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Evaluation of carbon paste electrodes modified with 1-furoylthioureas for the analysis of cadmium by differential pulse anodic stripping voltammetry

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Abstract

Two series of 1-furoylthioureas (FTHD) were used as modifiers of carbon paste electrodes (CPEs) for the analysis of Cd(II). The capacities of the newly FTHD-modified CPEs were calculated and the surface reactions during the preconcentration of Cd(II) were studied by cyclic voltammetry. The analyte was accumulated on the surface of the modified CPEs by complexing with FTHD 3,3-disubstituted (series **1**) and 3-monosubstituted (series **2**) and reduced at a negative potential (−1.0 V). It was then quantified by differential pulse anodic stripping voltammetry (DPASV) in Britton–Robinson buffer at pH 4. Experiments were conducted to establish the optimal carbon paste composition, electrolyte and pH of the determination, accumulation potential and time, and instrumental parameters. Under the optimized working conditions good linear correlations were obtained for the calibration graphs in the concentration ranges studied. For 5 min of accumulation time, detection limits using modified CPEs with ligands of series **2** were lower than that of series **1** (6×10^{-5} mg L^{-1} versus 3×10^{-3} mg L^{-1}, respectively, for the CPEs modified with 1-furoyl-3-*p*-tetradecylphenylthiourea and 1-furoyl-3-benzyl-3-phenylthiourea taken as models of both series). For a series of seven determinations of Cd(II) at 0.5 mg L^{-1} relative standard deviations below 3.9% were achieved for CPEs with ligands of both series. Only Pb(II) and Cu(II) apparently affected the electrochemical response of Cd(II).

Keywords: Chemically modified carbon paste electrode; Differential pulse anodic stripping voltammetry; Cadmium(II); 1-Furoylthioureas

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1. Introduction

Cadmium is one of the most toxic heavy metals of prime environmental and health concern. Cadmium toxicity may be manifested by a variety of syndromes and effects on human health [1,2]. Sensors for obtaining real time ppb-level cadmium concentration would reduce time and costs associated with the most common methods for the characterization and treatment of hazardous waste sites. Stripping voltammetric techniques are favourable methods for the determination of heavy metal ions, including Cd(II), because of their speed, remarkable analytical sensitivity, relative instrumental simplicity and minimum sample pre-treatment required prior to analysis. These attractive features have resulted in rapid development and wide application of stripping voltammetry [3–5]. A number of analytical determinations of Cd(II) based on stripping voltammetry at hanging mercury drop electrode have been reported [6–8]. However, mercury drop electrodes have the disadvantage of being mechanically unstable during various steps of the assay procedure and issues related to the use and disposal of toxic mercury, thus they are less desirable than solid-state sensors in routine field applications [9,10]. In the past two decades, more and more works has been performed at mercury free modified electrodes [11–16]. Carbon paste electrodes chemically modified are endowed with many good qualities, such as easy fabrication and renewal, low background current, low cost, ease of handling and applicability to anodic oxidations [3–5]. Different modifiers for carbon paste have been reported in the last years for the electrochemical stripping analysis of Cd(II): bismuth-powered [17], carbamoylphosphonic acid [18], organofunctionalized amorphous

