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ELECTROANALYTICAL DETERMINATION OF LEAD WITH CARBON PASTE MODIFIED STEEL ELECTRODE

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ABSTRACT: We report a sensitive electrochemical voltammetric method for analyzing lead (II) using a carbon-coated steel electrode. Operational parameters have been optimized, and the stripping voltammetric performance has been studied using square wave voltammetry and electrochemical impedance spectroscopy. The peak current was linearly dependent on the concentration of lead ions from 1.5 x 10^{-5} mol/L to 3 x 10^{-5} mol/L.

KEYWORDS: Electroanalysis; Modified electrodes; Lead; Electrochemical impedance spectroscopy; Square wave voltametry

INTRODUCTION

Lead is a toxic heavy metal that appears in the environment mainly due to industrial processes, it is a microelement naturally present in trace amounts in all biological materials, it has no physiological function in the organism. Lead is absorbed by plants through roots where most of the lead is also accumulated. Lead enters the organism with food and air. In children it affects most the central nervous system [1]. Therefore sensitive methods must be established for the trace amounts of lead quantification in human's body fluids, water samples, plants and animals. Some of the methods used for the determination of lead are Atomic Absorption Spectrometry (AAS) [2-3], atomic emission spectrometry (AES) [4] and mass Spectrometry (MS). These methods, although highly sensitive, require relatively large volumes of sample for analysis, complicated operation, costly maintenance, expensive apparatus and low electrical power requirement [5].

Electrochemical methods are well known as very powerful techniques for determination of diverse range of metallic and biological targets in environmental, biological and industrial samples.

Modified electrodes are also attracting interest [6-7]. Recent works, reported in the literature, have shown several applications and electro analytical methodologies employing micro-electrodes as working electrodes [8-12].

Mercury based electrodes such as, mercury film electrodes and hanging mercury drop electrodes, has been traditionally used in stripping techniques because of their advantages such as high sensitivity, reproducibility, purity of the surface, high hydrogen over potential, and possibility of the amalgam formation and they have been recognized as the most sensitive electrodes for determination of heavy metals [14]. It has been shown that bismuth film electrodes maintain all the advantages of mercury electrodes and, at the same time, are environmentally friendly as the toxicity of bismuth and its salts is negligible. In addition to their lower toxicity, bismuth film electrodes resulted in compared to the performance of mercury electrodes were less sensitive to dissolved oxygen and had a wide potential window for analysis. However, the determination of copper using bismuth film electrodes has been relatively ignored due to the similar stripping potentials of copper and bismuth with only a few reports in the open literature [11-12].

Many researchers detected heavy metal ions at modified carbon paste electrode [12], but no researchers using deposited carbon paste onto steel as electrode for the detection of Pb (II) were reported.

In this work we prepared and characterized the carbon modified steel electrode, which successfully exploits the favourable mechanical and electrochemical properties of carbon paste electrodes.

EXPERIMENTAL

***Reagents**: Potassium nitrate was dissolved into Bi-distilled deionized water (BDW) to form 1mg.L^{-1} stock solutions. Working standards for calibration were prepared by diluting the primary stock solution with BDW. Carbon paste was supplied from (Carbon, Lorraine, ref. 9900, French). All chemicals were of analytical grade and used without further purification.*

***Substrat preparation and electrodeposition of carbon paste:** The cathode electrode was a steel plate, with a dimension of 1 cm x 1 cm x 0.1 cm, was* *polished on wet SiC paper (grade 600) and immersed in H_2SO_4 solution for 5 min to dissolve the air-formed oxide film on the surface and the anode electrode was a platinum plate. The current was maintained by a galvanostat with a function generator. Then, the electrodes were immersed in electrolyte of carbon paste gel contained glass chamber, and subjected to anodic oxidation by applying DC for 48h at room temperature. The deposit of carbon paste on steel surfaces was processed at 20 V.*

Substrat/carbon paste characterization: *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 steel/carbon paste.*

