Electrochemical Sensor Based on 2-Benzimidazolethiole Modified Carbon Paste Electrode for Lead Chelation Therapy

Sakina Touzara, Rachida Najih and Abdellilah Chtaini*

Equipe d’Electrochimie Moléculaire et Matériaux Inorganique, Faculté des Sciences et Techniques Beni Mellal, Université Sultan Moulay Slimane, Maroc

Abstract

The performance of organic compounds such as, benzimidazolothiole, modified carbon paste electrode was investigated as an electrochemical sensor in the determination of lead in 0.1m phosphate buffer solution at pH 6. The organic product, 2-benzimidazole thiol, was synthesized in the laboratory to be used as modifier of the carbon paste electrode (CPE), and its complex formation with Pb (II) was studied by square wave voltammetry and cyclic voltammetry. It was found that the organic film modified electrode shows a better performance than the carbon paste electrode (CPE). Under optimal conditions, the electrode showed a good linear response to lead (II). The proposed method was applied for possible chelating agent for heavy metals.

Keywords: Square wave voltammetry; Lead; Sensor; Chelation therapy

Introduction

The overload of lead is a highly toxic substance, exposure to which can produce a wide range of adverse health effects. Both adults and children can suffer from the effects of lead poisoning, but childhood lead poisoning is much more frequent. Lead was classified as prevalent toxic metal even at very low concentration and has damaging effects on the plants [1]. Lead is a persistent toxic metal that has the facility to accumulate in humans, animals and plants. According, finding the sensitive, fast and simple analytical method for precise determination and chelating of Pb⁺⁺ is mandatory.

There are some reviews on the use of electrochemical sensors due to the advantages such as high sensitivity, rapidity of response, simplicity, low cost, miniaturized and automated devices [2,3]. The research activities in the preparation of electrochemical sensors for detecting heavy metals have dramatically increases over the past decades with the development of new materials and novel fabrication process [4,5].

Recently assembly of organic layers onto surfaces has been widely used in constructing the electrochemical sensors due to their unique characteristics such as high surface area and strong adsorption ability [6,7].

Carbon paste electrodes chemically modified are endowed with many good qualities, such as ease of handling and applicability to anodic oxidations [8,9]. Different modifiers for carbon paste have been reported in the last years for the electrochemical stripping analysis of heavy metals.

Recently, methods involving radical–based mechanisms have been developed for the modification of carbon surfaces with covalently attached layers of organic species. The deposition of mono or multilayers at the carbon paste surfaces serves the purpose of electrode functionalization for analytical purposes, like electroanalysis of heavy metals [10].

In this paper, a novel electrochemical sensor was developed by incorporation of organic molecules into the paste carbon electrode. These electrodes were used for the chemical preconcentration of lead at trace levels [11]. The organic molecule (2-Benzimidazolothiole) modified carbon paste electrode (MO-CPE) [12] can preconcentrate lead metal from aqueous solution to the surface of the modified CPE by forming complexes with these ions and greatly increasing the sensitivity of its determination. The experimental data show that some of the MO-CPEs have high sensitivity, adequate selectivity and reproducibility, and a wide operative linear range of concentrations for the determination of heavy metals in water samples. The MO-CPEs have the advantages of simple methods of toxic chelation therapy.

Experimental

Reagents and chemicals

All chemicals were of the highest quality. Graphite powder (spectroscopic grade RWB, Ringsdorff-Werke GmbH, Bonn-Bad Godesberg, Germany) was obtained from Aldrich and was used without further purification. PbSO₄ was obtained from Merck chemicals. Deionised water was used to prepare all solution. 2-Benzimidazolothiole was synthesized in our laboratory.

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 reference electrode was SCE and the counter electrode was platinum. All electrode potentials were referred to this reference electrode. The working electrode was MO-CPE.

Electrode preparation

Firstly, the carbon-paste electrode (CPE) 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.