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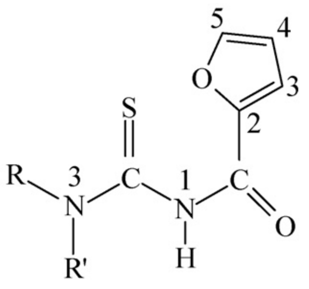
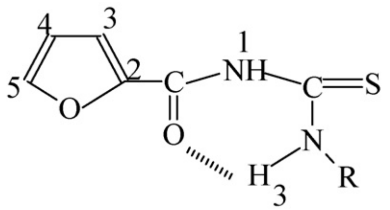
silica [19], diacetyldioxime [20], polycyclodextrin [21] and *N*-*p*-chorophenylcinnamohydroxamic acid [22]. The detection limits for these carbon paste modified electrodes are in the range from 0.0011 to 0.22 mg L^{-1}, with relative standard deviations from 2.6 to 6.5%. Due to its affinity by sulphurated species, modifiers containing sulphur in their structures are of interest in the preparation of carbon paste electrodes chemically modified for cadmium detection. Two series (Figs. 1 and 2) of 1-furoylthiourea derivatives (FTHD) have been successfully used as ionophores in ion selective electrodes (ISEs) for various heavy metal ions, including Cd(II) [23]. This application required a sharp modulation of the coordination strength of these ligands. Formation of very stable complexes is usually related to a short electrode lifetime due to the poisoning of the ISE membrane. The best performance in that application corresponded to 3-monosubstituted 1-furoylthioureas (series **2**) and it has been the main antecedent for using these ligands as Cd(II) complexing modifiers incorporated in carbon paste electrodes (CPEs). Recently we have first reported [24] the preliminary results concerning the preconcentration and voltammetric determination of Cd(II) by differential pulse anodic stripping voltammetry (DPASV) at these FTHD-modified CPEs in order to correlate the electroanalytical response (dependence of the binding capabilities of the FTHD-modified CPEs on the Cd(II) adsorption) with those changes observed in the FHTD Raman spectra after complexation with $CdCl_2$ in neutral media (ethanol), and the chemical yield of the complexes obtained, using the 1-furoylthioureas that gave response for both techniques [24,25]. The present work deals with the development and evaluation of these new chemically modified electrode systems suitable for the chemical preconcentration of Cd(II) at trace levels, using the 1-furoylthioureas that showed the best electrochemical behaviour. Some of the FTHD can preconcentrate Cd(II) from aqueous solution to the surface of the modified CPE by forming complexes with this ion and greatly increasing the sensitivity of its determination. The experimental data show that some of the FTHD-modified CPEs have high sensitivity, adequate selectivity and reproducibility, and a wide operative linear range of concentrations, for the determination of Cd(II) in water samples. The FTHD have the advantages of simple methods of synthesis and purification, and their low solubility in water.



No.	R	R'
1a	- CH_2 CH_2 CH_2 CH_2 CH_2- (piperidinyl)	
1b	-CH_2CH_3	-CH_2CH_3
1c	-C_6H_5	-C_6H_5
1d	-C_6H_5	-$CH_2C_6H_5$
1e	-C_6H_5	-CH_2CH_3
1f	-C_6H_5	-CH_3

Fig. 1. Series **1** ligands. The C=O and the C=S groups adopt a twist “S”-shaped conformation.



No.	R
2b	-C_6H_{11}
2c	-$CH_2C_4H_3O$
2d	-$CH_2C_6H_5$
2f	-C_6H_5
2g	-(o)$C_6H_5CH_3$
2h	-(o)$C_6H_5NO_2$
2j	-2-C_5H_5N
2k	-(m)$C_6H_5CF_3$
2m	-(p)$C_6H_5C_{14}H_{29}$

Fig. 2. Series **2** ligands. The C=O and the C=S groups adopt an “S”-shaped conformation due to the intra-molecular N_3–H···O=C– hydrogen bond bridge.

2. Experimental

2.1. Reagents and chemicals

Graphite powder (spectroscopic grade RWB, Ringsdorff-Werke GmbH, Bonn-Bad Godesberg, Germany), mineral oil (Sigma, St. Louis, USA), acetic acid (Merck, Darmstad, Germany), sodium hydroxide (Panreac Barcelona, Spain), boric acid (Merck), *ortho*-phosphoric acid (Panreac) and cadmium chloride (Merck) were used without further purification. Stock solutions of 1 mg L^{-1} Cd(II) were prepared in water. Working standard solutions of lower concentrations were prepared freshly by dilution. Nanopure water used throughout to prepare all solutions was obtained by passing twice-distilled water through a Milli-Q system (18 MΩ cm, Millipore, Bedford, MA).

The 1-furoylthioureas (series **1** and **2**) were synthesized as previously reported by Otazo-Sánchez et al. [23], and then recrystallized twice in ethanol. In order to provide certain continuity with previous studies on these families of thiourea derivatives [23–25], the same numerals there used are preserved.

2.2. Apparatus

Voltammetric measurements were performed with an Autolab PGSTAT20 (Ecochemie, Utretcht, The Netherlands) potentiostat/galvanostat interfaced with a personal computer, using the Autolab software GPES for waveform generation and data acquisition and processing. The experiments were carried out in a single-compartment three-electrode cell (25 mL), at room temperature (25 ± 1 °C), under stirring during the accumulation step. The electrochemical cell contains a working FTHD-modified CPEs with a surface area of 7 mm^2 (from Metrohm, Herisau, Switzerland), a platinum wire counter electrode and an Ag/AgCl/3 M KCl reference electrode.