Apparatuys: *Electrochemical experiments were performed using a voltalab potentiostat (model PGSTAT 100, Eco Chemie B. V., Utrecht, The Netherlands) driven by the general purpose electrochemical s systems data processing software (voltalab master 4 software).*

RESULTS AND DISCUSSION

Voltammetric characterisazation: *The cyclic voltammograms of both unmodified steel and carbon paste modified steel (CP-S) electrodes are shown in Figure 1. The carbon modified steel electrode voltammogram (Figure 1b) showed that the modified electrode is electro inactive at a reasonable broad potential range of approximatively -1500 mV to 1000 mV. There was also some indication that the modifier (carbon paste) is effectively deposited into steel plate.*

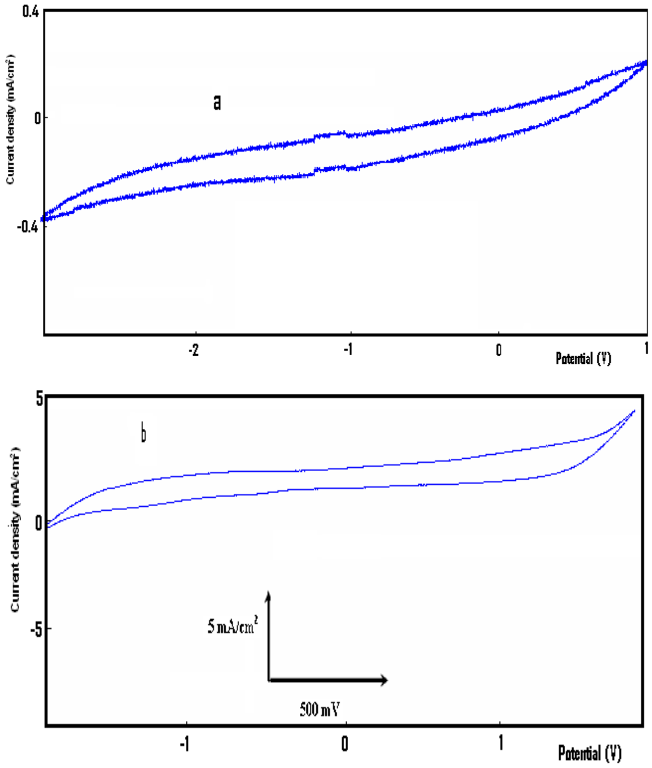

Figure 1. Cyclic voltammograms of unmodified steel (a) and carbon paste modified steel electrodes at scan rate of 100 mV/s in 0.1M Na_2SO_4 solution.

In the preconcentration step, the accumulated Pb^{2+} was found to be reduced at -1.05 V at which the lead ion is electrochemically deposited at the electrode surface. The deposited lead is oxidized at -0.5 V. The whole mechanism comprises of accumulation, reduction and stripping stages which can be represented, respectively, by the following:

$$(Pb^{2+})_{solution} + (CP\text{-}S)_{surface} \rightarrow (Pb^{2+} - CP\text{-}S)_{adsorption}$$

$$(Pb^{2+} - CP\text{-}S)_{adsorption} + 2^{e-} \rightarrow (Pb - CP\text{-}S)_{adsorption}$$

$$(Pb - S)_{adsorption} \rightarrow (Pb^{2+})_{solution} + (CP\text{-}S)_{surface} + 2^{e-}$$

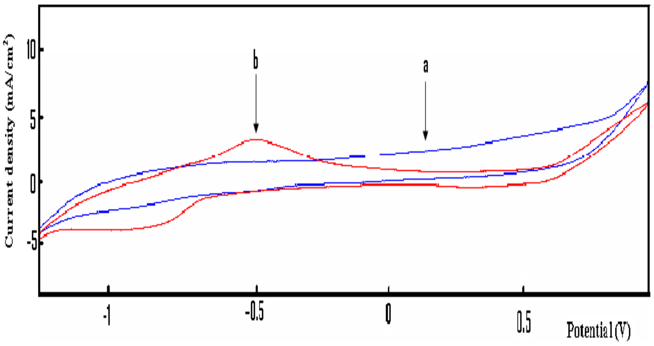

Figure 2. Cyclic voltammograms of carbon paste modified steel electrode at scan rate of 100 mV/s in 0.1M Na_2SO_4 solution (a) and in 0.1 M Na_2SO_4 solution container 10 mg/l Pb^{2+}.

