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EDTA-Modified Carbon Paste Composite for Electrochemical Determination of Pb(II) Ions

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Abstract

This paper studies the detection of Lead ions by using a Disodium ethylenediaminetetraacetate dihydrate (EDTA) modified Carbon Paste electrode. The modified electrode was used for the electrochemical analysis of trace lead ions by square wave voltammetry (SWV) technique. It was found that the EDTA-CPE electrode shows a better performance than the carbon paste electrode. Under optimal conditions such as modification method, pH, time of contact with the organic molecule and pre-concentration time of lead, the modified electrode proved the best linear response to lead (II). The proposed method has been applied to a possible electrochemical sensor for heavy metals in solution.

Keywords: Carbon electrode; Cyclic voltammetry; EDTA; Electrochemical sensor; Lead ion

Introduction

The toxic elements for example, lead, mercury are which can cause various dangers to human and the environment [1-5]. The Pb(II) ion has harmful effects on human health. It can enter the human body through the consumption of food, water and air, and cause serious health problems, brain damage, kidney damage, including decreased ability to learn the child, behavioral disturbances, disruption of the biosynthesis of hemoglobin and anemia [4]. As a result, many technologies and methods have been developed to increase the sensitivity and selectivity of metal ions. The most known techniques are spectrophotometry, liquid chromatography, inductively coupled plasma mass spectrometry, atomic emission spectroscopy, solid phase extraction coupled with atomic absorption spectroscopy [6-11] etc. But, these methods have many inconveniences as very expensive, require manipulators and long time to make analyzes.

Researchers have become increasingly interested in electrochemical techniques for detection of metal ions, for the advantages of these techenics such as rapid analytical response, simple manipulation and economic [12-14]. In adding, the complexation by organic molecules [15,16] and electrodes modified by chemical methods [17-22] could be applied in order to improve the sensitivity and selectivity of electrochemical methods. The desired sensitivity of chemical sensors can be achieved by a modification of electrode surfaces with suitable chemical reagents such as metals, semiconductors, carbon based materials and polymeric materials [23-26]. Chelating ligands are also used as metal ion complexing agents [27-31].

Carbon paste electrodes modified by chemical methods are enriched with numerous great qualities, for example, simplicity of handling and applicability to anodic oxidations [32,33]. Various modifiers for carbon paste have been accounted for in the most recent years for the electrochemical stripping analysis of heavy metals. In recent, techniques involving radical-based mechanisms have been developed for the modification of carbon surfaces with covalently immobilized layers of organic species. The deposition of mono or multilayers at the carbon paste surfaces provides the purpose of electrode functionalization for analytical purposes, like electroanalysis of heavy metals [34].

Experimental Section

Apparatus

The electrochemical studies were performed using a voltalab potentiostat (model PGSTAT 100, Eco Chemie B. V., Utrecht, The Netherlands) driven by a general purpose electrochemical systems data processing software (voltalab master 4). The three electrodes system consisted of a platinum as an auxiliary electrode, a saturated calomel electrode (SCE) (Ag-AgCl) serving as reference electrode, and modified paste electrode as the working electrode.

Reagents

All chemicals were of the highest quality. Graphite powder (Carbone, Lorraine, ref 9900, French) was used without further purification. All other regents used such as TrisHCl, $PbSO_4$, EDTA were of analytical grade. Bidistilled deionized water was used during the manipulations.

Preparation of the CPE

Preparation of carbon paste electrode is by mixing the graphite carbon powder with the paraffin oil. The resulting composite material was inserted into the electrode cavity of area 0.12. Electrical contact was established with a bar of carbon. The modified electrode (EDTA-CPE) was prepared by immobilization of EDTA molecule on electrode surface by soaking the CPE in a solution containing the EDTA solution (electroless) [35].

The mixing-modified carbon electrode was prepared by mixing the carbon powder and that of the organic molecule with equal percentages (50% carbon powder and 50% EDTA, the structure of which is given in Figure 1) [36].

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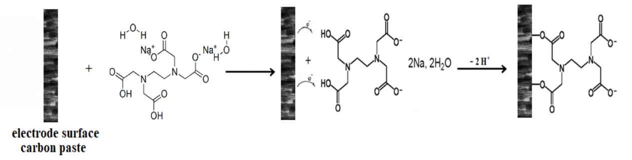
Results and Discussion

a) Optimization of experimental conditions

To examine the behavior of the EDTA film deposited on the graphite carbon, we present in Figure 2 the cyclic voltammograms corresponding to the two electrodes studied (CPE and EDTA-CPE). We can see that the shapts of the recorded CVs are different, which confirms that the surface of the carbon paste electrode is well modified by the organic molecule.

