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Electrochemical Detection of Lead Ions by 2-Benzimidazolethiol-modified Carbon Paste Electrode Prepared by Inset Modification: A Voltammetric Study

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Abstract

In this work, an electrochemical sensor was prepared by modifying a carbon paste with the organic molecule of 2-benzimidazolethiol (CPE/OM) by mixing methods (by combination of the organic molecules and the carbon electrode). The sensor was tested for detection of lead ions in an aqueous solution. All reactions studied took place on the modified electrode surface, the place of contact between the electrode and the electrolytic medium. For this reason, the electrochemical properties of the CPE/OM, including cyclic voltammetry and square wave voltammetry techniques, were used. Cyclic voltammetry studies have indicated the reaction involved. The determination of lead was carried out utilising the voltammetric technique at the surface of the modified electrode, and the correlation between the current of peak oxidation and the concentration of this ion showed a detection limit (DL) of $3.43 \cdot 10^{-6}$ mol l^{-1}. The experimental results proved that the carbon paste electrode modified with 2-benzimidazolethiol had high sensitivity toward lead ions and a wide linearity range.

Keywords

Cyclic voltammetry, heavy metals, organic molecule, sensor, modified electrode

1 Introduction

Lead overload is highly toxic; exposure to this substance can produce a range of adverse health effects.[1–4] Adults and children can suffer due to the effects of lead poisoning but lead poisoning in children is much more common. Lead has been classified as a toxic metal, even widespread at very low concentrations it has detrimental effects on plants. Lead is a persistent toxic metal that can accumulate in living beings and plants.[5–9] Finding the sensitive analytical method, rapid and simple determination, and precise chelation of Pb^{2+} is therefore mandatory.[10–15] Electrochemical analysis for heavy metals in solutions has been performed using organic and biological molecules as complexing agents.[16–18] Volumetric analysis of traces of lead was performed using electrodes modified by organic and biological molecules such as DNA, EDTA, *etc.*[19–21] In addition, a new, modified carbon paste electrode has been developed and used for the analysis of lead ions in ionic solutions.[22–24] The preconcentration and detection of lead was enhanced by modifying the CPE electrode with 2-benzimidazolethiol.[24] These analyses were performed for the purpose of determining heavy metals using the modifications of the electrode surface. However, for heavy metal analysis in a solution, further development of modification methods was required. For this purpose, another modification of the CPE electrode with 2-benzimidazolethiol was used to analyse the lead content in solution.

In this work, a new electrochemical sensor was employed by the incorporation of organic molecules into the carbon electrode. These new electrodes were used for the chemical preconcentration of lead to trace levels. The CPE modified by the organic molecule 2-benzimidazolethiol, whose structure is given in Fig. 1, can preconcentrate metallic lead in aqueous solution on the surface of the modified CPE by forming complexes with these ions, which greatly increases the sensitivity of its determination. Experimental data showed that some CPEs/OM's have high sensitivity, reproducibility, and a large operational linear range of concentrations for the determination of lead in solution.

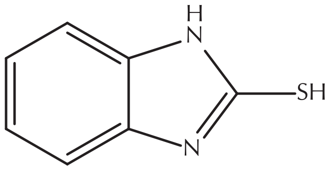

Fig. 1 – Structural formula of 2-Benzimidazolethiol

2 Experimental

2.1 Apparatus

In the electrochemical experiment, a conventional three-electrode cell configuration was used throughout, consisting of a working electrode (CPE or CPE/OM), a plati-

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num-plate counter electrode, and silver chloride electrode (Ag/AgCl) reference electrode. All manipulations were done by a Voltalab potentiostat (model PGSTAT 100, Eco Chemie BV, Utrecht, Netherlands) controlled by the Voltalab Master 4 software.

2.2 Reagents

All chemicals were of analytical grade and underwent no further purification. All solutions were made with double-distilled water. Tris-HCl buffer solutions (c = 0.1 mol m^{-3}) of different pH values were used as electrolyte carriers for the determination of lead. $PbSO_4$ was obtained from Merck KGaA (Darmstadt, Germany). Carbon paste (spectroscopic grade RWB, Ringsdorff-Werke GmbH, Bonn-Bad Godesberg, Germany) was acquired from Aldrich.

