

Electrochemical Chelation of Heavy Metals by 2-Benzimidazole

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Abstract

The performance of carbon paste electrodes modified with 2-Benzimidazole Thiol (BIT) was investigated as a modified electrode for the determination of lead. 2-Benzimidazole was developed and introduced as a new modifying agent for heavy metal chelation. The physical parameters that could influence the current densities were investigated and optimized. The prepared electrode showed a good linear response to lead ions in the different concentrations, the detection limit was $2,77 \cdot 10^{-9}$ mol/l. The behavior of Pb^{2+} is studied by Square Wave Voltammetry (SWV), Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS). Three peaks of oxidation of Pb^{2+} are observed successively at -0.7 V, -0.5 V and -0.42 V, the peak of reduction occurs at +0.43 V. The interference effect was studied.

Keywords: Lead; 2-Benzimidazole Thiol; Square Wave Voltammetry (SWV); Cyclic Voltammetry (CV); Electrochemical impedance spectroscopy (EIS)

Introduction

Pollution of the environment by heavy metals is mainly due to human activities but also to natural phenomena such as weather and volcanic eruptions [1-5]. Industrial sources include metal processing in refineries, coal in power plants, petroleum combustion, nuclear power plants and power lines, plastics, textiles, microelectronics, wood preservation and paper processing. Lead is a persistent toxic metal that has the facility to accumulate in humans, animals and plants. According, finding the sensitive, fast and simple analytical method for precise determination and chelating of Pb^{2+} is a priority.

There are some reviews on the use of spectrometric techniques such Atomic Absorption Spectrometry (AAS) [6,7], atomic emission spectrometry (AES) [8] and mass spectrometry (MS). Although, these methods proved their effectiveness and high but bring also some disadvantages such as complicated operation, expensive maintenance, expensive appliance and low electrical power requirement [9]. Recently, it has been demonstrated that the chemically modified carbon paste electrodes have received considerable attention due to their numerous advantages, such as easy manufacture, no poison, low prize [10-12].

In the present study, we proposed a new modified electrode based on carbon paste modified with 2-Benzimidazole Thiol and we also tested its ability to analyze lead, cadmium and mercury.

Experimental Section

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. PbSO_4 is obtained from Merck chemicals. Deionised water was used to prepare all solution. All organic molecules were synthesized in our laboratory.

Apparatus

Electrochemical experiments were performed using a Volta lab potentiostat (model PGSTAT 100, Eco Chemie B. V., Utrecht, The Netherlands) driven by the general purpose electrochemical systems data processing software (volta lab master 4 software). A conventional three-electrode system consisting of the 2BIT-modified carbon paste

working, platinum counter and SCE reference electrodes was used. The pH-meter (Radiometer Copenhagen, PHM210, Tacussel, French) was used for adjusting pH values.

Electrode preparation

The 2-Benzimidazole Thiol modified carbon paste electrode (BIT-CPE) was prepared by thoroughly hand-mixing of synthesis BIT and graphite powder (CP) to give BIT/CP ratios of 10% by weight (w/w). The obtained paste was dried at room temperature then a portion of the resulting paste was grounded and packed firmly into homemade PTFE cylindrical tube (geometric area 0.1256 cm^2) electrode. Electrical contact was established with a bar of carbon.

Procedure

The electrode, after having been washed with bidistilled water and heated at room temperature, was transferred into the sample cell (100 mL) (the sample was purged with pure nitrogen for 10 min). A pre-concentration step was necessary; the working electrode was immersed in water sample in open circuit. The initial working procedure consisted of measuring the electrochemical response of BIT modified carbon paste electrode in 0.1 M NaCl electrolyte at fixed concentration of Pb^{2+} . The cyclic voltammetry behavior of proposed modified carbon paste electrode was recorded from -1.5 to 1.5 V.

Results and Discussion

Figure 1 exhibit a cyclic voltammograms (CVs) recorded respectively, at BIT-CPE and CPE, in supporting electrolyte 0.1 M NaCl. The two curves (a and b) are not super imposable which confirms the modification of carbon paste electrode. We can see that the CVs recorded at BIT-CPE shows two well defined peaks, the first in the sense

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of anodic scanning at about -0.69 V corresponded of the oxidation of 2-Benzimidazole Thiol and the second is located at -0.07 V.

Electrochemical impedance spectroscopy (EIS) corresponding to CPE and BIT-CPE can be seen in Figure 2. In the case of the carbon-paste electrode, the impedance diagram shows three separate time constants, while the one recorded for the BIT-CPE electrode shows an unsymmetrical half circle.