Immobilization of the EDTA molecule on the surface of CPE (proposed mechanism) (Scheme 1):



Scheme 1: Immobilization of the EDTA molecule.

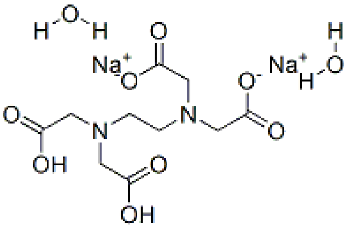


Figure 1: Disodium ethylenediaminetetraacetate dehydrate.

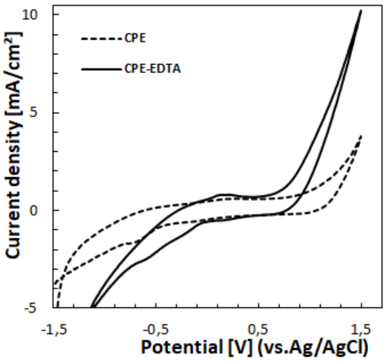


Figure 2: Characterization of used electrode by cyclic voltammogram in buffer solution. *Operating conditions: Scan rate: 100 mV/s, pH 5.06.

During the electroless modification, we followed the pH evolution of solution over time. We noticed that the fixation of EDTA molecule on carbon pate surface decreases the pH from 5.06 to 4.74, which confirms the release of the H$^+$ ions.

b) Comparison between electrode preparation methods

The results obtained by the voltammograms of square wave voltammetry (SWV) recorded in buffer solution, respectively for EDTA-CPE electrodes prepared by mixing and electroless method of the organic molecule, after preconcentration under optimal conditions in a solution containing the Pb^{2+} ions, are shown in Figure 3. The voltammograms have the same pace, which shows that the mechanism of the reaction is the same. The current densities are much higher in the case of the MO-CPE electrode where the organic film is developed by electroless. The electroless modification gives rise to an organic film, continuous over the entire surface, which promotes the attachment of Pb^{2+} ions.

c) Influence of pH

Figure 4 illustrates the effect of the pH of Pb^{2+} solution on the peaks current densities deduced from the square wave voltammetry. Curves show that the redox peak increases with decreasing pH. The peaks reach their maximums at slightly acid pH values. Probably the H$^+$ protons favor chelation of Pb^{2+} ions. The low current density peaks at pH~4 can be explained by the positive charges it carries at this pH. So, it does not have the power of electrostatic attraction to trap metal cations

d) Effect of contact time

The CVs recorded for the electrode EDTA-CPE, in electrolytic medium (pH 5.06), after preconcentration in a solution containing Pb^{2+} ions. In the direction of the anodic scanning, we can observe a well-defined peak at 0.6 V (Figure 5), attributed to the oxidation of the metallic lead trapped in the organic matrix, whereas in the cathodic scanning direction the reduction of the Pb^{2+} ions is translated by a strong current drop to negative values, probably due to a large amount of pre-concentrated Pb^{2+} on the surface of the EDTA film. The highest current densities are obtained by the electrode which is kept 24 hours in the EDTA solution.

e) Influence of preconcentration time of Pb^{2+} ions

For to be applicable to a measurement on site, an analytical method must be rapid and the accumulation step must be as short as possible. The variation in accumulation time was examined (Figure 6) for the solution of 100 mg /l Pb^{2+} in the time interval between 0 and 45 min. Peaks of oxidation currents gradually decrease with the accumulation

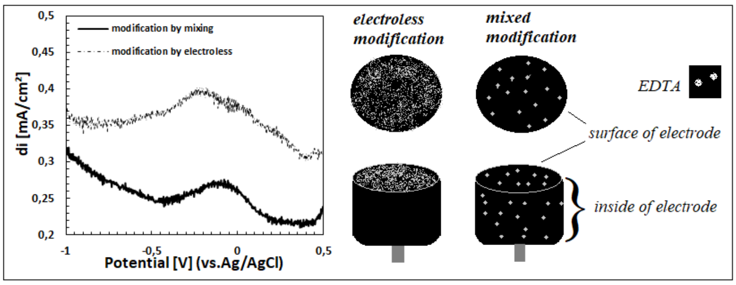


Figure 3: Comparison between electrode preparation methods recorded by square wave voltammograms for EDTA-CPE electrode in 0.1 M trisHCl. *Operating conditions: C$_{Pb(II)}$: 200 mg/l, pH 8.21, Scan rate: 25 mV/s, Pulse: 50 mV.

