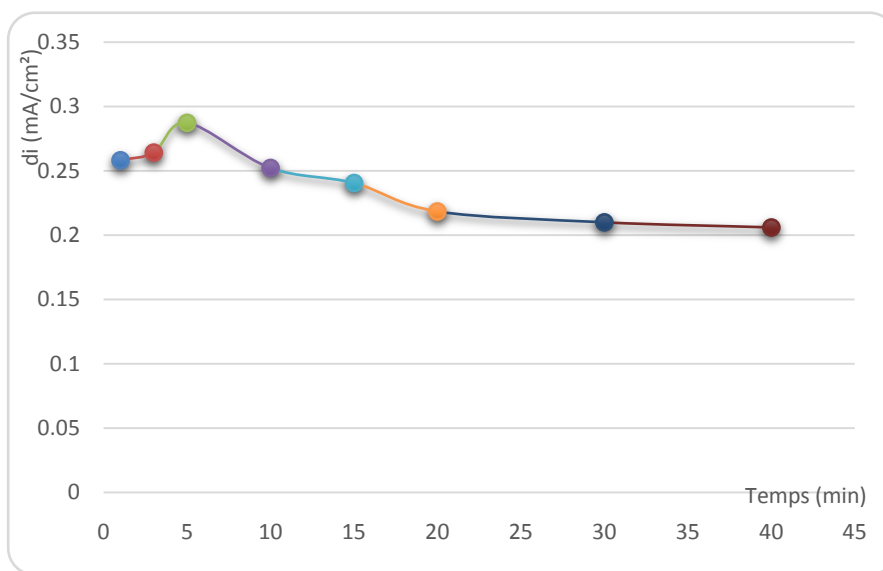


Figure 4: Effect of accumulation time on the oxidation peak of 0.602 mmol/l Pb^{2+} ($pH = 7$) in 0.1M TrisHCl on CPE-MO

Effect of Scan Rate

In Figure 5, we present the cyclic voltammograms, recorded for the carbon paste electrode modified by the organic molecule, at different scan rates (from 40 to 150 mV / S), in an electrolytic medium containing lead.

According to cyclic voltammograms, we observe that the anodic peaks move towards the positive potentials, as the scan rate increases.

In Figure 6, we show the linearity of the evolution of the anodic current densities with the scanning speed, As the current density and the potential of the anodic peak increases with the scan rate, diffusion controlled processes are to be taken into account.

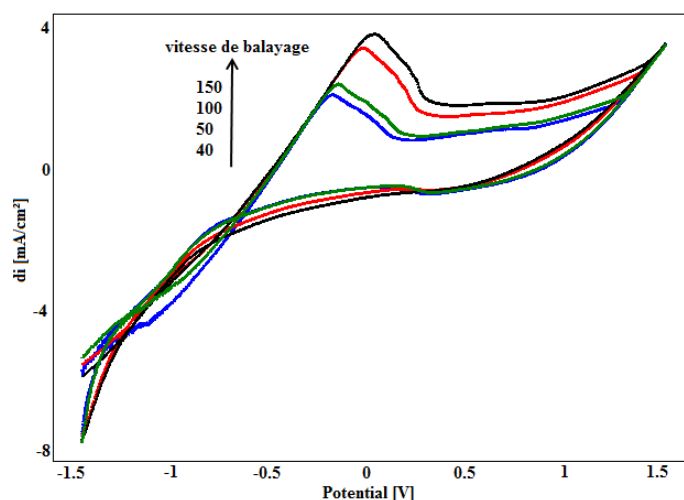


Figure 5: Cyclic voltammogram, recorded, in 0.1M tris HCl solution after accumulation of Pb^{2+} , at different scan rates, for CPE-MO electrode.

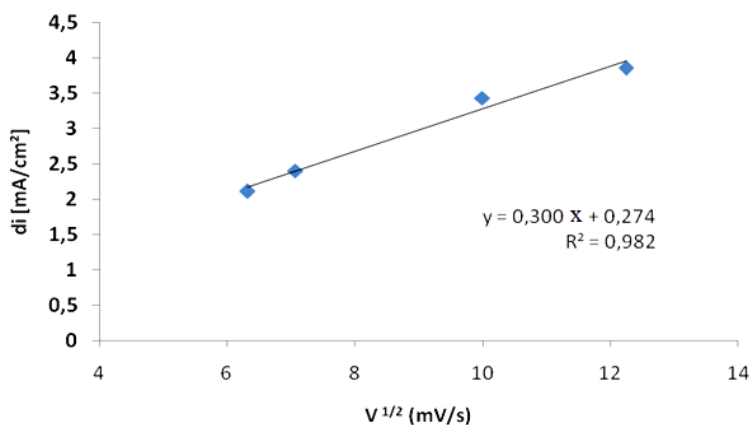


Figure 6: Influence of scan rate on oxidation peak intensities in 0.1M trisHCl solution after accumulation of Pb^{2+} (pH =7).