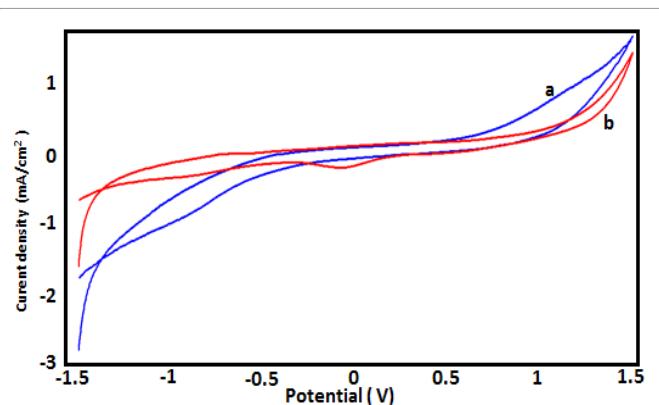


Figure 1: Cyclic Voltammograms recorded for: (a) bare carbon paste electrode (CPE) (b) carbon paste electrode modified with 2-benzeneimidazolthiole (CPE-BIT), in 0.1 M NaCl at 100 mv/s with 10% of CPE-BIT ratio and pH=7.

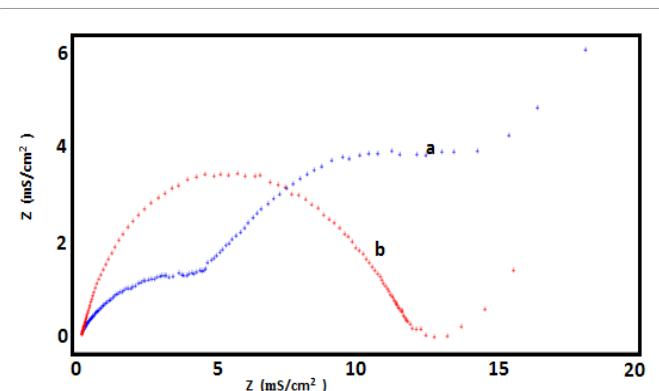


Figure 2: Electro-Chemical impedance spectroscopy (EIS) recorded for: (a) bare carbon paste electrode (CPE) (b) carbon paste electrode modified with 2-Benzeneimidazolthiole (CPE-BIT), in 0.1 M NaCl, scan rate 100 mv/s, 10% of CPE-BIT ratio and pH-7.

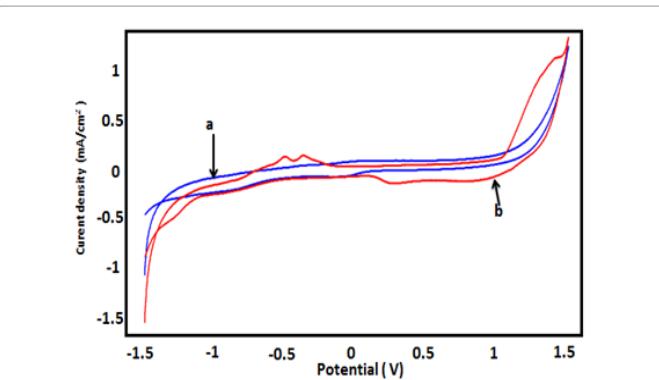


Figure 3: Cycle Voltammograms recorded for CPE-BIT: (a) in absence and (b) in presence of 0.6 mM pg Pb²⁺ in 0.1 M NaCl at 100 mv/s, pH=7, preconcentration time=1 min with 10% of CPE-BIT ratio.

Lead detection

The determination of lead was investigated by the Cyclic Voltammetry (CVs) (Figure 3) and the Square Wave Voltammetry (SWVs) (Figure 4) recorded for BIT-CPE before (curve a) and after 1 min of accumulation in a solution containing 0.6 mM of Pb²⁺ (curve b). In the anodic scanning direction, two oxidation peaks appear at $E_{p_1}=-0.7$ V and $E_{p_2}=-0.5$ V, whereas in the opposite direction of scanning, we observe one peak at $E_{p_3}=-0.42$ V.

The square-shaped voltammetry clearly shows these peaks which could be attributed according to the following mechanism (Figure 5):

At first, the Pb²⁺ ions are accumulated in the organic film of the electrode; it is the accumulation step then reduced in situ or in the solution. In the anodic scanning direction the lead formed is oxidized either in the solution or in the organic matrix, resulting in the appearance of two oxidation peaks.