The square wave voltammograms obtained for 10mg/L of lead ion present one peak at around -0.5V (Figure 3). This peak was associated to the oxidation of deposited Pb^{2+}. This peak can hence be used, with great success, for electroanalytical determination of lead ion in different samples.

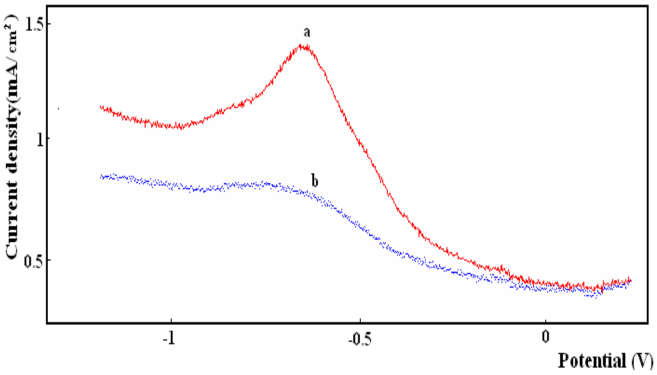

Figure 3. Square wave voltammograms recorded at CG-S electrode in a- 0.1M Na_2SO_4 solution containing 10 mg/L of lead (pH 7.0) and b- 0.1M Na_2SO_4 solution.

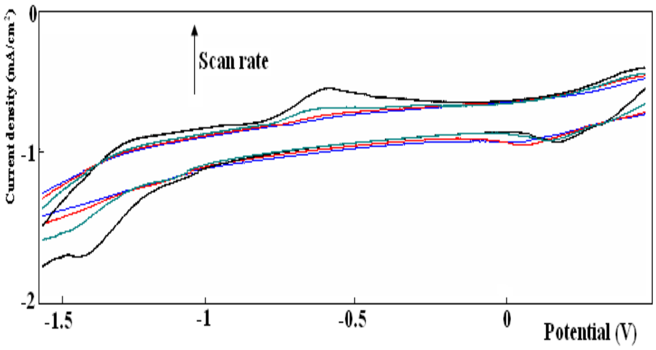

Figure 4. Cyclic voltammograms of carbon paste modified steel electrode at different scan rates in 0.1 M Na_2SO_4 solution container 10 mg/l Pb^{2+}.

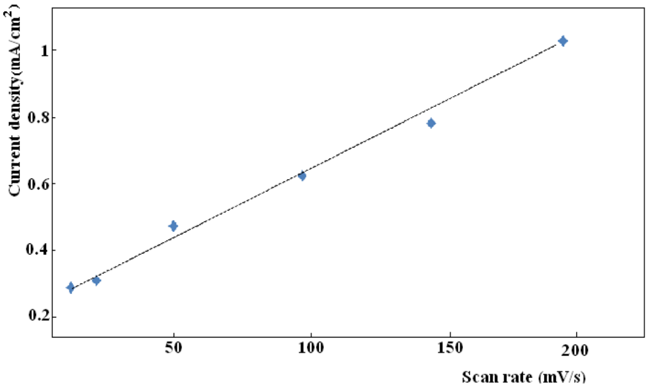

Figure 5. Influence of the scan rate on the oxidation peak intensity for 10 mg/L Pb^{2+} (pH 7.0) in 0.1M Na_2SO_4, preconcentration time 15 min.

Figure 4 shows the influence of scan rate was studied at CG-S electrode immersed for 15 min in 10 mg/L Pb^{2+}. The oxidation peak was found to vary linearly with the scan rate ranging from 10 to 200 mV/s (Figure 5). Lead ion diffused from the preconcentration solution towards the interstitial space existing in the paste carbon film.

