Lauriane et al., Pharm Anal Acta 2014, 5:4
DOI: 10.4172/2153-2435.1000295

Pharmaceutica Analytica Acta

Research Article Open Access

Electrochemical Sensor of Heavy Metals Based on Chelating Compounds

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Abstract

The analytical performance of developed organic film screen –printed sensors designed for the detection of metals was evaluated. The modified surface exhibited an affinity to chelating metal ions in solution, forming complexes. Square wave voltammetry combined with a pre-concentrating process and standard additions were employed for trace analysis. Finally, cyclic voltammetry technique was used to characterize the developed organic film surface behavior in presence of different metals.

Keywords: Cyclic voltammetry; Organic molecules modified electrodes; Heavy metals; Electrochemical sensors

Introduction

The determination of trace metals is important in the context of environment protection, food and agricultural chemistry. Environmental monitoring of heavy metals is of great important for ecological assessments as well as for understanding the dissemination of pollutants [1]. Contamination by metals is indeed widespread all over the word [2]. Pollution with heavy metals is a highly significant risk factor in predicting higher rates of crime, attention deficit disorder or hyperactivity, and learning disabilities. Exposure and uptake of heavy metals such, lead, copper and cadmium has been associated with industrial pollution. Detection of toxic trace metals in the environment is a challenging analytical problem. The major existing techniques for metal trace analysis are spectroscopic and inductively coupled plasma mass spectroscopy (ICP-MS), voltammetric and chronoamperometric. In recent years, applications of chemically modified electrodes have had great interest in various areas of research and development, such as material corrosion and inhibition, electrocatalysis, electronics, biosensors and electroanalysis [3-10]. For the analysis of trace metals, modified electrodes have shown some advantages over other analytical methods and have been employed as powerful tools for concentration determination and surface structure identification [11,12].

Recently assembly of organic layers onto surfaces have been widely used in constructing the electrochemical sensors due to their unique characteristics such as high surface area and strong adsorption ability.

Carbon paste electrodes chemically modified are endowed with many good qualities, such as ease of handling and applicability to anodic oxidations [13]. Different modifiers for carbon paste have been reported in the last years for the electrochemical stripping analysis of heavy metals.

Recently, methods involving radical–based mechanisms have been developed for the modification of carbon surfaces with covalently attached layers of organic species. The deposition of mono or multilayers at the carbon paste surfaces serves the purpose of electrode functionalization for analytical purposes, like electro analysis of heavy metals [14,15].

The aim of this investigation is to highlight the potential for using synthesized organic compounds for the fabrication of electrochemical sensors. These electrodes were used for the chemical preconcentration of different heavy metals at trace levels. The organic molecules modified carbon paste electrode (MO-CPE) can preconcentrate heavy metals from aqueous solution to the surface of the modified CPE by forming complexes with these ions and greatly increasing the sensitivity of its determination. The experimental data show that some of the MO-CPEs have high sensitivity, adequate selectivity and reproducibility, and a wide operative linear range of concentrations for the determination of heavy metals in water samples. The MO-CPEs have the advantages of simple methods of synthesis and purification and their low solubility in water.

Experimental

Reagents and chemicals

All chemicals were of the highest quality. Graphite powder (spectroscopic grade RWB, Ringsdorff-Werke GmbH, Bonn-Bad Godesberg, Germany) was obtained from Aldrich and was used without further purification. $CuSO_4$, $PbSO_4$ and $CdSO_4$ were obtained from Merck chemicals. Deionised water was used to prepare all solution. All organic molecules were synthesised in our laboratory.

Apparatus

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

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 MO-CPE.