Optimization of experimental conditions

In order to reveal the performance of BIT-CPE to detect lead, we carried out a series of manipulations which aim at the determination of the parameters influencing the electrochemical responses like BIT/CPE ratio, pH, and accumulation time (Figure 6).

Influence of accumulation time

The influence of preconcentration time was examined in 0.9 mM lead solution by SWV and EIS. From the SWVs obtained (Figure 7), we can observe that after only one minute of preconcentration the peak current reaches a maximum value, then begins to decrease gradually until 17 min preconcentration where its becomes stable. The EIS (Figure 8) has the form of a half circle which appears at high frequencies and corresponds to electron exchange phenomena. Then, the preconcentration time was fixed at 1 min for all further experiments.

Influence of scan rate

The influence of the scan rate on the redox peaks of Pb²⁺ was studied for BIT-CPE, at immersed time (1 min) in 2.1 mmol.l⁻¹ of lead. The Figure 8 shows both the anodic and the cathodic peak currents linearly decreases with the scan rate over the range from 30 to 120 mv/s, indicating that the electron transfers for Pb²⁺ at the CPE-BIT is adsorption controlled reaction. The Figure 9 shows the linear relationship between the scan rate anodic peak and cathodic peak currents of Pb²⁺ at the CPE-BIT.

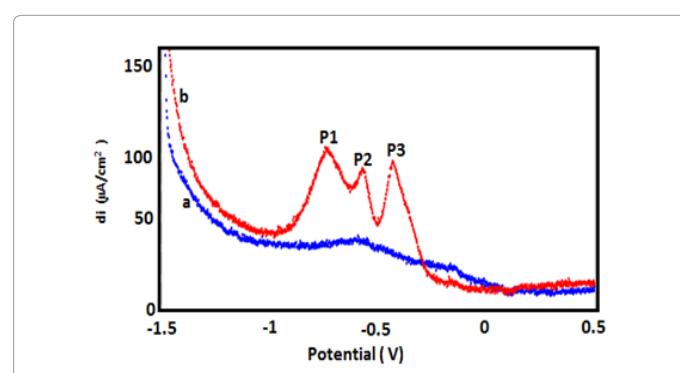


Figure 4: Square wave Voltammograms recorded for CPE-BIT: (a) in absence and (b) in presence of 0.6 mM pg Pb²⁺ in 0.1 M NaCl at 100 mv/s, pH=7, preconcentration time=1 min with 10% of CPE-BIT ratio.

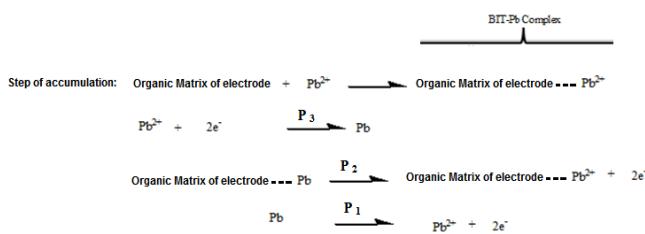


Figure 5: Mechanism of Pb^{2+} .

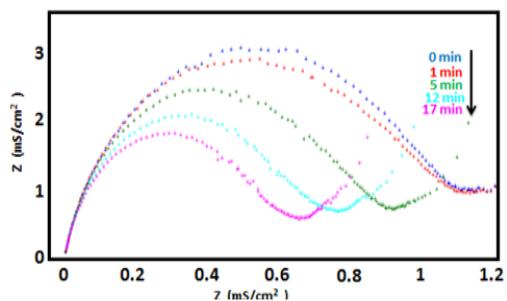


Figure 6: Bode diagrams recorded for CPE-Bit with 0.9 mM of Pb^{2+} in 0.1 M NaCl at different preconcentration time, pH=7 and 50% of CPE-BIT ratio.

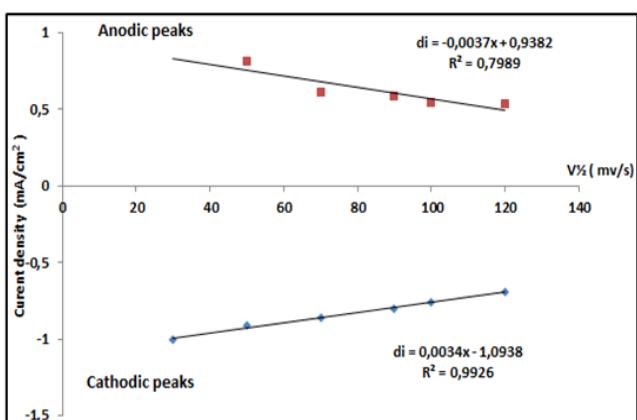


Figure 9: Plots of peaks current are versus scan rate.

