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ELECTROCHEMICAL DETERMINATION OF MERCURY (II) CONCENTRATIONS WITH CARBON PASTE ELECTRODE MODIFIED IN WASTEWATER

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ABSTRACT

The electrochemical determination of mercury (II) in industrial wastewater with a carbon paste electrode (CPE) modified with L_1 (N,N-dichromone-O-phenylenediamine) was studied using differential pulse voltammetry(DPV). For the optimization of this method, different parameters such as electrode composition, pH effect, preconcentration time, accumulation potential, accumulation time and interferences were studied. Hg (II) ions were preconcentrated on the modified electrode surface at open circuit by forming complex with L_1 (L_1-Hg). The results indicated that the peak current have a linear relationship with the concentration range from 0.1 to 10 nM, with a very good correlation coefficient of 0.996. The detection limit of the method was found to be 0.028 nM and the relative standard deviation was 1.4% for 10 successive determinations of 5.10^{-10}mol/L.

Keywords : *CPE (carbon paste electrode), L_1, mercury(II), differential pulse voltammetry.*

RÉSUMÉ

Détermination électrochimique de l'ion mercure (II) à l'aide d'électrode à pâte de carbone modifiée dans les eaux usées

La détermination électrochimique de mercure (II) dans des eaux usées industrielles à l'aide de l'électrode à pâte de carbone (CPE) modifiée avec L1 (N, N-dichromone-O-phénylène-diamine) a été étudiée en utilisant la voltamétrie à impulsion différentielle (DPV en anglais).

Pour cela, les ions de mercure (II) ont été préalablement préconcentrés sur la surface de l'électrode modifiée à circuit ouvert formant ainsi des complexes avec L1 (L1-Hg). Les résultats obtenus indiquent que le courant a une relation linéaire avec la concentration dans gamme 0,1 à 10 nM, avec un très bon coefficient de corrélation de 0,996. La limite de détection de la méthode est estimée autour de 0,028 nM et l'écart type relatif est de 1,4% pour les 10 déterminations successives de 5.10^{-10}mol/L. Pour l'optimisation de ce procédé, différents paramètres tels que la composition de l'électrode, l'effet du pH, le temps de pré-concentration, le potentiel d'accumulation, le temps d'accumulation et les interférences ont été étudiés.

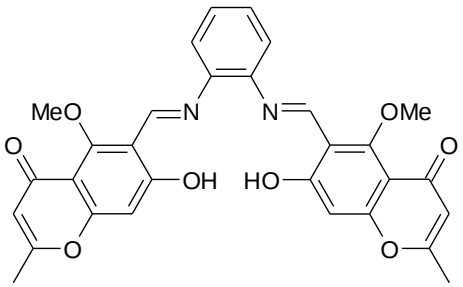
Mots-clés : *CPE (électrode à pâte de carbone), L1, mercure (II), voltamètrie à impulsion différentielle.*

I - INTRODUCTION

Mercury is one of the most toxic elements of the environment, because of its high reactivity, extreme volatility and relative solubility in water and living tissues [1]. It has crucial risk to human health [2]. In spite of the enormous effort done in research, the pollution of the environment caused by mercury remains a serious problem [3, 4]. It is very important to improve analytical techniques such as rapidity, sensitivity and selectivity. However, the instruments used in analytical methods such as gas chromatography (most frequently applied) [5], high performance liquid chromatographic separation [6], colorimetric [7], atomic fluorescence spectrometry (AFS) [8], cold vapor atomic fluorescence spectrometry [9], atomic absorption spectrometry [10] and so forth are very expensive, have longer experiment time and need qualification for their use.

To solve this problem, electrochemical techniques could be used for the determination of mercury (II) because of its easy application, low-cost materials and the analysis is not time consuming.Chemically modified electrodes (CME) have attracted great attention in the past decades since they improve the sensibility of electrochemical analysis methods [11]. CME have many advantages such as low cost, short analysis time, high sensitivity in electro analytical determination of different compounds [3-12]. In addition, the use of carbon paste electrode with appropriate modifier enhances the selectivity and sensitivity of electro analytical methods. There are several methods to modify the working electrode. These methods include electrochemical, chemical or physical methods. The sensor used in our work, L_1, is a Schiff-base.

The Schiff-base are obtained by condensation of a carbonyl compound with primary amines and are so regarded as privileged ligands [13-15]. Due to their capability to form complexes with different transition metals they can act as catalysts for many different reactions [16-18]. In this work, the elaboration and the analytical use of carbon paste electrode modified with **L_1** are proposed for the detection of mercury (II). The influence of parameters were studied and optimized by DPV.