Electrode preparation

The carbon paste unmodified was prepared by adding paraffin oil to carbon powder. Organic molecules-modified carbon paste electrodes

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Received February 12, 2014; **Accepted** April 22, 2014; **Published** April 25, 2014

Citation: Lauriane NTR, Najih R, Chtaini A (2014) Electrochemical Sensor of Heavy Metals Based on Chelating Compounds. Pharm Anal Acta 5: 295. doi:10.4172/2153-2435.1000295

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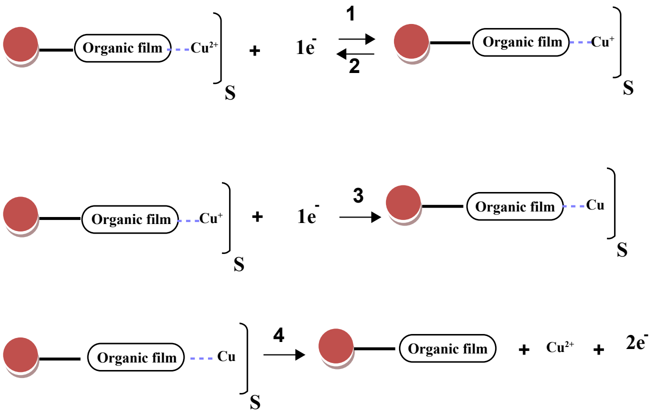
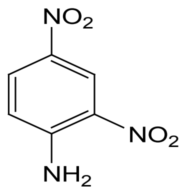
(MO-CPEs) were prepared by substituting corresponding amounts of the carbon powder by the organic molecules and the adding the paraffin oil and thoroughly hand-mixing in a mortar and pestle. The resulting paste was packed into the electrode and the surface was smoothed. The organic molecules used as modifiers are presented in scheme 1.

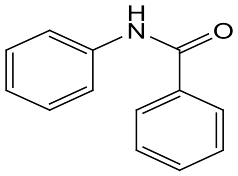
According to literature [15,16], the three studied molecules, include the diazonium reduction in the electrochemical measuring cell. The diazonium exchange one electron with the electrode surface and turns to an aryl radical; the latter establishes a covalent bond with the surface of electrode.



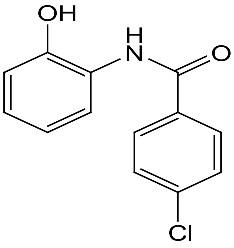
Peak 1: The Peak 4 corresponds, probably, to the release of copper from the organic matrix according to the reaction.



Molecule A



Molecule B



Molecule C

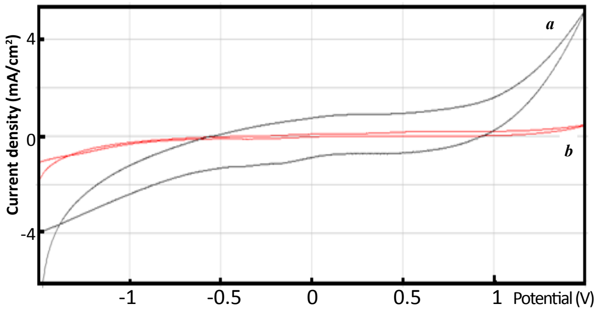


Figure 1: Cyclic voltammograms recorded in buffer solution (pH 7.2), at, a-CPE and b-MO (=molecule A)-CPE, scan rate 100 mV/s.

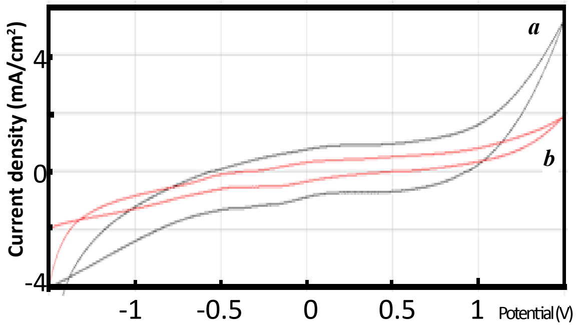


Figure 2: Cyclic voltammograms recorded in buffer solution (pH 7.2), at, a- CPE and b- MO (= molecule B)-CPE, scan rate 100 mV/s.

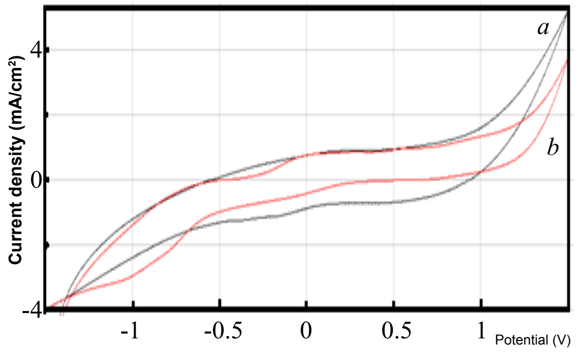


Figure 3: Cyclic voltammograms recorded in buffer solution (pH 7.2), at, a- CPE and b- MO (=molecule C)-CPE, scan rate 100 mV/s.

