

Development of Carbon Paste-2-Benzimidazolthiole-Polymer Biosensor for Heavy Metals Chelation Therapy

Touzara S^{1*}, Laghlimi C¹, Cheikh Ould S'id E², Chamekh M², Kheribech A³, Chtaini A¹

¹Molecular Electrochemistry and Inorganic Materials Team, Beni Mellal Faculty of Science and Technology, Sultan Moulay Slimane University, Morocco; ²Faculty of Science and Technology, University of Science, Technology and Medicine, B.P. 5026, Nouakchott, Mauritania; ³Faculty of Sciences, Laboratory of water and environment (Team Biomaterials and Electrochemistry), University Chouaib Doukkali, ElJadida, Morocco

ABSTRACT

The method used to fix the polymer on the surface of the new electrochemical biosensor the MO-CPE has proved its effectiveness for the detection and chelation of heavy metals. Its complex formation with Pb (II) was studied by square wave voltammetry and cyclic voltammetry. It was found that the polymer film modified MO-CPE electrode shows a better performance than the carbon paste electrode modified by 2-benzimidazolthiole organic molecule (MO-CPE).

Keywords: Biosensor; Heavy metals; Cyclic voltammetry; Polymer

INTRODUCTION

Heavy metals have high toxicity [1]. As a consequence, their presence in the water, which is a vital resource for life and for human activities, requires the realization of a device of alert and control immersed, fast and effective. 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]. The Carbon Paste Electrodes (CPEs) are cheaper and are suitable for preparing the electrode material with desired composition and predetermined properties [5,6]. 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, electropolymerization and immobilization method [7-11].

MATERIALS AND METHODS

Apparatus

Electrochemical experiments were performed using a voltalab potentiostat (model PGSTAT 100, Eco Chemie B. V., Utrecht, The

Netherlands) controlled by the general purpose electrochemical systems data processing software (voltalab master 4). 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 EDTA-CPE.

Reagents

All chemicals were of the highest quality. Graphite powder (Carbone, Lorraine, ref 9900, French) was used without further purification. All other reagents used were of analytical grade. Bidistilled deionized water (BDW) was used throughout the work.

Preparation of the CPE

The Carbon Paste Electrode (CPE) was prepared by thoroughly hand-mixing of graphite powder. The obtained paste was dried at room temperature then a portion of the resulting paste was grounded and packed firmly into homemade PTFE cylindrical tube (geometric area 0.1256 cm²) electrode. Electrical contact was established with a bar of carbon. EDTA-CPE's were prepared by immobilizing the EDTA by soaking the preformed carbon paste electrode in a solution containing the EDTA solution (Figure 1). And thereafter the surface of the prepared electrode is covered

Correspondence to: Touzara S, Molecular Electrochemistry and Inorganic Materials Team, Beni Mellal Faculty of Science and Technology, Sultan Moulay Slimane University, Morocco, E-mail: s.touzara@usms.ma

Received: June 02, 2019, **Accepted:** February 29, 2020, **Published:** March 13, 2020

Citation: Touzara S, Laghlimi C, Cheikh Ould S'id E, Chamekh M, Kheribech A, Chtaini A (2020) Development of Carbon Paste-2-Benzimidazolthiole-Polymer Biosensor for Heavy Metals Chelation Therapy. J Appl Pharm 12: 271. doi: 10.35248/2167-7956.20.9.271

Copyright: © 2019 Touzara S, et al. This is an open access article distributed under the term of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

by the polymer PSF/PAA: 95/05 (poly (acrylic acid) (PAA) of concentration equal to 5%, and Polysulfone (PSF) of concentration 95%), glued on the edges with Araldit [12,13].

