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Development of Carbon Paste Electrode/EDTA/Polymer Sensor for Heavy Metals Detection

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Abstract-The method used to immobilize the polymer on the Disodium ethylenediamine tetraacetate (EDTA) modified carbon paste electrode (CPE/EDTA) has proved its effectiveness for the detection and chelation of heavy metals in aqueous solution. Its complex formation with Pb(II) was examined by square wave voltammetry and cyclic voltammetry. CPE/EDTA electrodes are predisposed to the phenomenon of dissolution due to several factors, such as pH, we thought to cover these electrodes with a selective polymer synthesized (9% of the polysulfone and 91% of the polyacrylonitrile) for remedy this problem. It was found that the CPE/EDTA/polymer electrode shows a better performance than the carbon paste electrode modified by EDTA molecular (CPE/EDTA). The polymer used protects the surface of the electrode while preserving its activity. These modified electrodes developed in this study allow simple, rapid and inexpensive identifi1cation of lead ions with 1.08×10^{-9} mol/l of detection limit. The morphological study of polymer surface was examined by Atomic Force Microscopy (AFM).

Keywords- Atomic Force Microscopy; Sensor; Cyclic voltammetry; EDTA; Heavy metals

1. INTRODUCTION

Heavy metal ions are a form of hazardous water-soluble pollutants. Exposure to low concentrations of heavy metal ions be capable of cause: weight loss and hearing, diarrhea,

muscle weakness, growth failure, cardiovascular abnormalities, cancer, kidney failure and sleep disturbances [1–3]. Lead is famous for its high toxicity. It is part of heavy metals harmful to health, an excess of this metal can cause very serious diseases [4,5]. Nevertheless, scientists are developing techniques with the objective to better control the potable water quality and protect the water environment [6,7]. The possibility of developing electrodes based on non-toxic organic molecules represents an opportunity for human health with the intention of determine the concentration of this metal in the environment.

Carbon paste electrodes (CPE) are less expensive and appropriate for the elaboration of the electrode material with the chosen composition and the predetermined properties [8–10]. The electrochemical response of the CPE depends principally on the properties of the modifying species [11–14], for instance the electrochemical response of EDTA modified CPE was well analyzed for various ions viz. NH_4^+, NO_3^- and Pb^{2+} [15–17]. Moreover, there are materials and methods that contribute to the improvement of these electrodes to become more effective. There are numerous research for the detection of metal ions using polymers, complexes of chelating ligands with polymers [18–23].

In this study, we seek to develop an electrode based of EDTA capable of detecting lead in solution. In order to benefit from the EDTA chelating power and to avoid the problem of decomposition of electrode surface in the analytical solution, we have tried to protect the EDTA film deposited on the surface of the carbon paste by a polymer bonded on the surface of the modified electrode.

2. EXPERIMENTAL

2.1. Apparatus

Electrochemical experiments were carried out whit a voltalab potentiostat PGSTAT 100, (Eco Chemie B. V., Utrecht, The Netherlands) manipulated by voltalab master 4 software. CPE/EDTA/Polymer was used as working electrodes, SCE was used as the reference electrode and platinum as the counter electrode.

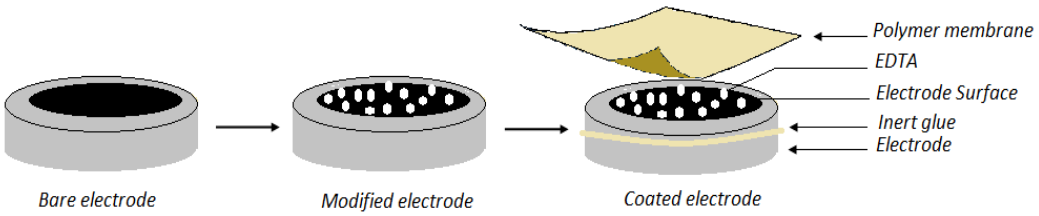
2.2. Reagents

All chemicals were of the highest quality and used as received. Graphite powder (Carbone, Lorraine, ref 9900, French). All other regents used were analytical reagent grade. Distilled water was used throughout the work.

2.3. Preparation of the CPE

The carbon paste electrode (CPE) was obtained by homogeneous mixing of graphite powder with a binder in a mortar and pester. The obtained paste was then inserted into the electrode cavity (geometric area 0.12 cm^2). The electrical contact was made by bar of carbon.