2.3. Electrode preparation

The carbon paste unmodified was prepared by adding 0.36 mL mineral oil to 1 g carbon powder. FTHD-modified CPEs were prepared by substituting corresponding amounts of the carbon powder (5, 10 and 20% weight-to-weight ratio) by the FTHD and then adding the mineral oil and thoroughly hand-mixing in a mortar and pestle. The resulting paste was packed into the electrode and the surface was smoothed. The FTHD-modified CPEs were renewed after each measurement and then polished with no. 1200 emery paper and wiped gently with weighing paper to get a fresh surface.

2.4. Procedure

Cyclic voltammograms (CVs) were carried out after purging the solutions for 10 min with nitrogen. CVs of the base line were run from −0.7 to 0.8 V and back (at scan rates from 10 to 500 mV s^{-1}) using Britton–Robinson buffer at pH 4 as electrolyte support. CVs of Cd(II) solutions in aqueous media were recorded from −0.4 to −1.1 V and back at the same scan rates.

All quantitative measurements were performed using DPASV to achieve the sensitivity required for trace analysis. Twenty-five milliliters of supporting electrolyte was added to the electrochemical cell, and then standard solution of Cd(II) was added into the cell. The mixture solution was stirred for 5 min at the potential of −1.0 V and let to settle for 5 s. The stripping voltammograms in the range from −1.0 to −0.5 V were recorded in the differential pulse mode, for which the scan rate was 20 mV s^{-1}, the pulse amplitude 100 mV, the pulse repetition time 0.6 s and the pulse duration 0.06 s.

3. Results and discussion

3.1. Electrochemical stripping

The performance of the newly FTHD-modified CPEs developed is based on the preconcentration of Cd(II) from aqueous solution onto the surface of the modified electrodes by forming complexes of different strength with the modifier [24]. By this means, the surface concentration of Cd(II) is much larger than those of the unmodified electrode and the sensitivity is greatly increased. The Cd(II) accumulated was reduced at −1.0 V and the product was then oxidized in the stripping stage. The steps can be described as follows:

- $(Cd^{2+})_{sol.} + (FTHD)_{surf.} \rightarrow (Cd^{2+}\text{-}FTHD)_{adsorb.}$ (the accumulation/complexing stage);
- $(Cd^{2+}\text{-}FTHD)_{adsorb.} + 2e^- \rightarrow (Cd^0, FTHD)_{adsorb.}$ (the accumulation/reduction stage);
- $(Cd^0, FTHD)_{adsorb.} - 2e^- \rightarrow (FTHD)_{surf.} + (Cd^{2+})_{sol./surf.}$ (the stripping step).

3.2. Cyclic voltammetry studies

After various preliminary studies using DPASV [24] the reactions of Cd(II) at the CPEs-FTHD modified in the presence of chloride as a complexing anion were investigated by cyclic voltammetry.

CVs of the FTHD-modified CPEs were recorded in the supporting electrolyte. In cycles between −0.7 and 0.8 V, no redox peaks were observed except for the CPE modified with ligand **2h**. In relation to the observed capacities, they were calculated by means of the equation $C_{obs} = i/v$, where i is the average anodic and cathodic current and v is the scan rate [26]. In these calculations, those parts of the voltammograms where faradaic intensities prevailed upon capacitive intensities were not considered. The capacities calculated for some of the FTHD-modified CPEs at scan rate of 100 mV s^{-1} are shown in Table 1.

In general, the values obtained are low for all the FTHD-modified CPEs. The high content of modifier in carbon paste mixture (20% in all the cases) and the non-homogeneity of the material could be the reason for that behaviour. The CPE modified with ligand **2h** had the highest capacity. The CV obtained with this electrode showed a signal in absence of any analyte, so this CPE is not appropriated for metal determination. Its behaviour is similar to a reversible system as much for the nearness of the anodic and cathodic peaks as the similar current peaks, with a i_{cp}/i_{ap} ratio close to the unity. The anodic current at 0.23 V should be caused by the oxidation of the reductive cleavage of the –NO$_2$ group of the ligand **2h**.