Electrochemical behavior of polymer modified electrode

Electrochemical characterization of the prepared electrode, Carbon Paste Modified by the Organic Molecule (CPE-MO), was performed by cyclic voltammetry (Figure 2). We find that the voltammogram recorded for the modified electrode (curve b) is remarkably different from that obtained for the electrode CPE (curve a). This confirms the deposition of the molecule on the surface of the carbon paste. The MO-CPE electrode prepared by electroless of a benzimidazolthiole film on the surface of the carbon paste electrode has shown great activity of chelation and analysis of Pb^{2+} ions [14]. However, these electrodes are predisposed to the phenomenon of dissolution due to several factors, such as pH for example, to remedy this problem, we thought to cover these electrodes with a selective polymer (polyacrylic synthesized), which protects the surface of the electrode while preserving its activity.

Electrochemical behavior of the Polymer-MO-CPE electrode

Foremost, we studied the electrochemical behavior of the carbon paste electrode (CPE) covered by the polymer, in a buffer solution to pH-7. Recorded cyclic voltammograms, respectively for electrodes CPE and polymer-CPE at 100 mV/s are given in Figure 3. It can be seen that the presence of the polymer (PSF/PAA: 95/05) on the surface of the CPE causes a decrease in the current density due to the lower conductivity of the electrode. The behavior of the MO-CPE electrode covered by the polymer is different; the cyclic voltammogram keeps the initial pace, that of the electrode MO-CPE (Figures 4 and 5).

Activity of the polymer electrode -MO-CPE

The activity of the polymer-MO-CPE electrode is evaluated with respect to the chelation of Pb^{2+} ions. Figure 6 illustrates the cyclic voltammograms recorded in an electrolytic medium, for the polymer-CPE electrodes and polymer-MO-CPE preconcentrated under optimal conditions in a solution containing the lead (II) ions. As we can see electrode polymer-CPE is less active than the electrode polymer-MO-CPE, confirming that the presence of the organic film catalyses the reduction of Pb^{2+} ions, by accumulating it on the surface, knowing that pre-concentration is the limiting step of the reaction.

Chelation of lead (II) ions

Electrochemical behavior, lead on CPE-MO-Polymer was studied by cyclic voltammetry in a 0.1 M solution of trisHCl and with a scan rate equal to 100 mV.s⁻¹. The results are shown in Figure 7.

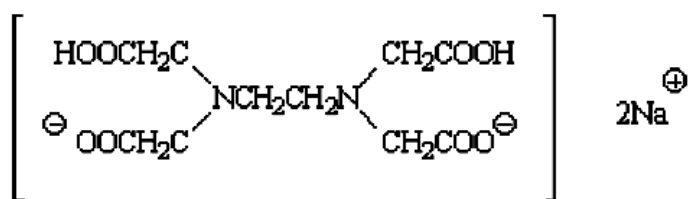


Figure 1: Disodium ethylene-diamine-tetra-acetate dihydrate.

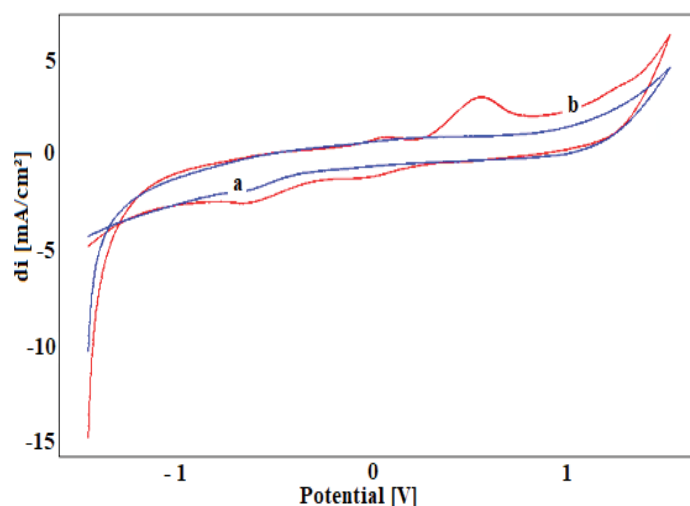


Figure 2: Cyclic voltammograms of CPE (curve a) and MO-CPE, recorded at a scan rate of 0.1 v/s in a solution of 0.1 M trisHCl, pH 7.