2.3 Preparation of the CPE and CPE/OM

The CPE electrode was made by mixing carbon powder with a binder. In this work, liquid paraffin was used which is a non-conductive binder. The paste obtained was shaped in an electrode body (geometric surface area of approximately 0.13 cm^2), the electronic conductivity was ensured by a carbon bar. The CPE/OM electrode was made in the same way as CPE; by mixing the carbon powder and the organic molecule (OM) powder at equal percentages by mass (50 % carbon and 50 % 2-benzimidazolethiol) in the presence of a binder.

2.4 Procedure

In order to test the power of CPE/OM electrode to detect lead ions, the electrode (CPE/OM or CPE), after being washed with double-distilled water, was transferred to the electrochemical capacity cell (100 ml). A preconcentration step was necessary; in this step, the working electrode was precentered in an analyte solution of Pb^{2+} at open circuit, followed by an electrochemical measurement of the preconcentrated analyte on the surface of the electrode in an electrolyte solution of background of 0.1 mol m^{-3} Tris-HCl without analyte.

3 Results and discussion

Firstly, the cyclic voltammograms were recorded, respectively, for the bare CPE and CPE/OM electrodes in acidic buffer medium and at 100 mV s^{-1} (Fig. 2). Comparison of the two voltammograms revealed that they were not of the same form, which in electrochemistry corresponds to a change in the morphology of the electrode surface. This change was characterised by a low current density and the appearance of an oxidation peak (around 1 V) attributed to a functional group carried by the organic molecule.

To study the impact of pH, the CVs were plotted in three electrolytic media: acidic buffer solution, neutral buffer solution, and basic buffer solution at different pH (4.6, 7.4, and 10.3), for the prepared electrode, before and after accumulation of Pb^{2+} ions (Figs. 3 and 4). In the absence of the preconcentration of the lead ions, the voltammograms practically had the same forms for the three pH values; they differed only in current densities, which were relatively high at acidic and neutral pH. After preconcentration of the modified electrode in a solution comprising Pb^{2+} ions, CVs recorded at acidic and neutral pH showed a well-defined anodic peak: at 0 V at acidic pH and 0.4 V at neutral pH. It could be observed that, at basic pH, the electrode showed almost no activity regarding reduction of Pb^{2+} ions. The highest current densities of the anode peak were obtained at pH 4.6. A pH below 4 was avoided to prevent the problem of electrode surface dissolution. The decrease in current density with increasing pH could be explained by the gradual increase in the formation of lead hydroxide $Pb(OH)_2$. Insert graph confirmed the results obtained by the voltammograms recorded by CV (Fig. 4), which shows that pH 4.6 gave the best result compared to other pH values, after the accumulation of Pb^{2+}.

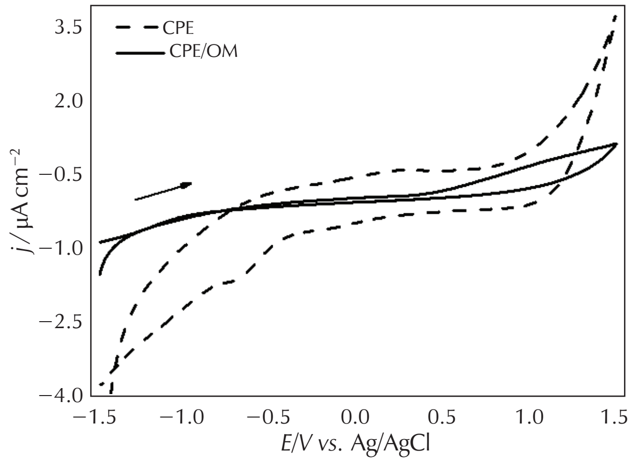


Fig. 2 – Cyclic voltammograms recorded in a buffer solution, at pH 4.6, scan rate 100 mV s^{-1}, potential interval from −1.5 to 1.5 V