Ions interference Hg^{2+} , Pb^{2+} and Cu^{2+}

We tested elements that can have some competition at the sites on theMO-CPE (figure 7). These tests were used under optimized conditions.

The voltammogram was traced after preconcentration of the electrode MO-CPE in aqueous solutions of lead nitrate, mercury and copper. the Anodic oxidation of lead occurs at the potential -0.5 V/ECS, less than mercury -0.1 V/ECS. the Peak the oxidation of metallic copper manifests at a potential of +0.21 V/ECS greater than that of mercury oxidation. The clear separation of the three peaks gives us the possibility of dosing the three metals simultaneously.

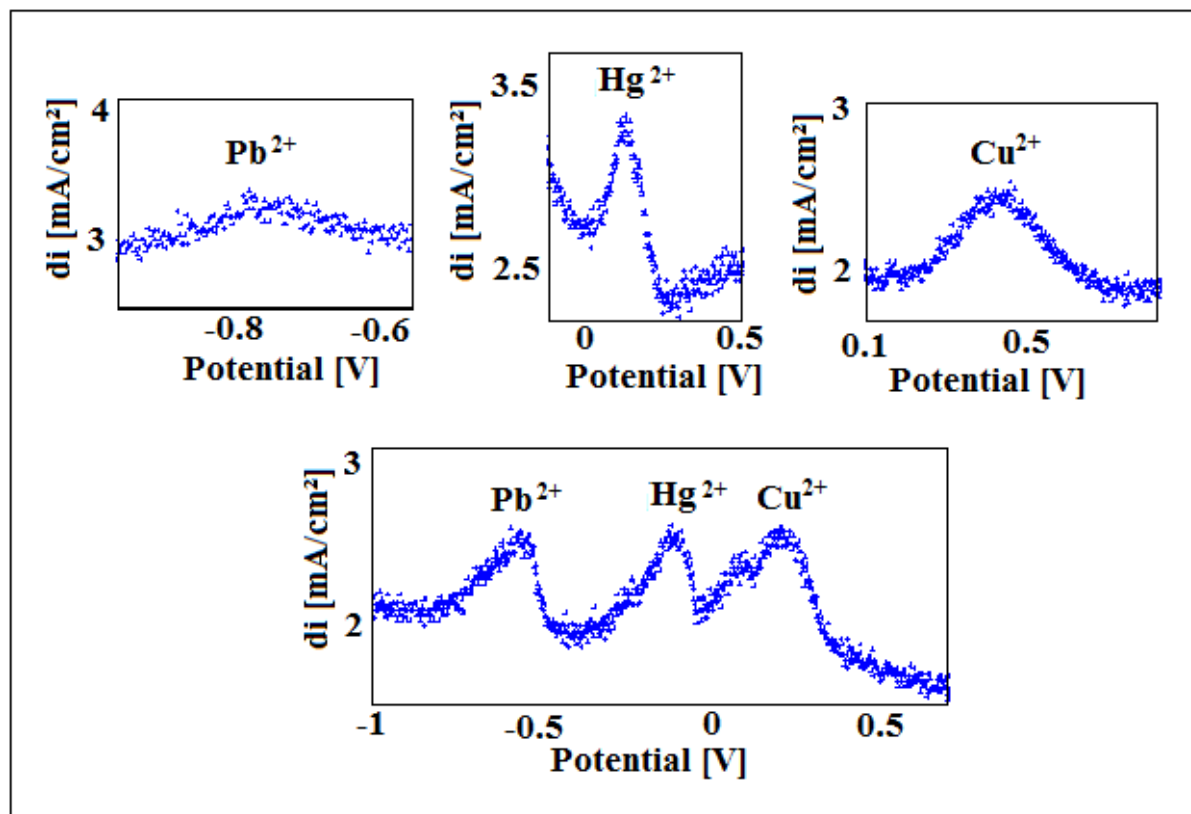


Figure 7: Effect of interferences of the three cations studied in buffer solution



Analytical Application: Orange juice and tap water

We tested the efficiency and sensitivity of the prepared electrodes, the analysis of traces of heavy metals in the orange juice and tap water of the Region de Beni Mellal-Khenifra.

The analysis of metal ions proves difficult, because of the affinity of the cations to form organic complexes. The Figure 8C represent cyclic voltammograms and square waves, recorded by the electrode MO-CPE (modified by electroless) after preconcentration, in optimal conditions, in a solution of orange juice containing 0.602 mmol/l of lead. We note that the cyclic voltammogram of the preconcentrated electrode in the orange juice solution containing the ions Pb^{2+} , is manifested by the appearance of two peaks, the first in the sense of cathodic scan, to approximately -1 V and the second of anodic nature to -0.4V. The two peaks are well defined and correspond respectively to the reduction of Lead (II) and the oxidation of Pb. This result is confirmed by SWV, which shows two intense peaks.