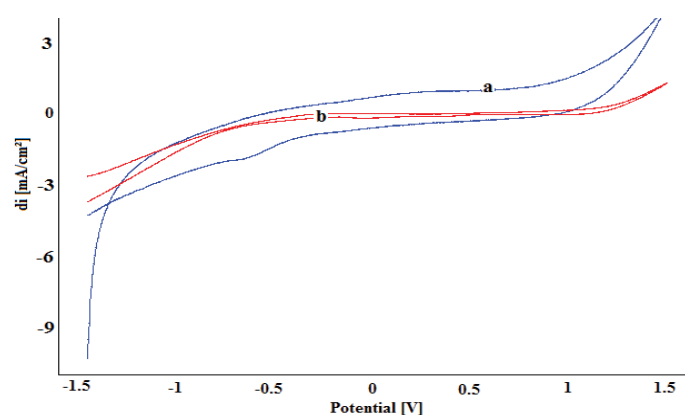


Figure 3: Cyclic voltammograms of CPE (curve a) and Polymer-CPE, recorded at a scan rate of 0.1 v/s in a solution of 0.1 M trisHCl.

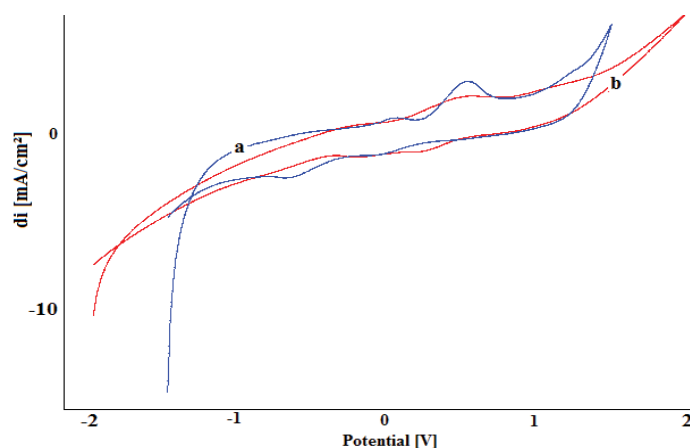


Figure 4: Cyclic voltammograms of the MO-CPE (curve a) and Polymer-MO-CPE (curve b), recorded at a scan rate of 0.1 v/s in a 0.1 M trisHCl solution.

After pre-concentration in a solution containing 0.602 mmol/L of lead (II). We see a considerable increase in current densities.

Variation of the scan rate

Figure 8 shows the cyclic voltammograms recorded for the Polymer-MO-CPE electrode, at different rates of scans. The general form voltammograms is not reached. On the other hand, the effect of the scanning rate is remarkable on the densities of the currents,

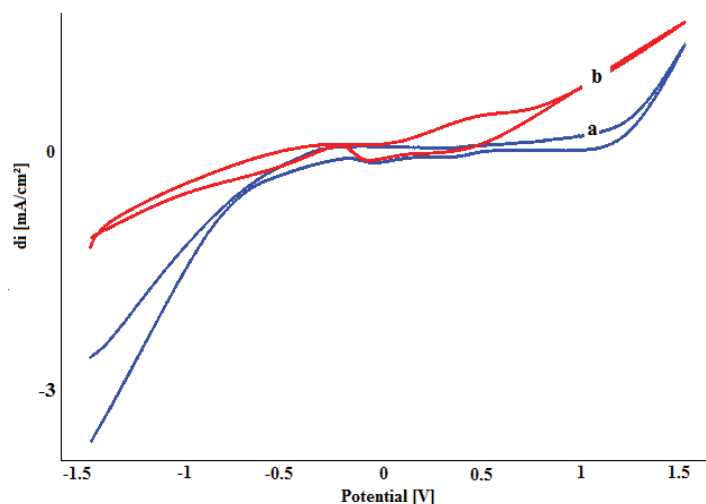


Figure 5: Cyclic voltammograms of CPE-Polymer (curve a) and Polymer-MO-CPE (curve b), recorded at a scan rate of 0.1 v/s in 0.1 M trisHCl solution.