CPE/EDTA's were prepared by immobilizing the EDTA (Figure 1) by soaking the prepared electrode (CPE) in a solution containing the 0.053 M EDTA solution for 24 hours [16]. And thereafter the surface of the prepared electrode is covered by the membrane [24], glued on the edges with Araldit (Scheme 1).



Scheme 1. Electrode surface coating by polymer membrane

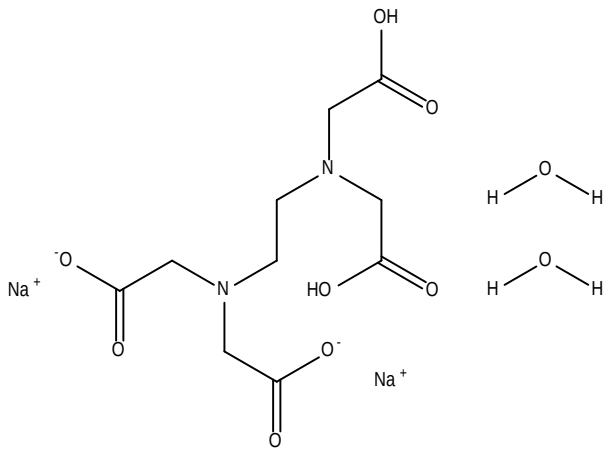


Fig. 1. Structural formula of disodium ethylenedi.minetetraacetate dihydrate

3. RESULTS AND DISCUSSION

3.1. Characterization

The membrane used is made up of a mixture of 9% of the polysulfone (PSf) and 91% of the polyacrylonitrile (PAN). The surface morphology of the polymer has been showed in Figure 2. The surface of the polymer or the membrane used has an asymmetrical structure, a rough surface with reliefs and the size of the aggregates is not identical over the entire surface, as the emonstrates atomic force microscopy (AFM) analysis.

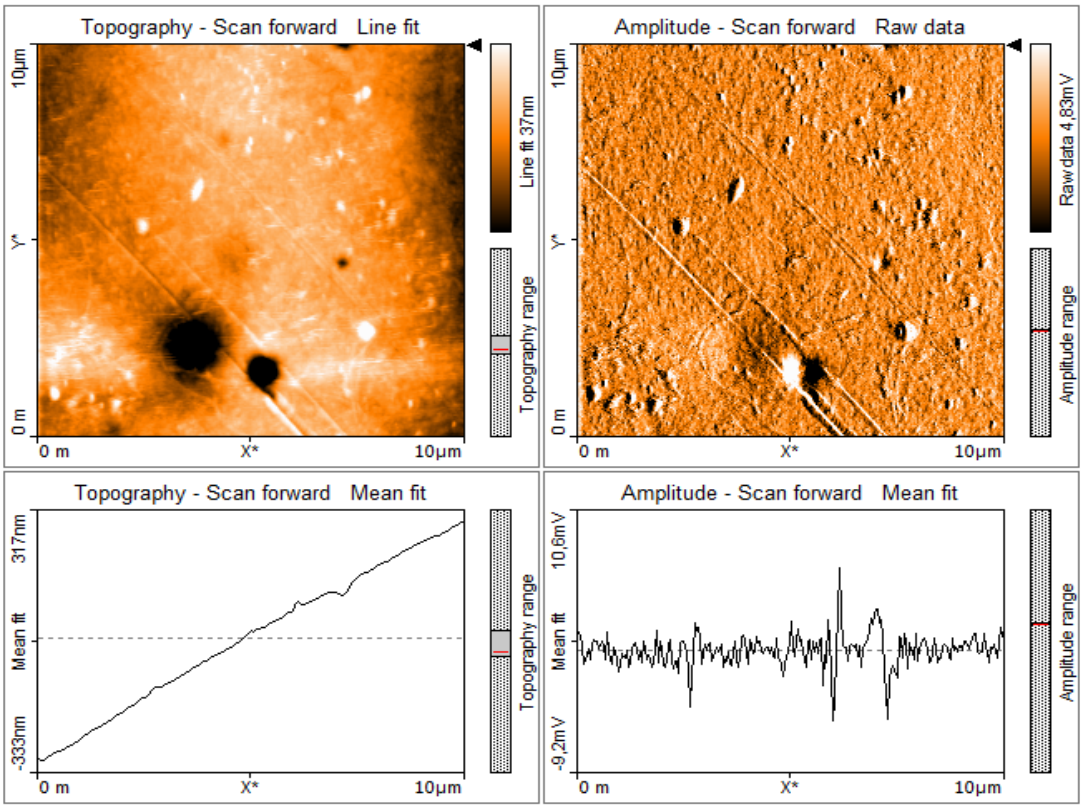


Fig. 2. AFM images of polymer used

In Figure 3 we have studied the behavior of the electrodes used. The cyclic voltammograms obtained for the bare electrode (CPE) and electrode modified by EDTA (CPE/EDTA) shows that the forms of the cyclic voltammograms are different, which confirms that the bare electrode is modified, suggesting that the organic EDTA molecule is well fixed on the surface of the carbon paste electrode.