The CVs of the CPEs modified with the series **1** and **2** ligands show small differences. In general, the CVs of the CPEs modified with the derivatives of series **2** show lower residual current and more symmetric anodic and catodic scans. These estimations agree with the higher C_{obs} values observed for the CPEs

Table 1
Some CPEs modified with 1-furoylthiourea derivatives of series **1** and **2**: capacities calculated at 100 mV s^{-1}

CPEs modified with	C_{obs} (μF/cm^2)
1c	8.6
1f	19.9
1d	12.4
1a	9.5
2f	2.8
2h	49.1
2j	1.8
2m	3.8
2d	2.9

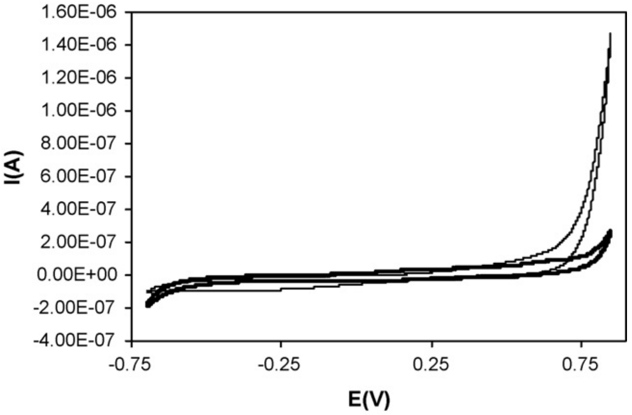


Fig. 3. Cyclic voltammograms obtained by **2m** (thicker curve) and **1d** CPEs modified at 100 mV s^{-1} in Britton–Robinson pH 4 electrolyte.

modified with the compounds of series **1** (Table 1). The useful potential range for the voltamperograms obtained with the CPEs modified with the derivatives of series **2** is wider in the anodic range while it is similar in the cathodic range for CPEs modified with both series. Fig. 3 shows the scans at 100 mV s^{-1} for the CPEs modified with the ligands **1d** and **2m** (selected as models of both series) where the differences commented above can be observed. In general, upon increasing the scan rate an increasing of the residual current and a higher distortion of the signals are observed. These effects are common for all the modified CPEs.

Figs. 4 and 5 show CVs for Cd(II) solutions obtained at CPEs modified with **1d** and **2m** in the range 10–500 mV s^{-1}. These 1-furoylthioureas showed similar electrochemical behaviour to the other compounds of the same series; they were selected, because they showed the highest sensitivity for each series, with the aim to realize a comparison. A similar behaviour is observed for both CPEs, which corresponds to an adsorption mechanism, with weak adsorption of the product [27–29]. The cathodic scan produces the reduced species of cadmium, 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), but not the reduction process. When the scan rate increases the contribution of the material that diffuses is low compared with the adsorption; the concentration of product of the cathodic reaction near the electrode is slightly enhanced because of adsorption, and this results in a lower cathodic peak, and in a marked increase of the anodic peak. Hence, it confirmed that the anodic stripping process must be shown as the more adequate, because the accumulation of the material after a previous reduction is favoured.

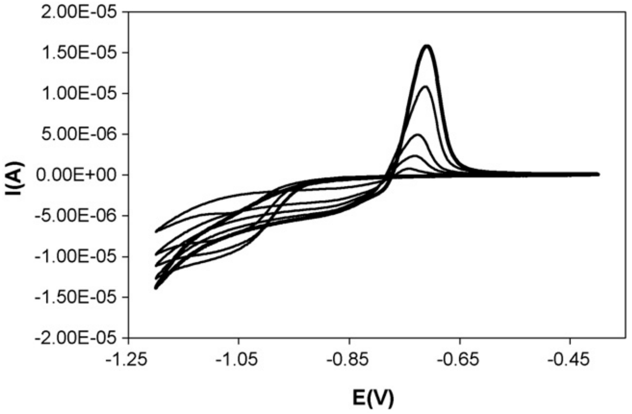


Fig. 4. Cyclic voltammograms obtained by **2m** CPE modified in the range 10–500 mV s^{-1} for 20 mg L^{-1} Cd(II) in Britton–Robinson pH 4 electrolyte. The thicker curve corresponds to the voltammogram obtained at 500 mV s^{-1}.