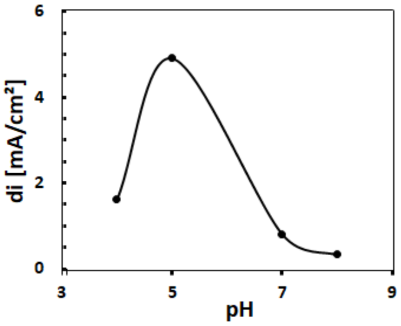


Figure 4: Evolution of the current the peaks densities of the Pb (II) concentration. *Operating conditions: $C_{Pb(II)}$: 100 mg/l, pH 5.06, $t_{pre[PbII]}$ 7 min, $t_{contact\ CPE\ whit\ EDTA}$ 24 h.

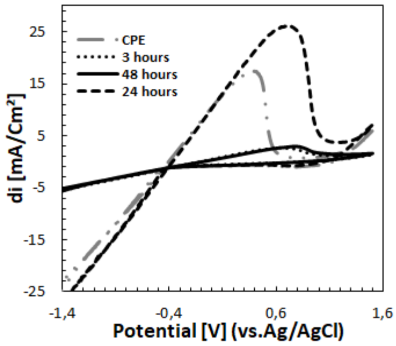


Figure 5: Cyclic voltammograms obtained by the EDTA-CPE and CPE electrodes at 100 mV/s, after preconcentration in a solution of Pb^{2+}.

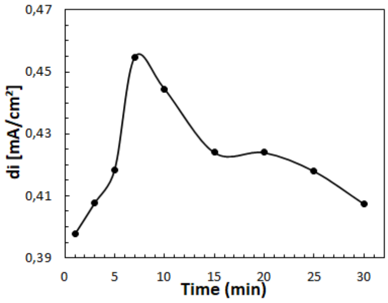


Figure 6: Influence of the preconcentration time on the intensity of the oxidation peak of Pb(II) ion in 0.1 M trisHcl for CPE-EDTA electrode, the current density values extracted from SWV oxidation peaks. *Operating conditions: $C_{Pb(II)}$: 100 mg/l, pH 5.06, $t_{contact\ CPE\ whit\ EDTA}$ 24 h.

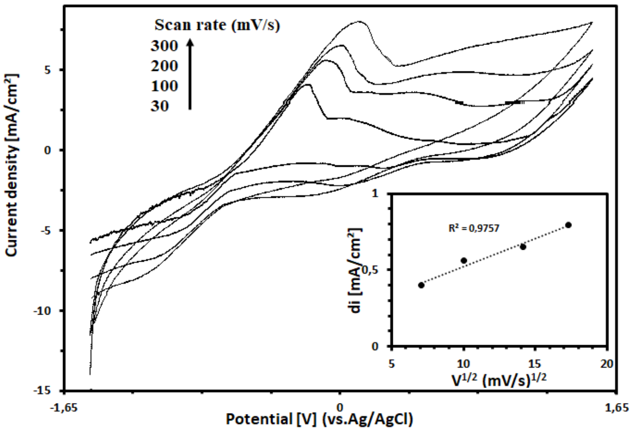


Figure 7: Influence of the scan rate on oxidation peak intensities in 0.1 M TrisHCl, after preconcentration in a solution of Pb^{2+}. *Operating conditions: $C_{Pb(II)}$: 100 mg/l, pH 5.06, $t_{pre[PbII]}$ 7 min, $t_{contact\ CPE\ whit\ EDTA}$ 24 h, Scan rate: 100 mV/s.

time which is between 0-7 min. After 7 min of accumulation, the amount of Pb^{2+} on the surface of the modified electrode decreases with increasing accumulation time. The preconcentration time 7 min which will be adopted thereafter.

f) Effect of scan rate

The influence of the scan rate was studied after a 7 min preconcentration step in a solution containing 100 mg/l of Pb^{2+}, then the electrode was transferred to the electrochemical measuring cell containing a 0.1 M tris-HCl solution, the voltammograms Cyclicals are presented in the. The intensity of the oxidation peak varies linearly with the scan rate ($V^{1/2}$) in the potential range between 30 and 300 mV/s (Figure 7). This linearity reflects a surface phenomenon, and lead ions have probably been scattered to the active sites of the organic film. The oxidation current can be expressed by Randles-Sevcik equation at 25°C:

$$Ip=(268600)\ n^{3/2}AD^{1/2}Civ^{1/2}$$

$$Ip=0,0363\ v^{1/2}+0,1612$$

Where

Ip: Anodic peak current.

n: Number of electrons involved in the reaction.

D: Diffusion coefficient of lead.

A: Electrode surface area.

C: Lead concentration.