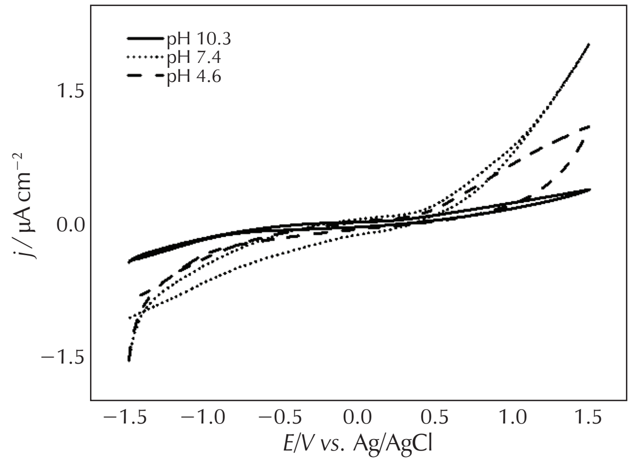


Fig. 3 – Voltammograms recorded in a 0.1 mol m^{-3} Tris-HCl solution at different pH for the CPE/OM electrode. Scan rate 100 mV s^{-1}. Potential interval from −1.5 to 1.5 V.

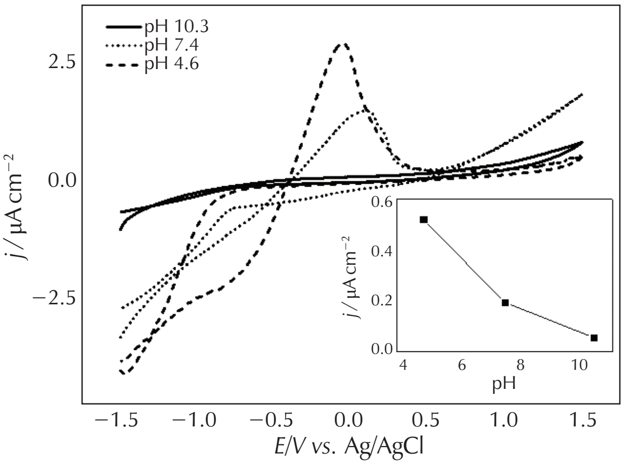


Fig. 4 – Voltammograms recorded in a 0.1 mol m^{-3} Tris-HCl solution at different pH for the CPE/OM electrode after the accumulation of Pb^{2+}. Scan rate 100 mV s^{-1}. Insert curve plotted: peak current densities *vs.* pH, potential interval from −1.5 to 1.5 V.

To study the mechanisms obtained by lead oxidation reduction by CPE/OM, cyclic voltammetry was used. The CVs presented in Fig. 5 show an intense peak P2 at −0.3 V; peak P2 is the oxidation peak of the organic film-Pb^{2+} complex. The P3 oxidation peak located at potential 1.35 V is the same peak P′ characteristic of the existence of the organic molecule OM (Fig. 5A). We notice in the other direction of scanning towards negative potential a reduction peak (P1 towards −0.8 V) of organic film-Pb^{2+} complex. These results were confirmed by the SWV method (Fig. 5B), representing two oxidation peaks similar to P2 and P3 detected by CV. We propose the mechanism according to Scheme 1.