Results and Discussion

Cyclic voltammetric (CV) experiments

Preliminary CV experiments were performed to study the behavior at carbon paste electrode (CPE) and MO-CPE.

The electrodes were first immersed in an electrochemical cell containing buffer solution (pH 7.2).

Comparing the two voltammograms, that recorded by the carbon electrode (Figure 1 curve b) and that obtained from the carbon electrode modified (Figure 1 curve a), we find that the shape has changed which corresponds to a change of the surface morphology. The electrical current densities are very low, probably due to the low conductivity of the developed organic film.

A similar behavior was observed by the carbon paste electrode modified by molecule B, but the current densities are higher and can distinguish the redox peaks (Figure 2).

Figure 3 illustrates the cyclic voltammograms obtained, respectively, from the carbon paste electrode (curve a) and the carbon paste electrode modified by molecule C. In this case, we can distinguish two electrochemical peaks, the first one, in the direction of the anodic scan, at about -0.1 V and the second, in the cathodic region, to about -0.9 V, the two peaks are far enough away that which suggests that they not correspond to a reversible system.

The developed organic films modified carbon paste electrodes were soaked, respectively, in solutions containing different concentrations of studied heavy metals for about 10 minutes, removed, then rinsed with pure water. The electrodes were then, respectively, transferred into the electrochemical cell only containing supporting electrolyte solution for cyclic voltammetry and square wave voltammetry. Figure 4 shows CVs for Pb (II) solutions obtained at CPE modified with molecule A. The cathodic scan produces the reduced species of lead, which is deposited on the electrode. This deposition favours the oxidation process and hence the current peak of this signal (i.e., the anodic peak). The peak current increased with an increase in Pb^{2+} concentration.

Even low metal ion concentrations, (MO=molecule B)-CPE presented a peak response in the investigated potential range (Figure 5). This observation suggests that the modified electrode has a strong affinity through surface coordination between metal ion and developed organic film.

Figure 6 shows the cyclic voltammograms recorded for the carbon paste electrode modified by the organic film formed from the molecule C. This voltammogram shows two oxidation peaks in the direction of the anodic scan (peaks 2 and 4 (Figure 6)), the first one at about 0.34 V, and the second to 0.7 V.

In the direction of cathodic scan, we observe also two peaks (1 and 3), which correspond to two successive reduction reactions, the first one is observed at about -0.2 V and the second at -0.6 V.

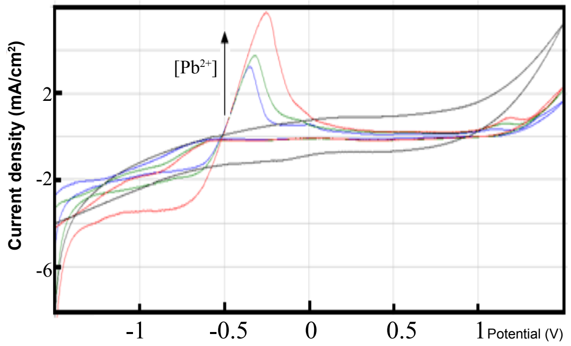


Figure 4: Cyclic voltammograms obtained by MO=A CPEs at 100 mV/s for different concentrations of lead, in buffer solution

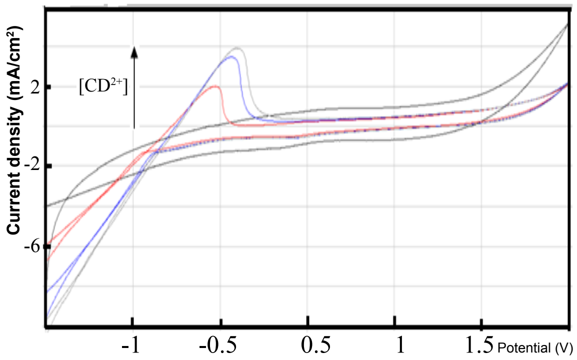


Figure 5: Cyclic voltammograms obtained by (MO=molecule B)- CPEs at 100 mV/s for different concentrations of cadmium, in buffer solution.