N,N-dichromone-O-phenylenediamine

Scheme 1 : *Structure of **L_1**(**N,N**-dichromone-O-PhenyleneDiamine)*

II - EXPERIMENTAL

II-1. Apparatus

Electrochemical experiments were carried out with an auto lab PGSTAT 30 potentiostat (Ecochemie, Utrecht Netherlands) controlled by GPES 4.8 software. The three electrode system consisted of carbon paste (Merck) or modified carbon paste electrodes as working electrodes (WE); the reference was an SCE (5M KCl) electrode (RE) and platinum wire was used as the counter electrode (CE). A fisher Scientific Accumet AB15BASIC pHmeter was used to prepare solutions at different pH.

II-2. Reagents

All chemicals products were of analytical reagent grade. L_1 was obtained from physical chemistry laboratory of Cairo University (Egypt). Mercury sulphate was obtained from Riedel-Dehaen. Solutions were prepared with distilled water. Standard mercury (II) stock solution was prepared by dissolving $HgSO_4$ in acidic solution. All experiments were carried out at room temperature (25°C).

II-3. Samples preparation

Wastewater samples were collected from a tannery Industry in Casablanca (Morocco)

II-4. Preparation of carbon paste electrode

The carbon paste electrode was prepared by mixing thoroughly 1g of graphite powder and 0.3mL of paraffin oil until homogeneous paste is obtained. The paste was then packed into the electrode cavity (2mm) with Ø=4mm. The electrical contact was made by means of a stainless steel wire. Before each use the electrode surface was rubbed with a piece of white paper until a smooth surface was observed.

II-5. Mercury determination

The surface of fresh bare CPE was immersed in aqueous solution containing:

- A certain concentration of $HgSO_4$ in 0.1mol/L HCl solution under stirring
- The preconcentration of Hg^{2+}ion was carried out at open circuit under stirring. After the preconcentration step, the stirring was stopped and the solution was left to equilibrate during 10s. An accumulation potential at -0.5V was applied during 60s in the range potential from -0.8 to +1.2 V using DPV: scan rate 50mV/s, potential step height of 10 mV, pulse amplitude 50mV.

II-6. Electrochemical characterization of bare carbon paste electrode (CPE) and modified carbon paste electrode (CPE/L_1) in acidic media (HCl).

The characterization of the bare carbon paste electrode (CPE) and modified carbon paste electrode with L_1 (CPE/L_1) were carried out in a solution of HCl 0.1 mol/L using as electrolyte support. To do this, the cyclic voltammetry and differential pulse voltammetry were used. The measurements were carried out with the silver electrode and converted with respect to the saturated calomel electrode.

III - RESULTS AND DISCUSSION

III-1. Cyclic voltammograms of the bare CPE

Figure 1 shows the cyclic voltammetry measurements carried out on bare CPE and electrode CPE/L_1 in hydrochloric acid medium. In this ***Figure***, the voltammogram B shows a high capacitive load, with the probably presence of peaks characteristic of the oxidation of L_1. Below -0.2 V and above 0.8 V, the current changes rapidly and between the two potentials, we noticed the two redox peak at 600 mV and 400mV and an irreversible peak at 100mV. These observations show that L_1 greatly changes the properties of the graphite electrode by causing an increase in the current intensity. The oxidation of L_1 peak appears at 600 mV vs/SCE and the cathodic peak at 400 mV vs/SCE.
As these peaks are not displayed with voltammogram A (absence of L1), it is clear that the peaks are characteristic of an electrooxidation L_1 at 600 mV, an irreversible peak at 100 mV vs/SCE and a peak corresponding to electroreduction of L_1 located at 388 mV vs/SCE.