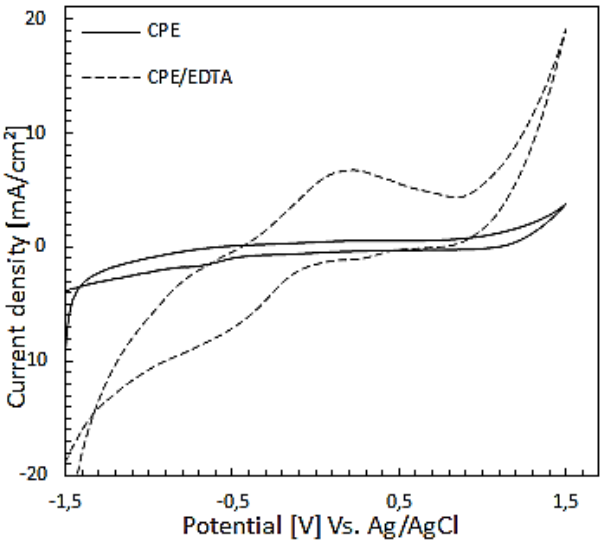


Fig. 3. Characterization of utilized electrode recorded by cyclic voltammogram in buffer solution; operating conditions: Scan rate: 100 mV/s, pH 5.06

3.2. Electrochemical study of the modified electrode CPE/EDTA/Polymer

Figure 4 indicates the cyclic voltammograms (CV) obtained, respectively, for the CPE/Polymer and CPE/EDTA/Polymer electrodes, under the suitable conductions of the lead chelation and detection in 0.1 M tris.HCl medium by EDTA fixed on CPE [16]. We find that the voltammograms obtained have different patterns, which confirms the existence of EDTA in the matrix of the electrode. As we can also notice that the CPE/EDTA/Polymer electrode has a higher active at the CPE/Polymer electrode which confirms that the presence of the organic film catalyzes the reduction of oxidation reduction of lead ions, by accumulating it at the surface, knowing that preconcentration is the limiting step of the reaction.

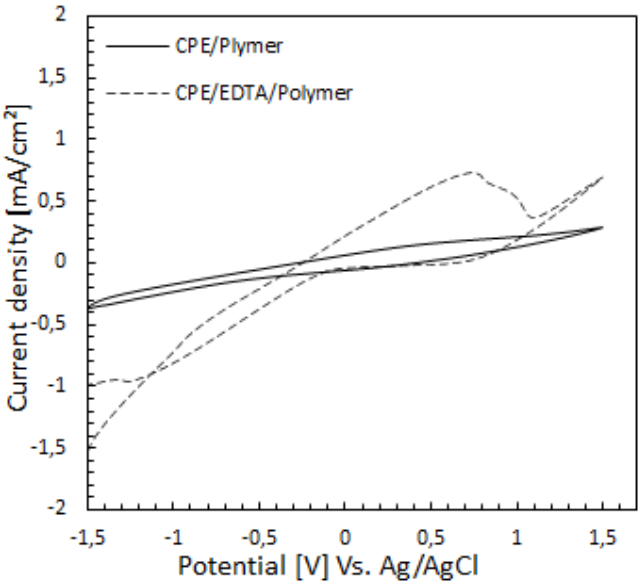


Fig. 4. Sensitivity evaluation of the existence of EDTA on protected electrode obtained by CV; operating conditions: $C_{\mathbf{Pb(II)}}$: 0.602 mmol/l, pH 5.06, $t_{pre[PbII]}$ 7 min, Scan rate 100 mV/s

3.3. Lead chelation

To estimate the performance of the modified CPE/EDTA/Polymer electrode, we recorded the cyclic voltammograms corresponding to this electrode, in a tris.HCl medium in the presence and absence of lead (Fig. 5). The addition of lead of 0.602 mmol /l to the solution of tris.HCl (0.1 M) result an increase in the densities of electric current, which shows that the prepared electrode responds actively to the redox of lead. The nature of the polymer texture characterized promotes the detection of lead ions and makes the chelation reaction easy.