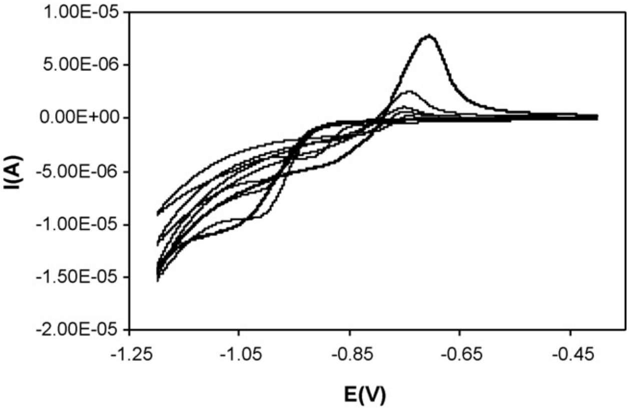


Fig. 5. Cyclic voltammograms obtained by **1d** CPE modified in the range 10–500 mV s^{-1} for 20 mg L^{-1} Cd(II) in Britton–Robinson pH 4 electrolyte. The thicker curve corresponds to the voltammogram obtained at 500 mV s^{-1}.

The anodic peak shows a typical scheme of product weakly adsorbed (see Figs. 4 and 5); increasing the scan rate the peak potential shifts to more positive values and the current peak is enhanced/increased.

On the other hand, the cathodic peak does not completely follow the sequence of a product weakly adsorbed, since a decrease of the peak current and a positive shift of the potential should be expected; the presence of the product adsorbed, and hence, its higher concentration in the nearby of the electrode, must be on account of a clear but slightly decreasing of the signal. However, this behaviour is only observed at high scan rates.

To explain these phenomena the following kind of reaction is proposed. Since, a modifier with binding capacities for the reduction reaction reactant (Cd(II) in this case) is used at the electrode surface, a double process of weak adsorption could be assumed, for both the reagent and the product (metallic cadmium) of the reduction reaction. The weak adsorption of the reagent implies an increasing of the cathodic current peak and a negative shift of the peak potential [27]. The increase of the scan rate implies an increasing reduction peak current. This is the effect observed over the cathodic peak with increasing scan rate for the CPEs modified with both series of ligands. When the scan rate is too high the effect of the adsorbed product dominates; the cathodic peak decreases for the reasons above mentioned, and the potential shifts to more positive values. On the other hand, for the anodic signal the effect of the product adsorption is always observed, with an increase of the peak current and a positive shift of the potentials with increasing scan rate.

The effects described above are observed in the CPE modified with **2m**; for this CPE the effect of product adsorption clearly prevails, as the i_{ap}/i_{cp} (anodic peak intensity/cathodic peak intensity) ratio is always over 1, and it increases with increasing scan rate.

The CPE modified with **1d** does not show such predominant effect of the product adsorption. The cathodic peak decreases for the highest values of scan rate (as it corresponds to the product adsorption), but the i_{ap}/i_{cp} ratio is below 1 even for the lowest scan rate. Although this ratio increases with increasing scan rate, it maintains values closed the unity in a wide scan rate range, as it should be expected due the reagent adsorption.

From these studies we can establish/say that the FTHD-modified CPEs show promising behaviour with respect to the base line. In the determination of Cd(II), the adsorption plays a very important role, emphasizing the weak adsorption of the product with oxidation signals of greater intensity than the reduction signals. It agrees with the preliminary results obtained by DPASV [24]. The FTHD-modified CPEs by series **2** ligands show a larger sensitivity. This fact will be confirmed in the following calibration studies and detection limits calculation.

The CPEs modified with **1d** and **2m** were the CPEs modified with ligands of each series that showed the most promising perspectives for Cd(II) determination by DPASV. We are now interested in experiments conducted to establish the optimal media conditions, and the electrochemical and instrumental parameters of the method.

3.3. Stripping voltammograms of Cd(II) at the CPEs modified with 1d and 2m

The determination of Cd(II) in aqueous solution at the CPEs modified by **1d** and **2m** was carried out by DPASV after 5 min of accumulation at −1.0 V in a solution containing Cd(II). The voltammograms are showed in Fig. 6. Two well-defined and enhanced peaks are observed for the modified CPEs as compared to the unmodified one. At the unmodified CPE a Cd(II) oxidation peak of 1.8 μA appears at −0.78 V, while the FTHD-modified CPEs exhibit an anodic peak at −0.77 V, with higher intensity for the anodic current (9.9 and 21.2 μA for **1d** and **2m** modified CPEs, respectively) in comparison with that observed at the unmodified electrode. The increase in anodic current at the FTHD-modified CPEs demonstrates that the FTHD play an important role in the accumulation process of Cd(II) on the electrode surface.