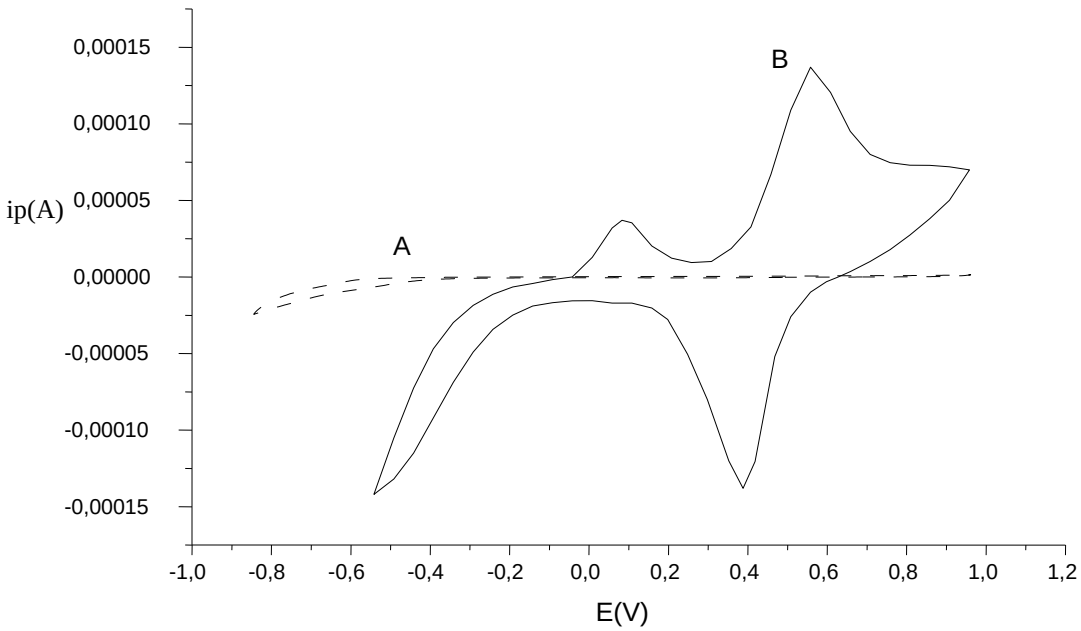


Figure 1 : *Cyclic voltammograms of the bare CPE (A) and modified L_1 (B) in 0.1 mol/L HCl with a scan rate of 50 mV/s*

III-2. Optimization of experimental conditions

After the accumulation step made with open circuit in solution containing 10^{-6} mol/L of Hg(II), the electrode was placed in the voltammetric cell with the supporting electrolyte (HCl 0.1mol/L) and a potential of 0.1V was applied at the beginning of the scan. When the potential scan reaches the value of 0.025V, an anodic peak is produced owing the oxidation of mercury as indicated by the ***Equation 1:***

$$Hg^0 \rightarrow Hg^{2+} + 2e- \qquad (1)$$

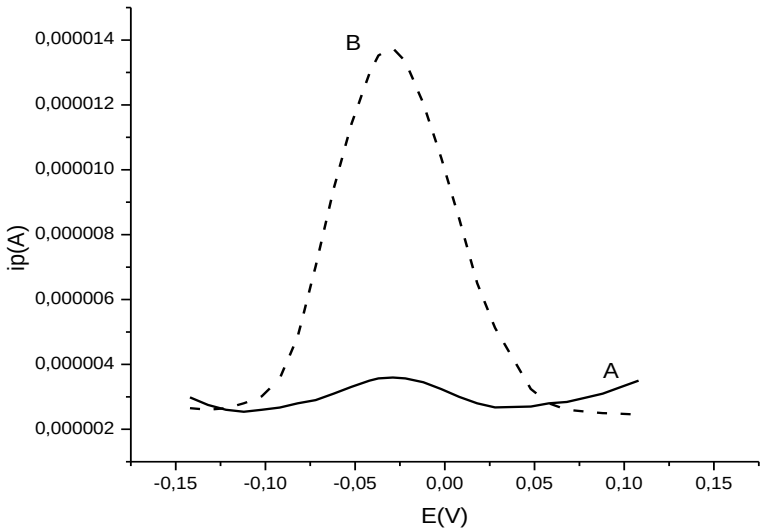


Figure 2 : *CPE voltammograms of bare CPE (A) and CPE/L$_1$ (B) in a solution of of 10^{-6} mol/L of Hg (II)*

The experimental conditions are 0.1 mol/L HCl, accumulation potential - 0.5 V for 20 s and the scan rate 50 mV/s.

III-3. Effect of preconcentration time

A parameter expected to be of primary importance to mercury (II) preconcentration was the length of time allowed for the deposition process to take place. The results reported in ***Figure 3*** show the variations of the mercury oxidation current for a preconcentration time varying from 3 to 10 min.

A decrease in the intensity of the peaks is observed for the oxidation of mercury in almost linear function of the increase in the preconcentration time, until a time of 5 min. A plateau is observed and then a further drop. This plateau should be the phenomenon of saturation of the surface. The peak current was larger and the dependence was not linear. The higher increase in current occurred at 3 min. Therefore, 3 min was chosen for the preconcentration step. This is consistent with the value obtained in the literature [21]. Comparing this value to previously reported rates of uptake of metal ions at various CMCPE (chemically modified carbon paste electrode) surfaces, this process was very fast [22-24].