*Corresponding author: Abdellilah Chtaini, Equipe of Molecular Electrochemistry and Inorganic Materials, Faculty of Science and Technology of Beni Mellal, Sultan Moulay Slimane University, Morocco, Tel: +212523485112; Fax: +212523485201; E-mail: a.chtaini@usms.ma

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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$^2$. A bare of carbon vitreous inserted into carbon paste provided the electrical contact. Organic compounds-modified carbon paste electrodes (MO-CPEs) were prepared by immobilizing the 2-Benzimidazolethiole compounds by soaking the preformed carbon paste electrode in a solution containing the organic molecular solution. The effect of the contact time of the CPE electrode with the organic molecular solution was studied. The compound studied in this work is shown in Figure 1.

**Procedure**

The electrode, after having been washed with bidistilled water (BDW) and heated at room temperature, was transferred into the sample cell (20 mL) (the sample was purged with pure nitrogen for 10 min). A preconcentration step was necessary; the working electrode was immersed in water sample in open circuit. The initial working procedure consisted of measuring the electrochemical response of MO-CPE electrode in 0.1 M phosphate buffer electrolyte.

**Results and Discussion**

The cyclic voltammograms (CVs) of the organic molecular modified carbon paste electrode (MO-CPE) [14] and carbon paste electrode (CPE) were recorded in the supporting electrolyte. In cycles between -1.5 and 1.5 V (Figure 2). The effect of the contact time of the CPE electrode with the organic molecular solution was also studied in Figure 2, three times have been considered, 3 hours, 24 hours and 48 hours.

The main comments about these CVs are:

- The shape of the cyclic voltammogram was modified in the presence of organic molecular at CPE surface, suggesting that the carbon paste electrode was effectively modified by MO.

- Appearance of two anodic peaks in the anodic scan, the first one at 0.1 V and the second at about 0.7 V, and one peak in the cathodic scan, at -0.3 V.

- The current density of the anodic and cathodic peaks is more important, when the contact time of the CPE with MO is 24 hours.

Figure 3, As can be seen, the peak currents at modified electrodes are significantly higher than that at CPE electrode because of the preconcentration ability of the modified electrode. It clearly indicated the high activity and feasible chelating of the lead (II).

The corresponding square wave voltammograms (Figure 4) confirm these results. The release peak of the Pb$^{2+}$ ion reduced at the cathodic scan is not well defined, due to complexation with the organic film formed on the electrode surface [15].

The anodic and cathodic peaks of Pb$^{2+}$ were measured by square voltammetry. As the curves shows in Figure 5, there is a positive correlation between the concentration of lead ion and the peaks current. The peak current increases linearly with the concentration of Pb (II).

The influence of pH on the lead ion chelating with organic molecular modified carbon paste electrode was studied in the pH range of 5 to 8. The results obtained (Figures 6 and 7) for MO-CPE (contact time=24 hours), show that the oxidation peak increased with decreased pH. The decrease in peak currents at higher pH values could be due to the formation of lead hydroxide complexes at basic pH values, which prevents the accumulation of Pb$^{2+}$. Among the various electrolytes, such Na$_2$SO$_4$, NaCl, phosphate buffer solutions were examined for the
After lead determination, the best results were obtained in the phosphate buffer media. Thus, a phosphate buffer solution of pH 5 was adopted as supporting electrolyte.

The Figure 8 shows the optical microscopic images, recorded respectively, for CPE (a) and MO-CPE (b) electrode after lead complexation. We note that the organic film forms a thin layer that covers the entire carbon surface.

**Conclusion**

In this study, we introduced a voltammetric sensor for the determination of lead ion based on an organic molecular modified carbon paste electrode. Organic compound was synthesized, and its complex formation with Pb²⁺ was studied by electrochemical means. The contact time of organic molecular with carbon paste electrode effect was studied, and the supporting electrolyte pH was examined. The effect of the amount of Pb²⁺ accumulated at the electrode surface was studied. In view of this, we work on the validation of the proposed method and also the study of the interference of different metals such as Zn²⁺, Cd²⁺, Fe³⁺, etc.

**References**