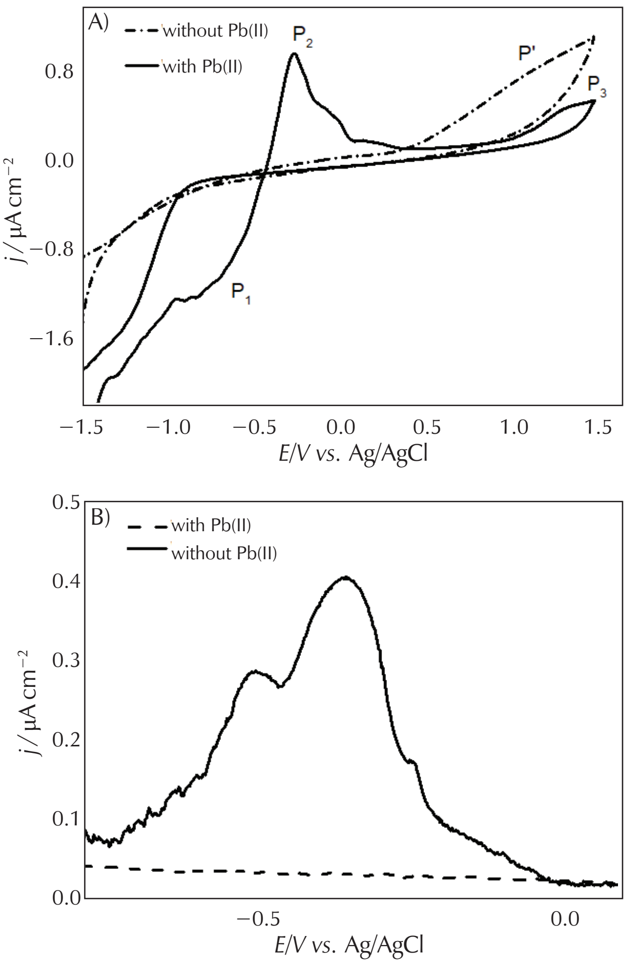
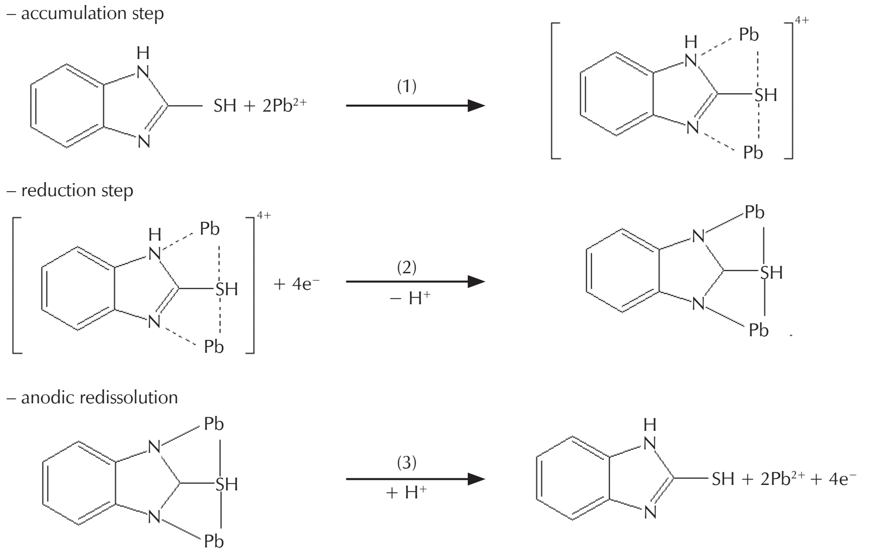


Fig. 5 – Voltammograms recorded in a CPE/OM buffer solution (pH 4.6) in the presence and absence of Pb(II), by the CV (A) and SWV (B) techniques. Scan rate of CV is 100 mV s^{-1} and potential interval from −1.5 to 1.5 V. Scan rate: 25 mV s^{-1}, pulse: 50 mV for SWV.



Scheme 1 – Reaction mechanism of Pb(II) with 2-benzimidazolethiol on the surface of the electrode CPE/OM

External calibration is a technique allowing us to have a calibration line of our CPE/OM electrode, from which we can determine the concentrations of the unknown lead. Fig. 6 shows a superposition of the voltammetry cycles obtained at lead concentrations ranging from 0.1 $g\,l^{-1}$ up to 1 $g\,l^{-1}$ with a step of 0.1 $g\,l^{-1}$. These current densities changed linearly with the concentration of the analyte, implying that the preconcentration step was critical (Fig. 6). The calculated relation is:

$$jp_2 = 8564\ \mu A\,cm^3\,mol^{-1}\,cm^{-2}\,[Pb^{2+}] + 0.401\ \mu A\,cm^{-2} \quad (1)$$

where jp_2 (oxidation peak) is expressed in $\mu A\,cm^{-2}$ and $[Pb^{2+}]$ in $mol\,cm^{-3}$. R^2 was 0.9342.

On the other hand, according to the data in Table 1, certain studies have shown that the response of a carbon paste electrode modified by organic 2-benzimidazolethiol carbon molecule possessed a response and sensitivity, which depended on the electrode preparation method and the measuring conditions. Experimentally, the electrodes prepared by mixing keep their modification over the entire electrode paste, remaining resistant against the phenomenon of surface dissolution. Otherwise, some electrodes which were modified only on the surface,[27] were exposed to this problem.