V: Scan rate.

g) Comparative study of bare CPE and EDTA modified–CPE electrodes towards Pb(II) ion sensing

In order to study the impact EDTA on sensing, the comparative study sensing abilities of bare CPE and EDTA modified CPE for the determination of Pb(II) ion concentration was investigated. The bare CPE and EDTA-modified were preconcentrated in the analyte solution containing 200mg/l of Pb(II) ions in an trisHCl buffer solution, pH 5.06. The EDTA-modified CPE electrode has two overlapped redox peaks of SWV significant for Pb (II) ions, however, the CPE bare electrode has a lower current density than that of the modified electrode (Figure 8). The better response was observed for EDTA-CPE due to selective chelation ability of EDTA molecules towards Pb(II) ions.

h) Electrochemical response of EDTA-CPE towards Pb(II) ion concentration

The SWV peak currents registered during Pb(II) ion determination over the potential range between −1 V to 0.5 V. SWV voltammograms for different Pb(II) ion concentrations determined by EDTA-CPE are presented in Figure 9. The dotted line represents the reference curve recorded for blank solution without Pb(II) ions.

Results obtained show that SWV linearly varies with the concentration of lead ions. The calibration curve was constructed from

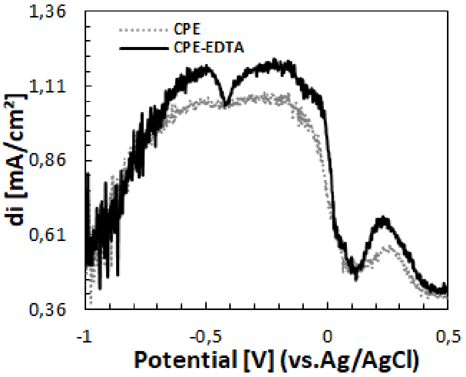


Figure 8: Sensitivity evaluation of the presence of EDTA on CPE electrode recorded by SWV.

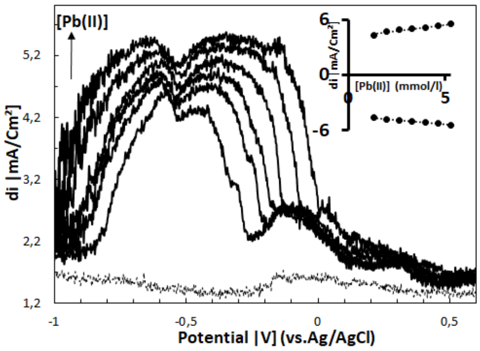
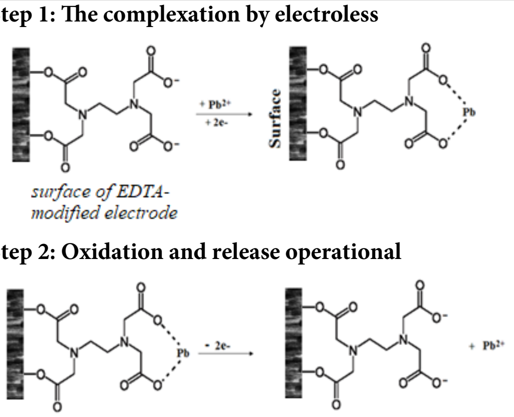


Figure 9: Effect of the variation of the quantity of Pb (II) on the square wave voltammograms recorded for the EDTA-CPE in an electrolytic trisHCl (0.1 M) pH 5.06, $t_{pre[PbII]}$ 7 min and $t_{contact\ CPE\ whit\ EDTA}$ 24 h, inset: Calibration curves obtained by analyzing lead ions in the range comprised between 1.31 and 5.27 mmol/l.

EDTA-CPE redox peak currents of SWV in optimized conditions. Linear regression analysis gave a correlation coefficient of 0.9721 of the oxidation peak. The detection limit (DL, 3s) and the quantification limit (QL, 10s) are calculated from the Miller-Miller equation were, respectively, $5.87.10^{-5}$ mol l^{-1} and $1.92.10^{-4}$ mol l^{-1}.

$$Ip=0.2754[Pb(II)]+4.055$$

The proposed mechanisms for the chelation of lead by the EDTA-CPE (Scheme 2).


Step 1: The complexation by electroless

Step 2: Oxidation and release operational

Scheme 2: Mechanisms for the chelation of lead by the EDTACPE.

Conclusion

An electrochemical characterization confirmed the difference in electrochemical behavior between bare CPE and EDTA-CPE. The EDTA-modified CPE was constructed by the modification of CPE by EDTA using the electroless method. The results gotten show that the prepared EDTA-CPE electrode can be considered as a true electrochemical sensor with sensitivity and reproducibility for the determination of various chemical pollutants in aqueous solution; the EDTA molecule serves as an agent that provides advanced sensitivity to metal ions because of its chelating ability. The prepared electrode sensitivity was measured by analyzing the Pb(II) ion studied. However, further research is needed to increased sensitivity and applique this sensor under real samples.

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