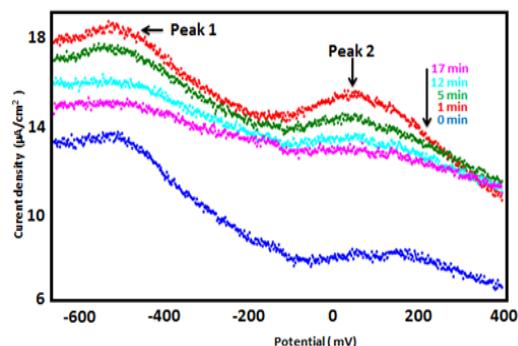


Figure 7: Square Wave Voltammograms recorded for CPE-BIT: with 0.9 mM pf Pb²⁺, in 0.1 M NaCl at different preconcentration time, scan rate 20 mV/S, pH=7 and 50% of CPE-BIT ratio.

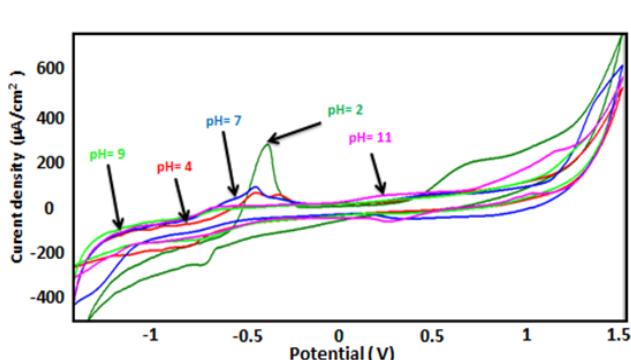


Figure 10: Cyclic Voltammograms recorded for CPE-Bit with 0.6 mM of Pb^{2+} in 0.1 M NaCl at different pH, scan rates 100 mV/S, $t_p=1$ min and 50% of CPE-BIT ratio.

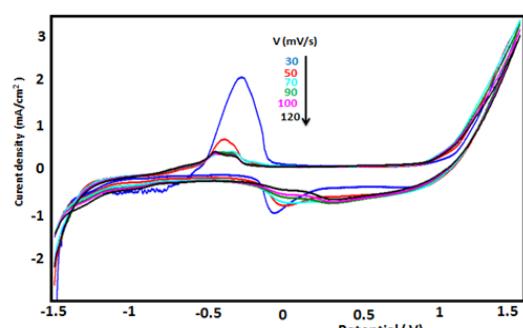


Figure 8: Cyclic Voltammograms recorded for CPE-Bit with 2.1 mM of Pb^{2+} in 0.1 M NaCl at different scan rates from 30 to 120 mV/S, pH=7 and $t_p=1$ min

Influence of pH

The pH effect on the BIT-CPE peak currents of lead ions was studied in the pH range of 4 to 11. The results obtained (Figure 10 and 11) show that the oxidation peak current increased when the pH value decreases (Figure 12). The decrease in peak currents at higher pH values could be due to the formation of lead hydroxide complexes at higher pH values, which hinders the accumulation of Pb^{2+} [13].

Influence of the BIT loading

The influence of the amount of 2-Benzimidazole Thiol on the sensitivity of the electrode is studied. The results obtained (Figure 13) showed that the peak current decreased with increasing the BIT

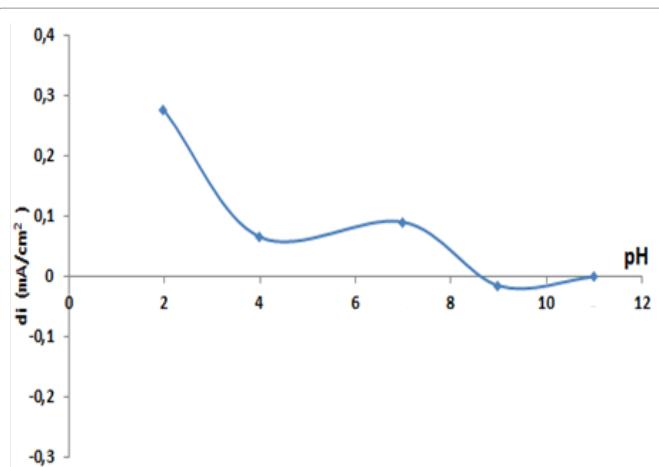


Figure 11: Plots of the relationship between solution pH and the redox peak current.