4 Conclusion

In this study, a carbon paste electrode modified by an organic molecule as an amperometric sensor for the determination of lead ions was developed. An electrochemistry study was performed of the organic compound and its complex formed with Pb^{2+} to examine the effects of the concentration of Pb^{2+} accumulated on the surface of the electrode and the pH of the medium. After fixing the optimum conditions, we examined the CPE/OM electrode prepared by the mixing method, where organic matter was introduced squarely into the dough. The latter showed a great activity towards the detection of Pb^{2+} ions. Monitoring the release peak (oxidation) of Pb^{2+} ions offered the possibility of analysing lead(II) in the electrolytic solution.

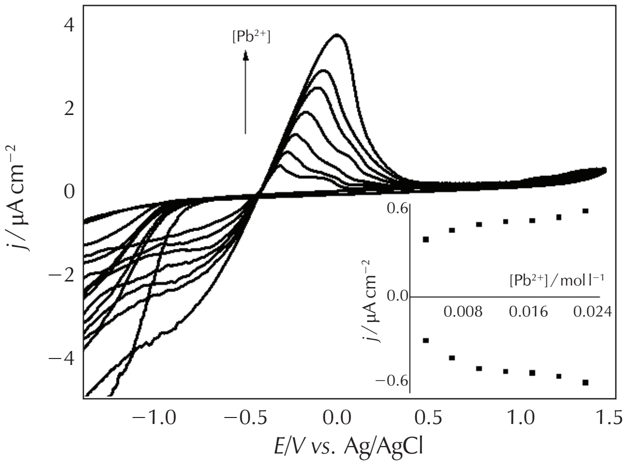


Fig. 6 – Cyclic voltammograms of CPE/OM with different concentrations of lead ions using 0.1 $mol\,m^{-3}$ Tris-HCl (pH 4.6). Insert of calibration curve plotted: the current densities of the peaks *vs.* concentration of lead ion at CPE/OM in 0.1 $mol\,m^{-3}$ Tris-HCl (pH 4.6), potential interval from −1.5 to 1.5 V.

List of abbreviations
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SCE – saturated calomel reference electrode
CPE/OM – carbon paste electrode modified by 2-benzimidazolethiol
DL – detection limit
CPE – carbon paste electrode
CV – cyclic voltammetry
DNA – deoxyribonucleic acid
EDTA – ethylenediaminetetraacetate
SWV – square wave

Table 1 – Comparison of detection power of certain species using sensors developed by different modification methods with 2-benzimedazolethiol

Modified electrode	Electrolytic medium	Modification method	Detection of Pb(II) ion	DL / $mol\,l^{-1}$	Ref.
CPE/2-benzimidazolethiol	0.1 $mol\,m^{-3}$ NaCl	mixing (inset)	inset of the electrode	$2.77 \cdot 10^{-9}$	25
CPE/2-benzimidazolethiol	0.1 $mol\,m^{-3}$ phosphate buffer solution	electroless (on the surface)	in preconcentration solution	$3.57 \cdot 10^{-6}$	24
CPE/2-benzimidazolethiol/Polymer	0.1 $mol\,m^{-3}$ Tris-HCl	electroless (on the surface)	in preconcentration solution	$1.77 \cdot 10^{-8}$	26
CPE/2-benzimidazolethiol	0.1 $mol\,m^{-3}$ Tris-HCl	mixing (inset)	in preconcentration solution	$3.43 \cdot 10^{-6}$	this work

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SAŽETAK

Detekcija iona olova elektrodom od ugljikove paste modificirane 2-benzimidazoletiolom: voltametrijska studija

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U ovom je radu pripravljen elektrokemijski senzor (CPE/OM) modificiranjem ugljikove paste s organskom molekulom 2-benzimidazoletiolom. Ispitana je primjenjivost senzora za detekciju iona olova u vodenoj otopini. Sve proučavane reakcije odvijale su se na modificiranoj površini elektrode, tj. na mjestu kontakta elektrode i otopine. Stoga su upotrijebljene ciklička voltametrija i voltametrija kvadratnog vala. Ciklička voltametrija je pokazale koje se reakcije odvijaju. Određivanje olova provedeno je voltametrijski na površini modificirane elektrode, uz granicu detekcije (DL) od $3{,}43 \cdot 10^{-6}$ mol l^{-1} . Eksperimentalni rezultati pokazali su da elektroda modificirana 2-benzimidazoletiolom ima visoku osjetljivost prema ionima olova te veliko područje linearnosti.

Ključne riječi
Ciklička voltametrija, teški metali, organska molekula, senzor, modificirana elektroda

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