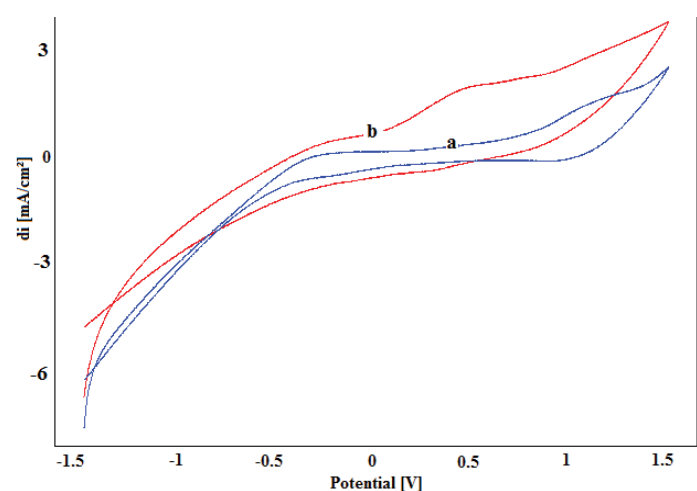


Figure 6: Cyclic voltammograms of CPE-Polymer (curve a) and Polymer-MO-CPE (curve b), recorded at a scan rate of 0.1 v/s in a solution of 0.1 M trisHCl, after the accumulation of 0.602 mmol/L of lead.

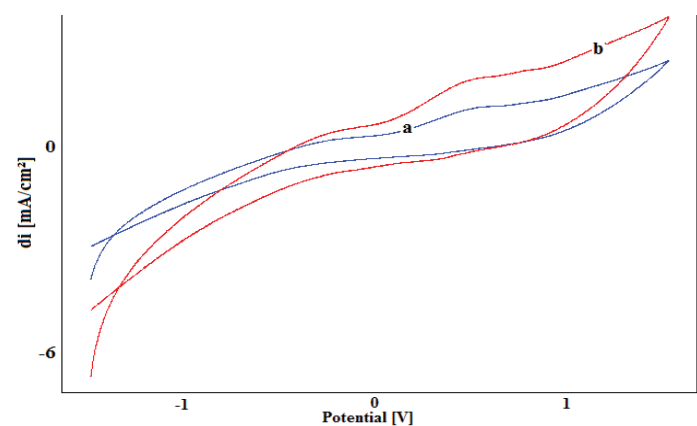


Figure 7: Cyclic voltammograms of Polymer-MO-CPE in absence (curve a) and presence of 0.602 mmol/l of Lead (curve b) recorded at a scan rate 0.1 v/s.

when the scanning rate increases the current density increases, due to the release of active sites.

Calibration curve

The change in current density as a function of lead concentration was followed by square wave voltammetry in a solution 0,1M of

trisHCl, after pre-concentration of the electrode in solutions containing different concentrations of Pb²⁺ (Figure 9). We have established the calibration curve, given in Figure 10. Current densities increase linearly with the concentration of lead. This linearity is expressed by the following relation [15,16]:

$$di = 1.0467 [\text{lead}] + 0.1378 \quad R^2 = 0.9517$$

- The limit of detection: $1.77 \times 10^{-8} \text{ mol.L}^{-1}$
- The limit of quantification: $4.4 \times 10^{-8} \text{ mol.L}^{-1}$