This same experiment was conducted with tap water (Fig. 8D). The VC shows only the peak oxidation of lead, the reduction is poorly defined, because of the strong interference Pb^{2+} with water cations. The SWV does not allow to separate the two peaks (oxidation and reduction) that remain overlapped.

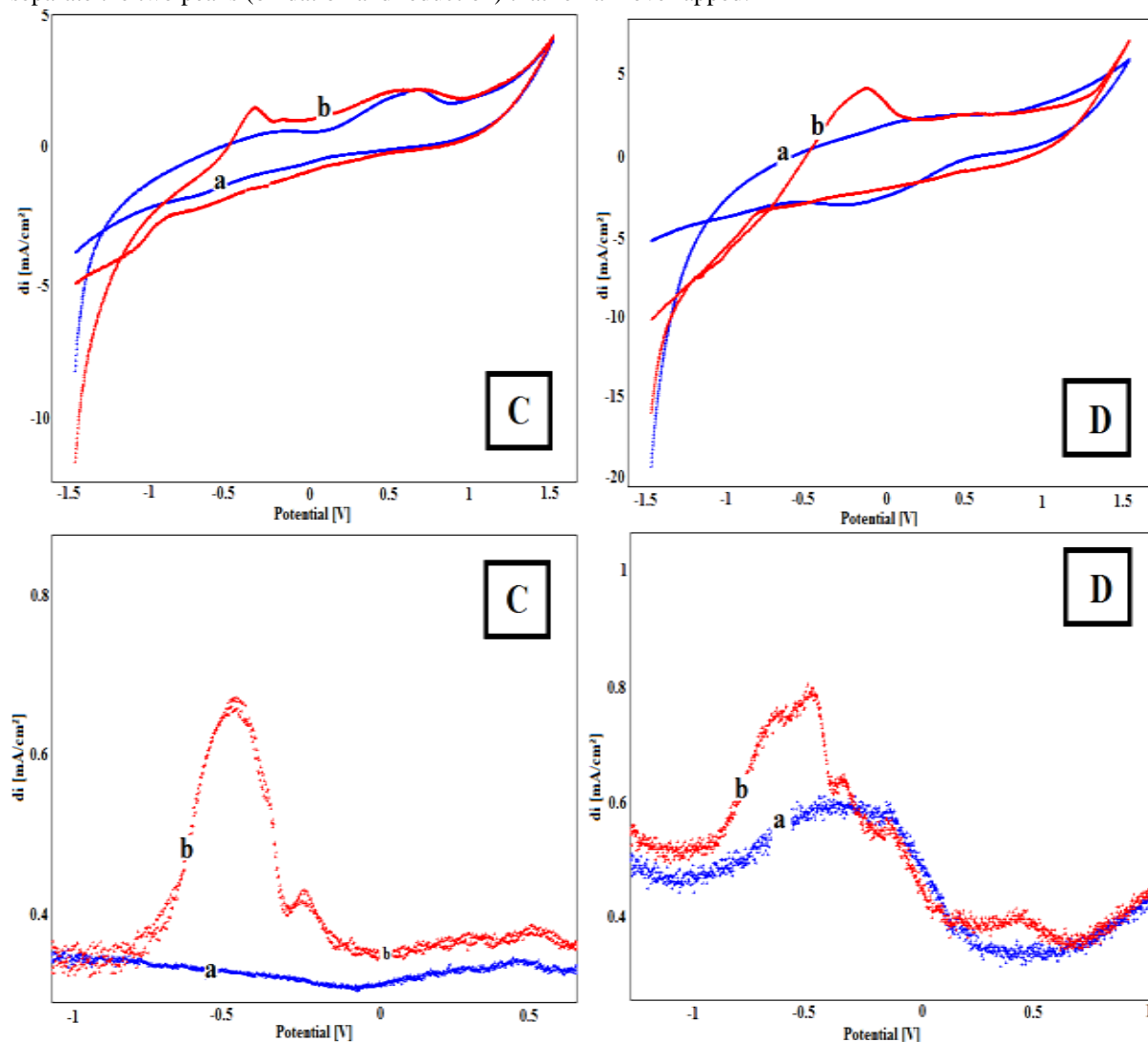


Figure 8: Voltammograms recorded in the two orange juice media (C) and the tap water (D) of the CPE-MO electrode in the presence (b) and absence (a) of lead (II).



Conclusion

The carbon paste electrode modified with 2-Benzimidazolethiole by electroless showed a great activity for chelation of ions Pb^{2+} . The analytical application to real solutions has shown efficiency that despite the effect of interference, the analysis of lead (II) is possible, by following the peak of release (oxidation) of Pb^{2+} ions in the electrolytic solution.

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