***Optimization parameters:** The effect of accumulation time on the stripping peak currents of 10 mg/L de Pb^{2+} was shown in Figure 6. The stripping peak currents decreased gradually with the accumulation time in the range of 0 - 10 min. After 10 min of accumulation, amounts of lead ion on the surface of modified electrode increased with the increase of accumulation time, which resulted in the increase of oxidation peak currents.*

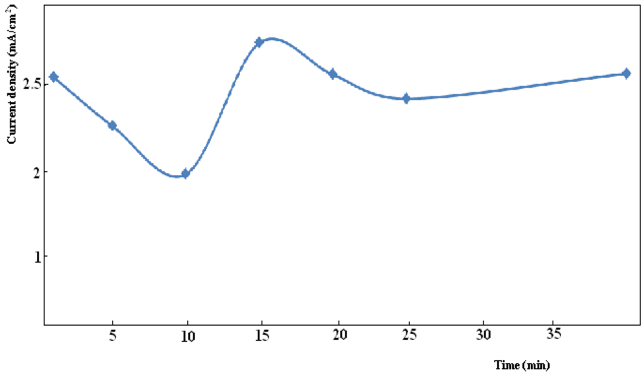

Figure 6. Influence of preconcentration time on the oxidation peak of 10 mg/L lead pH 7.0 on square wave voltammograms at CP-S electrode in 0.1M Na_2SO_4 solutions

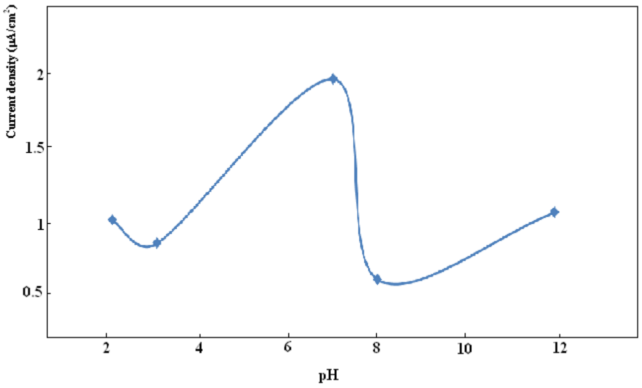

Figure 7. Effect of the pH on square wave voltammogram peak height of 10 mg/L Pb^{2+} in 0.1M Na_2SO_4, accumulation time: 15 min

With further increase of accumulation time, the peaks currents reached a flat caused by the complete coverage of active points on the surface of carbon paste modified steel electrode by lead. Taking account of the sensitivity and the efficiency, accumulation time was 15 min in the following experiments.

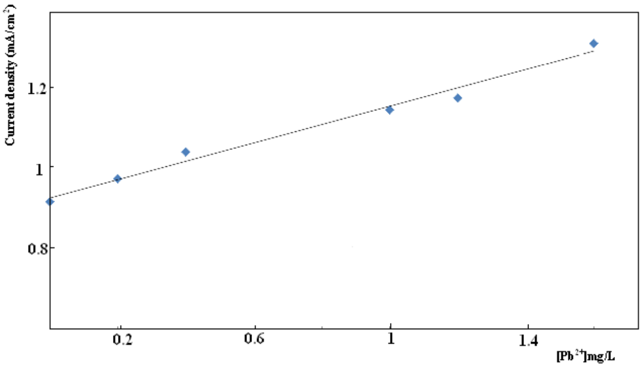

Figure 8. Influence of concentration of lead on the peaks intensity at CP-S electrode under the optimized conditions

The effect of pH on the preconcentration solution is shown in Figure 7. Results showed that the current peak decreased above pH 7. An increase in pH led to an increase in peak current up to pH 7. This is also the same with a study [18] which demonstrated that lead belongs to the first class of metals where metal ion can tightly bind and is rapidly bound at pH ≥ 5.0.

***Calibration plots:** The calibration graph of peak current vs lead ion concentration in the range 0.2 - 20 mg/L is shown in Figure 8. The calibration graph was linear. The regression straight line has the following equation:*

$$i_P = 0.4592\,[Pb^{2+}] + 0.64$$

where i_P is expressed in mA/cm^2 and the concentration in mg/L and the correlation coefficient was 0.9837.