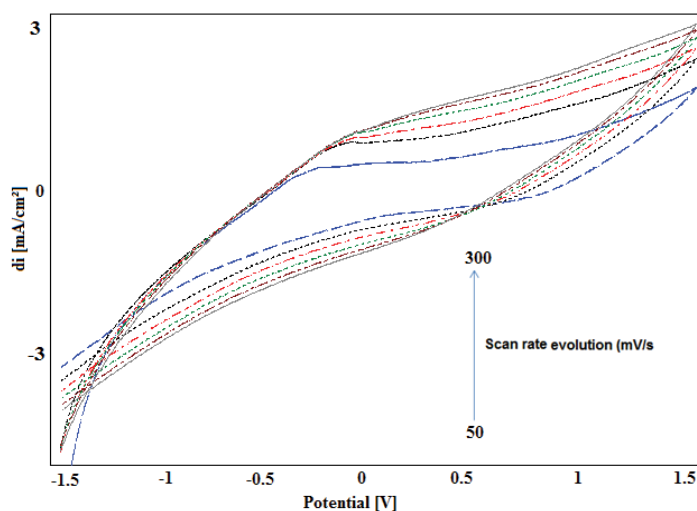


Figure 8: Cyclic voltammograms of Polymer-MO-CPE, recorded at different scan rates in 0.1M trisHCl solution after accumulation of 3.01 mmol/L of lead.

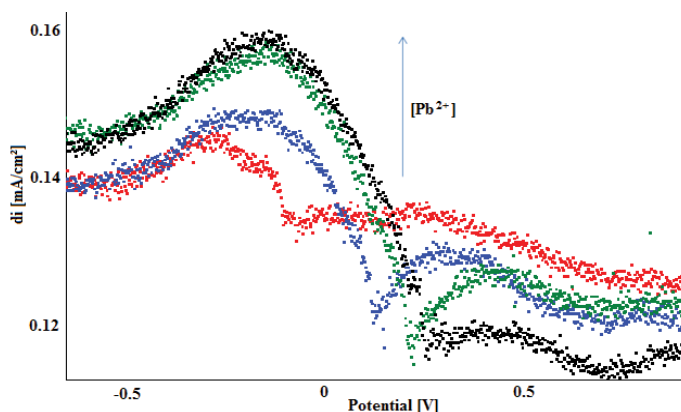


Figure 9: Square wave voltammograms of Polymer-MO-CPE, recorded at scan rates of 0.1 mv/s in a 0.1M solution of trisHCl at different lead concentrations.

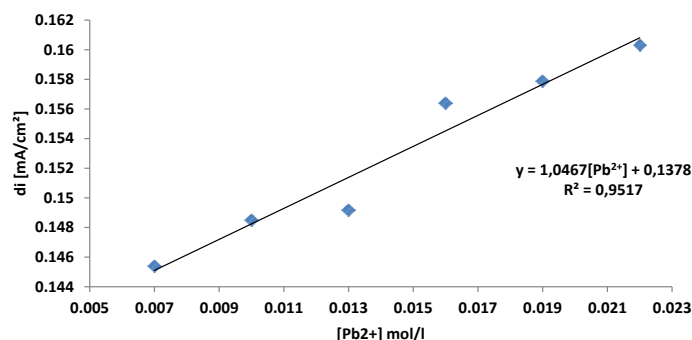


Figure 10: Evolution of the electrical density with the concentration of lead.

Table 1: Comparison between MO-CPE and polymer-MO-CPE electrodes.

S. No	Electrodes	DL (mol.l ⁻¹)	QL (mol.l ⁻¹)
1	CPE-MO	3.57×10^6	1.19×10^5
2	CPE-MO-Polymer	1.77×10^8	4.4×10^8

We find that the presence of the polymer increases the sensibility of the electrode (Table 1). As has been demonstrated previously, the polymer used ensures a selectivity of Pb²⁺ ions which, once passed through the membrane, will be chelated by the protected organic film.

CONCLUSION

In this work, a new electrochemical sensor has been developed by deposition of organic molecules on the surface of the carbon electrode and coating the surface of this electrode with the polymer. These electrodes have been used for chemical preconcentration of lead at trace levels. The modified carbon paste electrode (MO-CPE) by the organic molecule (2-benzimidazolethiole) and coating by polymer can preconcentrate the metallic lead in aqueous solution on the surface of the modified CPE by forming complexes with these ions and considerably increases the sensitivity of its determination. Electrodes modified with 2-benzimidazolethiole revealed remarkable electroactivity after polymer coating with 2-benzimidazolethiole as an anchor layer, the polymer coating has shown improved performance for this modified electrode, which confirms that the deposited film is protected by the polymer coating.