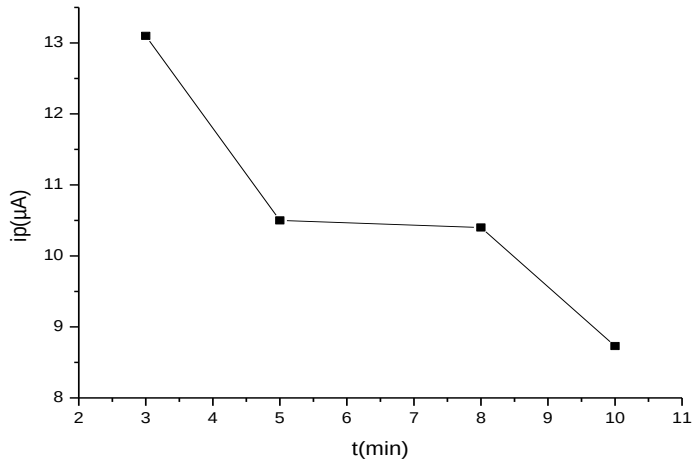


Figure 3 : *Dependence of anodic peak current on preconcentration time at 1.10^{-6}mol/L of mercury*

The experimental conditions are 0.1 mol/L of HCl, accumulation potential - 0.5 V for 20 s and the scan rate 50 mV/s.

III-4. Effect of accumulation time

The effect of accumulation time for mercury (II) determination was studied from 10 to 150s ***(Figure 4)***. The peak current increased with increase in accumulation time up to 60s and then remained nearly constant between 60 and 150s. Before 60s, the rapid increase of the peak current explains the increasing formation of complex between mercury (II) ions and L_1. After 60s, the step of stability was attained. Therefore; 60s was selected for all the subsequent measurements.

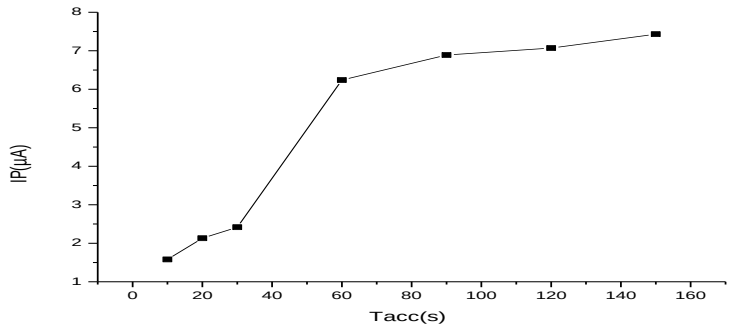


Figure 4 : *Effect of accumulation time on the peak current of mercury (II)*

The experimental conditions are 0.1 M HCl, accumulation potential - 0.5 V for 20 s and the scan rate 50 mV/s.

III-5. Effect of accumulation potential

Figure 5 shows the influence of the accumulation potential on the peak current of Hg (II), which was studied over the potential range from -0.9 to -0.5V. As can be seen, in ***Figure 5***, the peak current increases with the increase in accumulation potential up to -0.8V, and then decreases from -0.8 to -0.7 V and becomes constant until -0.5V. This phenomenon could explain the beginning of saturation of the surface of the electrode. Therefore, we chose -0.8 V as optimum accumulation potential for further work. This value is the same obtained by Sevgi et al [25].

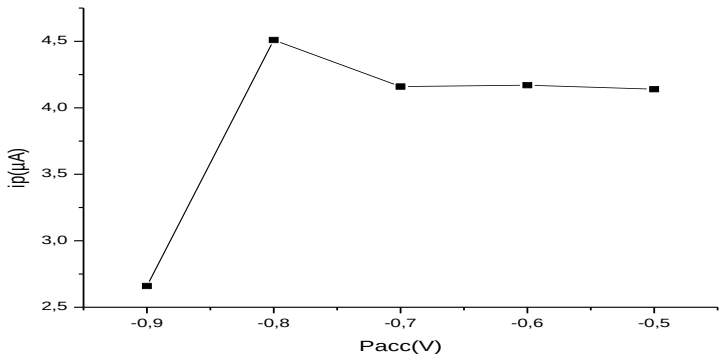


Figure 5 : *Effects of accumulation potential on DPV peak current for 1.10^{-4}mol/L of Hg^{2+} at L_1modified CPE electrode)*

The experimental conditions are 0.1 M HCl, accumulation potential - 0.5 V for 20 s and the scan rate 50 mV/s.