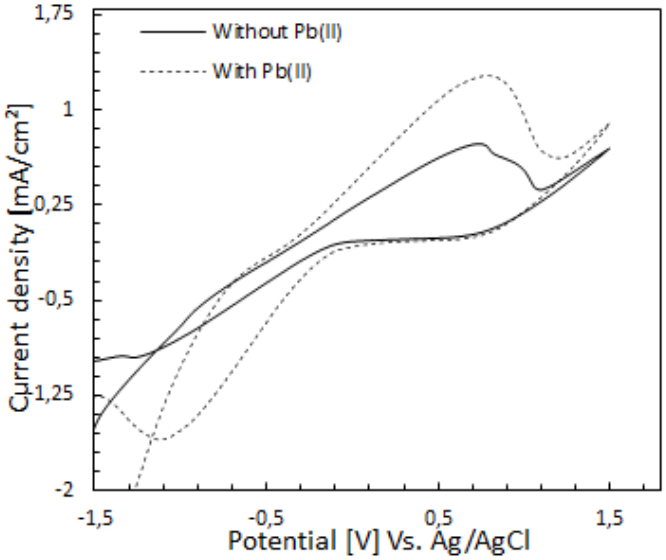


Fig. 5. Cyclic voltammograms to evaluate the sensitivity of the CPE/EDTA/Polymer electrode; operating conditions: $C_{\mathbf{Pb(II)}}$: 0.602 mmol/l, pH 5.06, $t_{pre[PbII]}$ 7 min (preconcentration time), Scan rate 100 mV/s

3.4. Scan rate variation

The effect of the scan rate on the recorded cyclic voltammograms of the CPE/EDTA/Polymer electrode was studied in the values range between 50 and 250 mV/s (Fig. 6), after the preconcentration step in a solution contain 6.02 mmol/l of Pb(II). We find that the anodic peaks displace towards the positive potentials, gradually, as the scan rate increases. The current density of the lead oxidation peak increases linearly with the scan rate or square root of scan rate ($V^{1/2}$) according to Equation (1). This linearity explains by the diffusion phenomenon:

$$I_{peak} = 0.0656\ (V^{1/2}) - 0.2301 \qquad (1)$$

In Figure 7, we represent the effect of the concentration of the Pb(II) ions on the current densities of the redox peaks. We find that the current densities increase linearly with the concentration, which proves that the matrix of the electrode has a considerable number of active sites. The redox peaks are interlocked due to the reversibility of the system. The calculated lead correlation Equations (2) are:

$$Ip = 0.4888\ [\text{plomb}] + 0.0841 \qquad R^2 = 0.9852 \qquad (2)$$

with *Ip*(oxidation peak) is expressed in mA.cm² [lead] in mol/l.

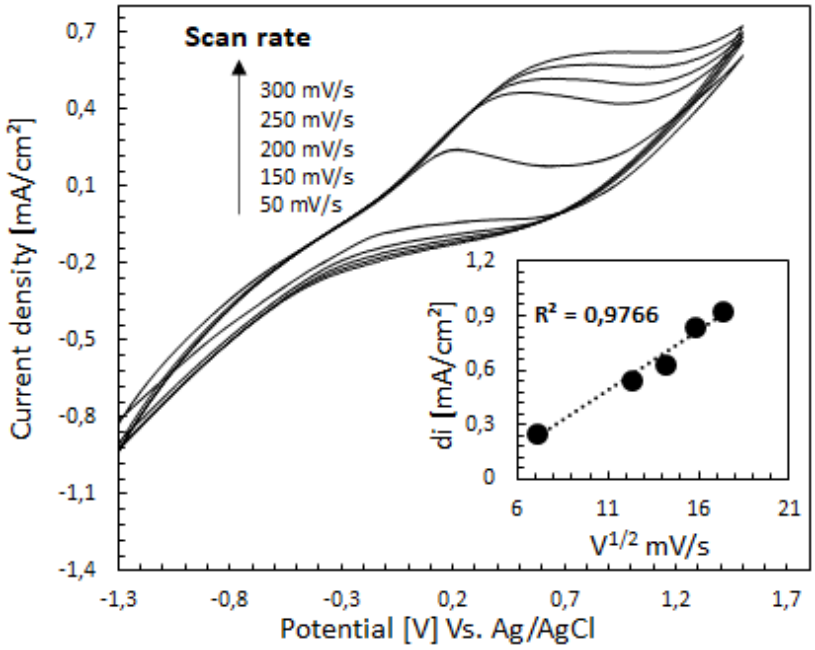


Fig. 6. Effect of the scan rate on oxidation peak intensities in 0.1M TrisHCl, after preconcentration in a solution of Pb(II); operating conditions: $C_{\mathbf{Pb(II)}}$: 6.02 mmol/l, pH 5.06, $t_{pre[PbII]}$ 7 min