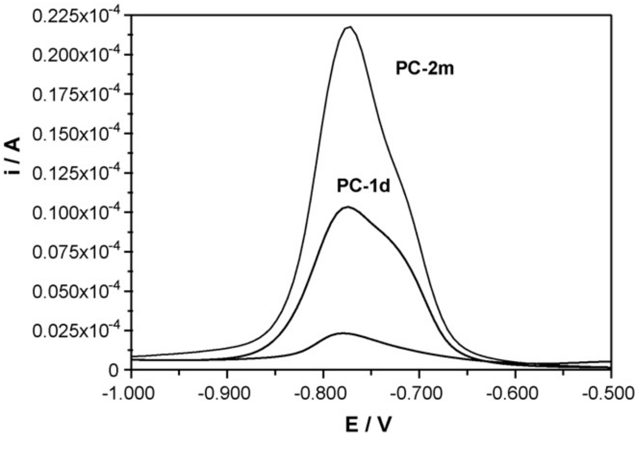


Fig. 6. DPASV voltammograms of Cd(II) in Britton–Robinson electrolyte pH 4 at the CPEs modified with **2m** and **1d** (larger current peaks) and unmodified CPE; accumulation time: 300 s; accumulation potential: −1.0 V; differential pulse amplitude: 100 mV; scan rate: 10 mV s^{-1}; **2m** (**1d**)/graphite powder: 20% (w/w).

3.4. Effect of carbon paste composition

The amount of FTHD in the carbon paste must significantly affect the height of the voltammetric signal. The anodic peak of cadmium was increased with FTHD-modified CPEs. This obviously indicates that the voltammetric response results from the accumulation of Cd(II) at these electrodes by means of the complex formation reaction between the metal ion, Cd(II), and the modifier, FTHD. The effect of carbon paste composition on the peak current was tested using FTHD-modified CPEs prepared with 5, 10 and 20%. The anodic peak current increased with increasing amount of modifier, because the concentration of FTHD on the surface of the modified CPE increased correspondingly. Higher modifier quantities in carbon paste usually load to a decreasing of the conductive area at the electrode surface [19,20,22]. Hence, we did not study carbon paste with FTHD/carbon powder weight ratio over 20%. Consequently, a carbon paste composition of 20% of FTHD was used in further studies.

3.5. Effects of pH and electrolyte

The influence of pH on the determination of Cd(II) was investigated. From pH 2.0 to 8.0, the peak current increased at first until the peak current reached a maximum value around pH 4. The continuous increase of pH led to a decrease of peak current and a broadening of the signal, which is due to the hydrolysis of Cd(II). Also, the FTHD can slowly dissolve in basic solution for the acidity of the amidic proton NH and lose its ability of complexing Cd(II).

The effect of another buffer electrolyte of pH 4, such as HAc/NaAc was studied. When the measurements were performed in this electrolyte, the shape of the stripping peak current was similar, but a smaller peak height was obtained. Thus, buffer solution Britton–Robinson (pH 4) was suitable as supporting electrolyte.

3.6. Effects of accumulation potential and time

Accumulation potential is an important parameter for stripping techniques and has non-negligible influence on the sensitivity of determination. The effect of accumulation potential on the stripping peak current of Cd(II) was studied in the range from −0.9 to −1.2 V. The peak increased with the negative shift of the accumulation potential. The increase of the reduction potential beyond −1.0 V (in negative sense) led to a steady-state current. At the same time, over this potential of −1.0 V another metal ions can be reduced and cause interference on Cd(II) determination. Hence, a reduction potential of −1.0 V was chosen for all subsequent experiments to allow a difference of about 200 mV from the peak potential observed.

Similarly, the accumulation time is a decisive factor in any technique dealing with a preconcentration step. The quantity of Cd(II) reduced over the surface of the FTHD-modified CPEs increased with increasing accumulation time in the range 0–10 min. Beyond this period, the current peak reached a flat level caused by the complete coverage of active sites on the surface of the modified CPEs. Taking account of sensitivity and efficiency, accumulation time was 300 s in the following experiments.