III-6. Calibration curve

The performance of the proposed method was evaluated with respect to the range of linearity, the limit of detection. Mercury calibrating curve was performed in an optimum analytical condition and linearity of peak current versus mercury concentration was checked. The peak current value linearly increases with Hg^{2+} concentration in the range from 0.1 to 10 nM. The analytical curve was linear according to equation:

$$i_p = 1{,}867 + 0{,}427\ C_{Hg2+} \qquad (2)$$

where i_p in µA and C_{Hg2+} in nM. With correlation coefficient $R^2 = 0.999$. The detection limit (DL=3S.D/analytical curve slope) was found to be 0.028 nM. The relative standard deviation of 10 determinations of 0.5nM is 1.4%.

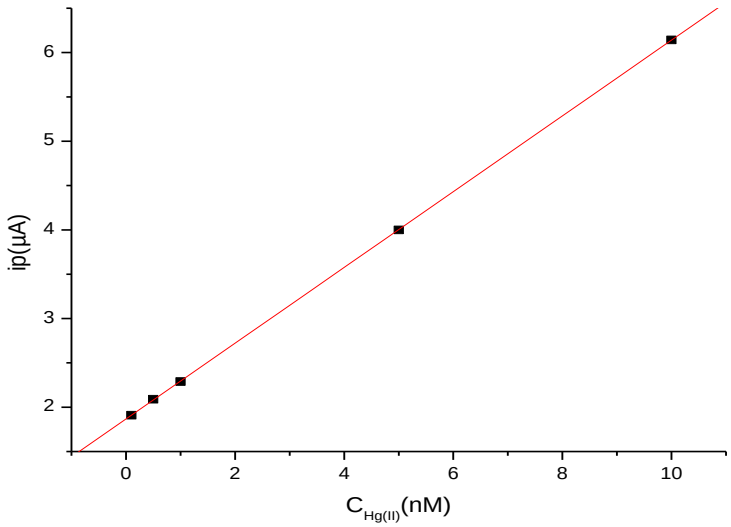


Figure 6 : *Calibration plot for mercury (II) in 0.1 M HCl, preconcentration time 3min, concentration range 0.1 to 10 nM*

The experimental conditions are 0.1 M HCl, accumulation potential - 0.5 V for 20 s and the scan rate 50 mV/s.

III-7. Interferences

The interference studied were carried out by evaluating the interference effects of Pb^{2+}, Fe^{3+}, $Fe^{2+}$and Zn^{2+}under optimized experimental conditions at CPE/L_1: Pacc=-0.8 V, Tacc= 60 s, $t_{préc}$ = 3min.

Table 1 : *Effect of interfering metal ions on the peak current of mercury observed after preconcentration in 2µM of Hg^{2+} solution in the presence of interfering metal ions*

cation	Concentration of the interferent (µmol/L)	Change in peak current, %
Pb^{2+}	1	68,8
Fe^{3+}	1	-16,7
Fe^{2+}	1	-33,3

The method used for calculating the percentage is as followed:

$$I\,\% = \frac{I_1 - I_2}{I_1}.100\,, \qquad (3)$$

I_1 signal of Hg^{2+} and I_2 signal of interference. As indicated in the table, Pb^{2+} could interfere the determination of Hg^{2+}. Interference of Pb^{2+} must be eliminated using appropriate masking agent.

III-8. Analytical Application

In order to evaluate the performance of the proposed method, it was applied to the determination of mercury (II) in industries wastewater samples under optimized conditions. The samples were collected from a tannery industry of Casablanca (Morocco) and adjusted to pH< 2. In order to take into account the matrix effect, we applied the standard addition method. The regression equation was:

$$i_p(\mu A) = 6.311 + 13.597\, C_{Hg2+}, \qquad (4)$$

where ip in µA and C_{Hg2+} (R^2 = 0,999) and the detection limit was found to be 0.011 nM. These data indicate that this method is promising for water samples containing the concentrations of Hg^{2+} examined in this study.

The analysis of real samples showed that, although our propose method was sensitive to allow the determination of mercury in wastewaters [24], it may represent an extremely useful approach for the analysis of water contaminated by heavy metals. Therefore, the developed CPE/L_1 represents easy electrode handling and modifying

IV - CONCLUSION

We have developed an effective method for the determination of metal ions by L_1 modified CPE. We showed that, after optimization of the experimental conditions, the electrode prepared was suitable for the determination of Hg with satisfactory. This method developed was applied to real samples to determine Hg^{2+} contents about nM.

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