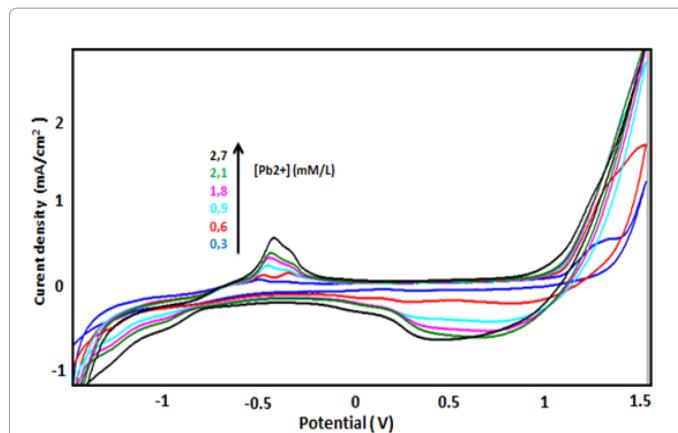


Figure 14: Cyclic Voltammograms recorded for CPE-Bit at different concentrations of Pb^{2+} in 0.1 M NaCl, $\text{pH}=7$, scan rates 100 mV/S, $t_p=1$ min and 10% of CPE-BIT ratio.

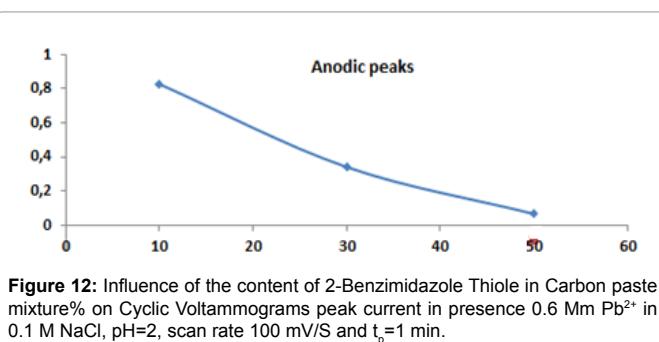


Figure 12: Influence of the content of 2-Benzimidazole Thiole in Carbon paste mixture% on Cyclic Voltammograms peak current in presence 0.6 Mm Pb^{2+} in 0.1 M NaCl, $\text{pH}=2$, scan rate 100 mV/S and $t_p=1$ min.

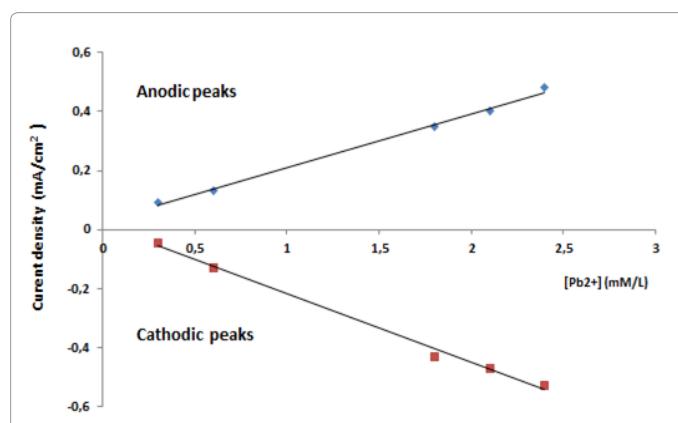


Figure 15: Plots of peaks are versus added concentration of Pb^{2+} .

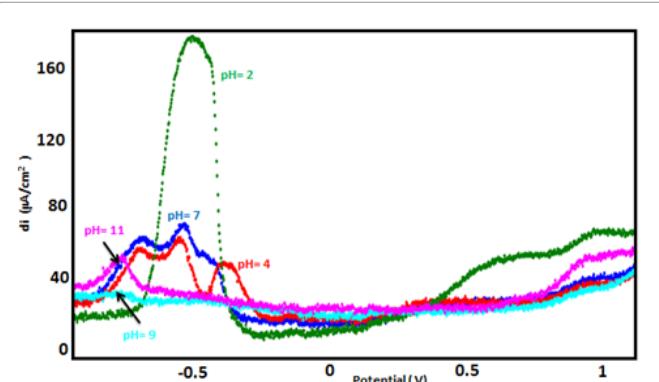


Figure 13: Square Wave Voltammograms recorded for CPE-Bit with 0.6 mM of Pb^{2+} in 0.1 M NaCl at different pH, scan rates 20 mV/S, $t_p=1$ min and 50% of CPE-BIT ratio.

concentration. This decrease is probably due to the decrease of the conductivity of the surface of the electrode.