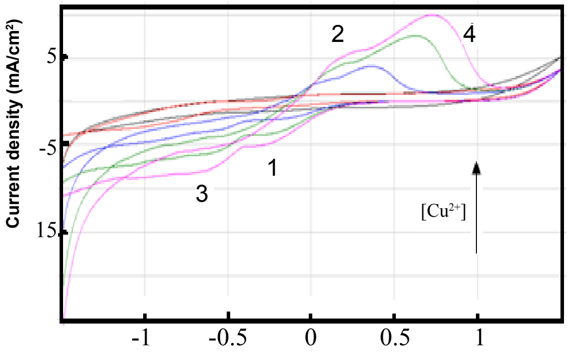


Figure 6: Cyclic voltammograms obtained by (MO=molecule C)- CPEs at 100 mV/s for different concentrations of copper, in buffer solution

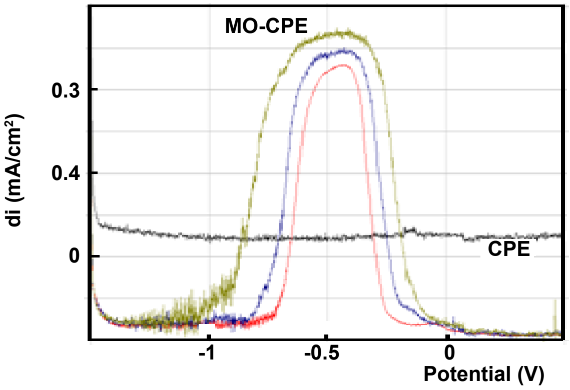


Figure 7: SQW voltammograms of different concentration of lead (pH 7.2), in buffer solution, accumulation time 10 min.

Integrations of the peaks to determine the number of electrons involved in each reaction. We find that each peak 1, 2 and 3 reactions undertake one electron, and four electrons investigated in peak 4, suggesting the following mechanism:

The Peak 4 corresponds, probably, to the release of copper from the organic matrix according to the reaction:

The determinations of heavy metal traces (Pb^{2+}, Cu^{2+} and Cd^{2+}) were performed by square wave voltammetry (SQWV); however, the behavior of each metal was also studied by CV in order to understand the affinity of developed organic film towards them.

The SQWV's recorded at carbon paste electrode modified with molecule A, after exposure, 10 min, to different concentrations of lead, in stirred solutions, are shown in Figure 7.

The peak current of lead at the MO-CPE electrode is intense than that of unmodified electrode. Thus there is a substantial enhancement in lead oxidation peak current when modified electrode is used.

The concentration range from 3×10^{-6} to1.5×10^{-6} mol/L was examined for proportionality of MO-CPE signal with concentration of lead by analyzing model solutions containing appropriate additions of Pb2+. The linear calibration plots (Figure 8).

were obtained under optimal conditions. The regression straight line has the following equation:

$$i_p=0.091\,[Pb^{2+}]+1.213$$

where i_p is expressed in µA and the concentration in µmol/L and the

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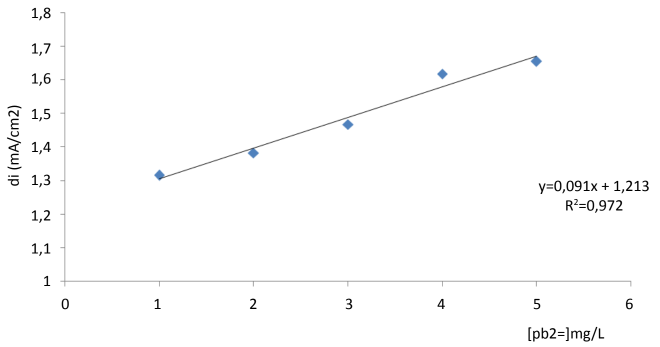

Figure 8: Influence of concentration of lead on the peak intensity at (MO= molecule A)-CPE under the optimized conditions.