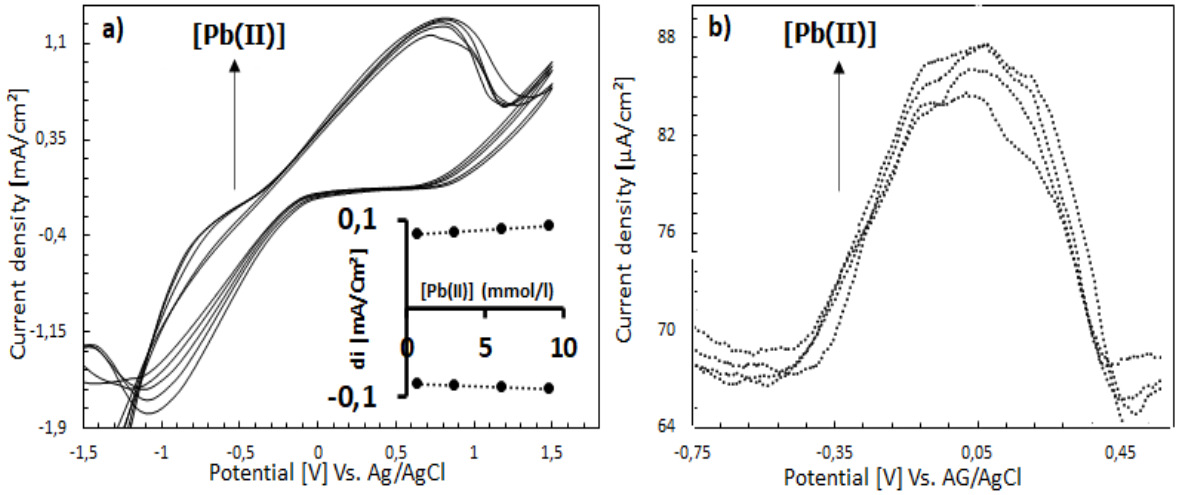


Fig. 7. Influence of the variation of the quantity of Pb(II) on the cyclic voltammograms (a) and square wave voltammograms (SWV) (b) obtained for the CPE/EDTA/Polymer in an electrolytic trisHCl (0.1M) pH 5.06, $t_{pre[PbII]}$ 7 min, Scan $rate_{\mathbf{(VC)}}$ 100 mV/s, Scan $rate_{\mathbf{(SWV)}}$ 25 mV/s. insert: Calibration curves obtained by square wave voltammograms for analyzing lead ions in the domain comprised between 0.602 and 9.03 mmol/l

Table 1. Comparison between CPE/EDTA and CPE/EDTA/Polymer electrodes

Electrodes	DL (mol/l)	QL (mol/l)
CPE/EDTA [16]	5.87×10^{-5}	1.92×10^{-4}
CPE/EDTA/Polymer	1.08×10^{-9}	3.6×10^{-9}

In this paragraph we clearly notice the effect of polymer use in the conditions established, in the presence of the polymer the sensitivity of the electrode increases depending to the results illustrated (Table 1). We can explain this improvement by efficiency of polymer for two things; one to protect the organic film or all of the surface of the electrode modified by the dissolving problem and also it ensures a well selectivity of the Pb(II) ions.

4. CONCLUSION

The results obtained indicate that the electrode prepared CPE/EDTA/Polymer be able to become as a true electrochemical sensor with high sensitivity and reproducibility for the detection and chelation of numerous chemical pollutants in aqueous solution. The prepared electrode chelating power was evaluated by analyzing the Pb(II) examined. The method used to fix the polymer on the surface of the electrode CPE/EDTA makes it possible to retain the surface state and prevent the dissolution of the powders constituting the electrode. The existence of the polymer on the surface did not affect the sensitivity and activity of the electrode due to the selectivity of the polymer.

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