3.7. Effect of pulse amplitude and scan rate

The influences of parameters of DPASV on the measurements of Cd(II) were studied. The results showed that the stripping peak current increased with increasing differential pulse amplitude and it remains nearly constant when differential pulse amplitude is larger than 100 mV. Thus, 100 mV was chosen as the differential pulse amplitude.

Scan rate can also influence the determination of Cd(II) by DPASV. The peak current increased with the increasing of scan rate, but slightly over 20 mV s^{-1}. However, the shape of stripping peak became apparently asymmetry when scan rate was larger than 20 mV s^{-1}. For that reason, 20 mV s^{-1} was chosen as the scan rate.

3.8. Calibration graph, detection limit and precision

The sensitivity of the method was studied by recording differential pulse anodic stripping voltammograms at different Cd(II) concentrations. For the CPE modified with **2m** a calibration plot influenced by the electrode surface saturation was observed. Depending on the ranges it could be obtained linear ranges described by different regression equations. For the lower range (0.0010–0.0075 mg L^{-1}) the linear regression equation was $I_{pa}(\mu A) = 0.20 + 168.33$ [Cd(II)] (mg L^{-1}), with a correlation coefficient of 0.999. The anodic peak current at the carbon paste modified electrode PC-**1d** was proportional to the concentration of Cd(II) in the range 0.01–0.1 mg L^{-1}, with a correlation coefficient of 0.993. The linear regression equation was: I_{pa} $(\mu A) = 0.13 + 18.80$ [Cd(II)] (mg L^{-1}). From 0.1 mg L^{-1} a deviation from linearity was observed due to the saturation of the electrode surface.

The detection limits in the linear range for both modified CPEs, calculated [30] as the signal of the blank plus three times its standard deviation are also reported. The detection limits obtained were 6×10^{-5} and 3×10^{-3} mg L^{-1} for the CPEs modified with **2m** and **1d**, respectively.

The results obtained for the detection limits of these modified CPEs with two FTHD (taken as models of the behaviour of the derivatives of both series) show that the ligands of series **2** (1-furoylthioureas 3-monosubstituted) have greater sensitivity toward Cd(II). This fact is consistent with the results previously reported for the complexes of these ligands with cadmium chloride [24,25].

The relative standard deviations were found to be 3.9% for seven determinations of 0.5 mg L^{-1} Cd(II) in the experimental conditions previously optimised. The results indicate that the FTHD-modified CPEs have good reproducibility.

3.9. Effects of other ions

The influence of Hg(II), Zn(II), Ag(I), Pb(II) and Cu(II) on Cd(II) peak current was also evaluated at a 1:1 interferent:analyte mass ratio. Hg(II), Zn(II) and Ag(I) do not interfere the determination of Cd(II). However, the presence of Cu(II) or Pb(II) interfere significantly by suppressing the Cd(II) signal up to 40–50%, because they form complexes with the modifier and prevent the complex formation and accumulation of Cd(II) at electrode surface; peak potential for Pb(II) signal is near to that of Cd(II), and overlapping is also observed.

3.10. Applications to real water samples

Some tests were carried out for spiked superficial water (collected from San Pedro river, Puerto Real, Cádiz, Spain) and spiked drinking water samples; Cd(II) concentrations in cell of 0.05 and 0.01 mg L^{-1} for the CPE modified with **2m**, and 0.25 and 0.05 mg L^{-1} for the CPE modified with **1d** were used. The results show recoveries of 92–96%; the standard addition method was used for the determinations. In all cases the paste was removed from the electrode, giving relative standard deviations for the repeated measurements below 4%. As a previous step, the absence of Cd(II) in the real samples was tested by ICP (inductively coupled plasma).

4. Conclusions

A simple and effective electrode system for the determination of Cd(II) was developed. The concentration of Cd(II) at the surface of the FTHD-modified CPEs is increased by the formation of cadmium complexes of the FTHD, specially for the 3-monosubstituted ligands (series **2**). The FTHD and their cadmium complexes show thermal and physical stability, high temperature of decomposition and a pH operational range from slightly acid to neutral; the moderate stability constants of the complexes favour the reversibility during the stripping step and the adsorption process, as it has been confirmed by the CV studies. The FTHD-modified CPEs showed good capacities, stability, sensitivity and reasonable selectivity.

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