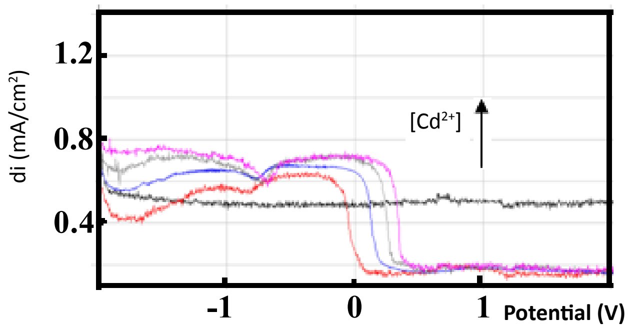

Figure 9: Influence of concentration of cadmium on the peak intensity at (MO= molecule B)-CPE under the optimized conditions.

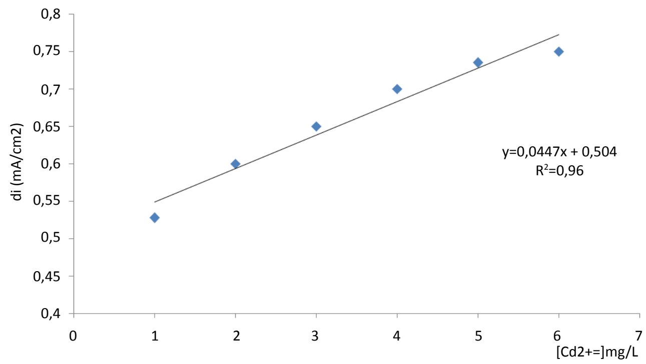

Figure 10: Influence of concentration of Cd²⁺ on the peak intensity at (MO= molecule B)-CPE under the optimized conditions.

correlation coefficient was 0.972.

In the case of electro analysis of cadmium by the carbon paste electrode modified by the molecule B, we find that the square wave voltammograms (Figure 9) gives rise to an ill-defined peak to about -0.2V, the intensity of this flattened peak increases with the concentration of Cd^{2+} ion, the correspond calibration curve is given in Figure 10.

The analytical study of copper by molecule C modified carbon paste electrode is shown in Figure 11. The corresponding calibration curve is shown in Figure 12.

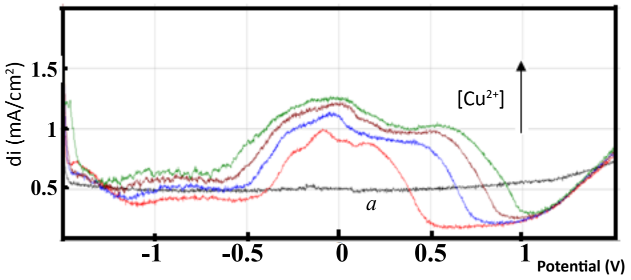

Figure 11: Influence of concentration of copper on the peak intensity at (MO=molecule C)-CPE under the optimized conditions.

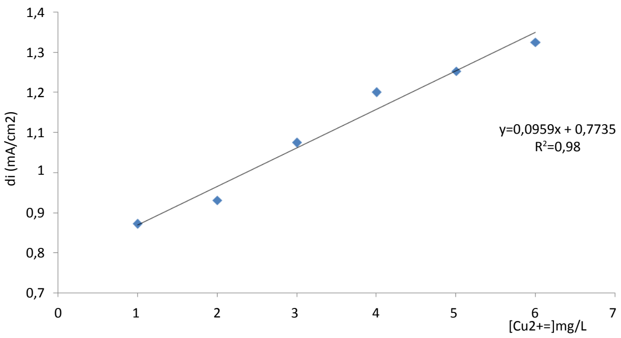

Figure 12: Influence of concentration of Cu²⁺ on the peak intensity at (MO=molecule C)-CPE under the optimized conditions.

Conclusion

In conclusion, it was possible demonstrating the potentiality of the proposed electrodes for determining heavy metals. Such a sensor is characterized by a higher sensitivity and reproducibility than those of the unmodified carbon paste electrode.

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