REFERENCES

1. Yi Y, Yang Z, Zhang S. Ecological risk assessment of heavy metals in sediment and human health risk assessment of heavy metals in fishes in the middle and lower reaches of the Yangtze River basin. *Environ Pollut.* 2011;159(10):2575-2585.
2. El-Ouafy T, Chtaini A, Oulfajrete H, Najih R. Electrochemical studies and cyclic voltammetry of 3-nitroptalic acid. *Res & Rev Electro Chem.* 2014;5(4):118-123.
3. Gao H, Qi X, Chen Y, Sun W. Electrochemical deoxyribonucleic acid biosensor based on the self-assembly film with nanogold decorated on ionic liquid modified carbon paste electrode. *Anal Chim Acta.* 2011;704(1-2):133-138.
4. Wang J. Nanoparticle-based electrochemical DNA detection. *Anal Chim Acta.* 2003;500(1-2): 247-257.
5. Švancara I, Vytras K, Barek J, Zima J. Carbon paste electrodes in modern electroanalysis. *Crit Rev Anal Chem.* 2004;31(4):311-345.
6. Rice ME, Galus Z, Adams RN. Graphite paste electrodes: Effects of paste composition and surface states on electron-transfer rates. *J Electroanal Chem Interfacial Electrochem.* 1983;143(1-2):89-102.
7. Reddy S, Swamy BK, Chandra U, Sherigara BS, Jayadevappa H. Synthesis of CdO nanoparticles and their modified carbon paste electrode for determination of dopamine and ascorbic acid by using cyclic voltammetry technique. *Int J Electrochem Sci.* 2010;5(1)10-17.
8. Tanuja SB, Swamy BEK, Vasantakumar KP. Electrochemical response of dopamine in presence of uric acid at pregabalin modified carbon paste electrode: A cyclic voltammetric study. *J Anal Bioanal Tech.* 2016;7(1):1-6.
9. Gilbert O, Chandra U, Swamy BK, Char MP, Nagaraj C. Poly (alanine) modified carbon paste electrode for simultaneous detection of dopamine and ascorbic acid. *Int J Electrochem Sci.* 2008;3(1):1186-1195.
10. Gilbert O, Swamy BK, Chandra U, Sherigara BS. Electrocatalytic oxidation of dopamine and ascorbic acid at poly (Eriochrome Black-T) modified carbon paste electrode. *Int J Electrochem Sci.* 2004;4(1):582-591.
11. Shankar SS, Swamy BK, Ch U, Manjunatha JG, Sherigara BS. Simultaneous determination of dopamine, uric acid and ascorbic acid with CTAB modified carbon paste electrode. *Int J Electrochem Sci.* 2009;4(1):592-601.
12. Nguyen QT, Alexandre S, Zimmerlin I. Fabrication of ion-exchange ultrafiltration membranes for water treatment: I. Semi-interpenetrating polymer networks of polysulfone and poly (acrylic acid). *J Memb Sci.* 2006;278(1-2):10-18.
13. Chtaini A, Touzara S, Cheikh Ould S'Id E, Chamekh M, Mabrouki M. Development of graphite-DNA polymer composites as electrode for methanol fuel cells. *Mat Sci Eng.* 2014;6(1):333-340.
14. Touzara S, Najih R, Chtaini A. Electrochemical sensor based on 2-benzimidazolethiole modified carbon paste electrode for lead chelation therapy. *J Biomol Res Ther.* 2016;5(1):137-142.
15. Paneli MG. Applications of adsorptive stripping voltammetry in the determination of trace and ultratrace metals. *Electroanalysis.* 1993;5(5-6):355-373.
16. Kotkar R, Srivastava K. Voltammetric determination of paraaminobenzoic acid using carbon paste electrode modified with macrocyclic compounds. *Sensors and Actuators.* 2006;60(1):271-279.