Influence of lead concentration

Figure 14 shows the CV curves recorded at BIT-CPE, after pre concentration in solutions containing different concentrations of Pb^{2+} , in the range of 0.3 mM to 2.7 mM. Under optimized conditions the elaborated electrode showed a typical linear response (Figure 15), which can be expressed according to the following equation:

The detection limit (DL, 3s) and quantification limit (QL, 10s)

were, respectively, $2.77 \cdot 10^{-9}$ mol/l and $9.24 \cdot 10^{-9}$ mol/l. The two regression lines correspond to the oxidation peaks and reduction peaks are represented by the following two equations (I is expressed in mA and the concentration in mmol/L):

$$I_{\text{oxidation}} = 0.1823[\text{Pb}^{2+}] + 0.0278 \quad R^2=0.9957$$

$$I_{\text{reduction}} = -0.2332[\text{Pb}^{2+}] + 0.0151 \quad R^2=0.9947.$$

Interferences studies

Natural samples such as tap water, plasma, river water, etc. have several chemical elements that affect the health of living beings, which presents a great challenge for chemical analysis laboratories. For this reason, we thought to test the capacity of BIT-CPE to identify with precision three elements at a time such Pb^{2+} , Cd^{2+} and Hg^{2+} .

Figure 16 shows the Square Wave Voltammograms recorded at BIT-CPE pre concentrated respectively, in solution containing, 1.6 mmol/L Cd^{2+} (curve a), 1.5 mmol/L Pb^{2+} (curve b), 1.8 mmol/L Hg^{2+} (curve c) and after adding all these elements in the same solution (curve d) in 0.1 M NaCl while respecting the optimal conditions. From the negative potential range, the appearance of the oxidation peak of Cd^{2+} at -0.84 V immediately followed the oxidation peak of Pb^{2+} at -0.7 V, but as soon as we slightly exceed the negative field potential, we are facing the oxidation peak of Hg^{2+} exactly at +0.03 V.

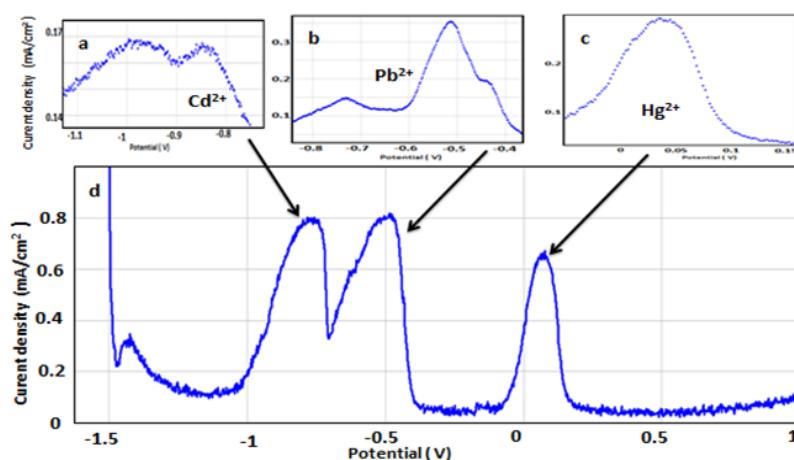


Figure 16: Cyclic Voltammograms recorded for CPE-Bit in presence of 1.6 mM/1 Cd²⁺ (a) 1.5 mM/1 Pb²⁺ (b) 1.8 mM/1 Hg²⁺, (c) after adding all these elements in electrolytic solution and (d) 0.1 M NaCl, pH=7, scan rates 20 mV/S, and 10% of CPE-BIT ratio.

Conclusion

In this study, we proposed a new modified electrode BIT-CPE for the simultaneous determination of Pb²⁺, Cd²⁺ and Hg²⁺. We have seen through this work that the realized electrode is very sensitive and very selective with regard to several chemical elements which give it the opportunity to analyze them without disruption or overlap. The prepared electrode is not soluble in water, non-toxic and non-polluting.

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