***Interference studies**: Several other metal ions were examined for their possible interference in lead (II) analysis using the prepared electrode. The determination of a 10 mg/L Pb^{2+} using the optimized conditions was not affected by the presence of cadmium and copper ions.*

The voltammograms has been recorded after the preconcentration of CP-S electrode in aqueous solutions containing Pb^{2+}, Cd^{2+} and Cu^{2+} (Figure 9). The anodic oxidization of the cadmium occurs to the potential of -0.7 V, lower to the potential oxidation of lead -0.45 V. The oxidization peak of copper ion appears at a potential + 0.1 V superior to the potential oxidation of lead. The clean separation of the three potential peaks offers us the possibility of the simultaneous determination of lead, cadmium and copper.

PRACTICAL APPLICATION OF PROPOSED ELECTROANALYTICAL METHOD - In orange juice

The same methodology has been applied with success in orange juice under the optimized conditions. Interference is possible because of the complexity of the matrix. The presence of the organic substances in the matrixes of the orange juice has a considerable effect on the response of lead at the electrode surfaces. (Figure10).

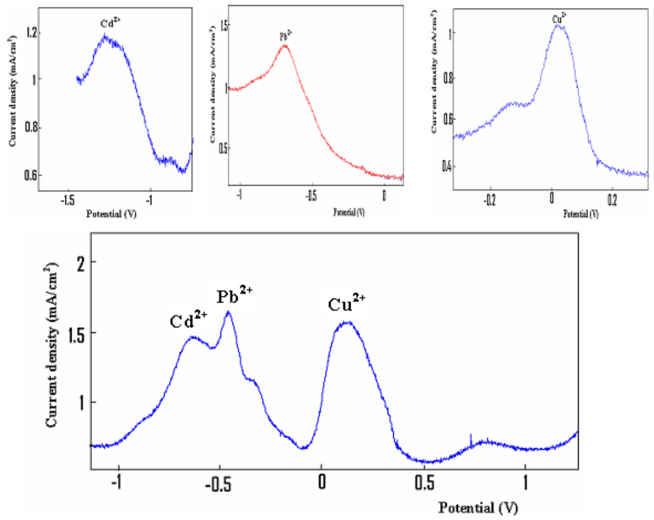

Figure 9. Cyclic voltammograms of 10 mg/L lead, 10 mg/L cadmium and 10 mg/L copper at CP-S electrode, pH 7.0, 15 min of preconcentration time in 0.1M Na_2SO_4.

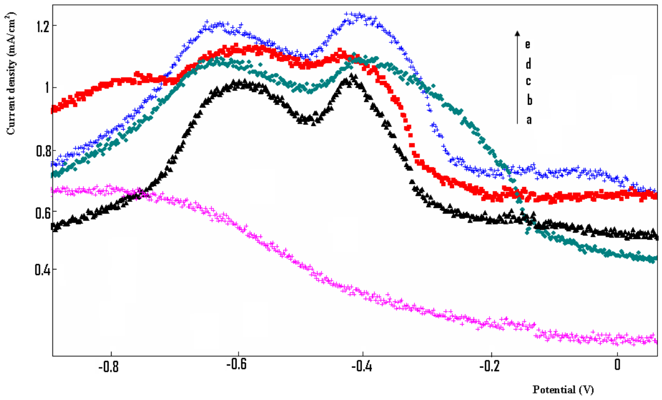

Figure 10. Square wave voltammograms in 0.1M Na2SO4 under the optimized conditions at CP-S electrode of lead (II): a- 0 mg/L, b- 5 mg/L, c- 8 mg/L, d- 10 mg/L and e- 20 mg/L.

CONCLUSIONS

An edge plane steel electrode was modified with an in-situ electro-deposition of carbon paste and was then successfully utilized for the simultaneous determination of Pb^{2+}, Cd^{2+} and Cu^{2+} in standard and real samples.

Under the optimal conditions lead ions can be detected in the concentration range from 1.0×10^{-5} mol/L to 3.0×10^{-5} mol/L.

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