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Determination of lead and cadmium using a polycyclodextrin-modified carbon paste electrode with anodic stripping voltammetry

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Abstract This work reports the use of α and β -cyclodextrin-modified carbon paste electrodes (CPE $_{\alpha\text{-CD}}$ and CPE $_{\beta\text{-CD}}$) to determine simultaneously Pb(II) and Cd(II) by means of the electrochemical technique known as anodic stripping voltammetry (ASV). Both modified electrodes displayed good resolution of the oxidation peaks of the said metals. Statistic analysis of the results strongly suggests that the CPE $_{\beta\text{-CD}}$ exhibited a better analytical response than the CPE $_{\alpha\text{-CD}}$, while the detection limits obtained for Pb(II) were 6.3×10^{-7} M for the CPE $_{\alpha\text{-CD}}$ and 7.14×10^{-7} M for the CPE $_{\beta\text{-CD}}$, whereas for Cd(II) they were 2.51×10^{-6} M for the CPE $_{\alpha\text{-CD}}$ and 2.03×10^{-6} M for the CPE $_{\beta\text{-CD}}$.

Keywords Cyclodextrins · Carbon paste electrode · Anodic stripping voltammetry · Lead · Cadmium

Introduction

It has been a matter of deepening interest to quantify heavy metals in natural media such as air, soil and water, as much as in foodstuffs and biological fluids, because the growing environmental health concern has singled them out as closely related to poisoning. Therefore, there has been a noticeable drive to develop diverse analytical techniques capable of detecting trace levels of the said metals in various matrices.

One of the electrochemical techniques that has been mostly used to determine heavy metals is anodic stripping voltammetry (ASV) in combination with the hanging drop-

ping mercury electrode HDME, as the most frequently employed working electrode. The latter offers a continuously renewed surface, an elevated hydrogen overpotential, the ability to dissolve metals and low detection limits (2×10^{-7} M to Pb(II), Cd(II) and Zn(II) with a deposition time of $t_d=30$ min) [1, 2]. Hg(II) is a highly toxic heavy metal and is considered to be a dangerous polluting agent, which after prolonged exposure is liable to cause severe damage to the central nervous system (CNS) [3] alike Parkinson's disease. In view of such considerations it has been fundamental to search for effective alternatives to determine the metals in question using other analytic techniques with no contaminating electrodes.

An alternative has been found in which the HDME is substituted for a carbon paste electrode (CPE), and such electrodes have been amply used in electroanalysis and biosensors [4, 5]; these electrodes are inexpensive and indeed useful, because their surfaces are deliberately modified to display specific qualities to suit well-defined analytic purposes. As an expected outcome, the wide field of application of the CPE is still growing mainly due to a combination of interesting features such as low manufacturing costs offset by a wide potential window, ease of preparation and a surface that is modifiable without having to use other contaminating chemical species; these have turned them into selective, versatile and renewable analytical devices [6]. Modification of the CPE electrodes can be effected by means of a mix of electroactive compounds [4, 5, 7, 8, 9, 10], by adsorption or electrodeposition [11, 12]. To get a response similar to that of the HDME a CPE has been modified with Hg electrodeposits to determine Pb(II) obtaining low detection limits (2.5×10^{-9} M with a $t_d=10$ min) [12, 13, 14, 15]. Notwithstanding, the Hg pollution problem is not solved, since the electrode is modified with this heavy metal.

Thus several other modified electrodes have been studied with different chemical species that also present lower detection limits for the determination of heavy metals such as Pb(II) and Cd(II). Among the species used for the determination of Pb(II), various complex-forming agents have been used, such as the *N-p*-chlorophenylcinnamohy-

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droxamic acid having a detection limit of 2×10^{-8} M and a $t_d=6$ min [16], the dibenzo-18-crown-6 and cryptand with 1×10^{-6} M and 0.5×10^{-6} M detection limits [17], respectively, and lichen with 2×10^{-5} M [18], 1-(2-pyridylazo)-2-naphthol and Nafion [19], among others. Further, the determination of Pb(II) and Cd(II) has been carried out potentiometrically using a PVC membrane that incorporated cyclodextrins modified with polymethylhydrosilane [20].

Therefore, this work aims at developing a CPE modified with natural cyclodextrins (CDs) [21] to study the determination of heavy metals (Pb(II) and Cd(II)), based on the fact that the cyclodextrins are innocuous and biodegradable chemical species [22].

As chemical species the cyclodextrins are widely used for the modification of diverse substrates [23, 24, 25]. They have a molecular structure resembling, as it were, a hollow truncated cone or basket with a cavity that displays receptor-like features, which can interact with other chemical species to form inclusion complexes [26]. The cyclodextrins belong to the family of cyclic oligosaccharides formed by various D-glucopyranose units, held together by (1-4)-glucosidic bonds: the better-known members of the family are the α -, β - and γ -cyclodextrins, which have six, seven and eight D-glucopyranose units, respectively [27], thus providing features such as selectivity and sensitivity.

There is evidence that it is possible to form inclusion complexes between the cyclodextrins and metal ions like Cu(II) and Ni(II) [28, 29]. However, for the case of heavy metals, apparently there are no references to be linked to the study of Pb(II) [30] and Cd(II), which is why this research works aims at studying both species.

Therefore, in this work a carbon paste electrode modified with α -cyclodextrin and β -cyclodextrin (CPE $_{\alpha\text{-CD}}$ and CPE $_{\beta\text{-CD}}$) was developed to carry out the determination of Pb(II) and Cd(II) using ASV. The interest in studying both metals stems from their potential as chemical polluting agents and their associated toxicity even at low concentrations.

Experimental

Reagents

All solutions used were prepared with deionised water (18.2 M Ω) and analytical grade reagents. The cyclodextrins were dissolved in 1 M HClO₄ to reach a 0.01 M concentration. The lead solutions were prepared with Pb(NO₃)₂ (J. T. Baker), to a 0.1 M concentration; other solutions were prepared by dilution to reach a given range of interest ($2 \times 10^{-7} < M < 1 \times 10^{-5}$). The cadmium solutions were prepared with CdCl₂ (Sigma) to a 0.1 M concentration and as before, other solutions were prepared by dilution to reach the range of interest ($2 \times 10^{-7} < M < 1 \times 10^{-5}$).

The CPE was prepared from a 1:1 mixture of single-crystal-grade high-purity graphite 99.99% (Alfa AESAR) and Nujol (Fluka) to give an easily handled paste.

Instruments

The electrochemical studies were carried out using a BAS-100 W potentiostat and a typical three-electrode cell with Ag/AgCl as ref-

erence electrode while a graphite bar was the counter electrode and the modified CPE was the working electrode.

Preparation of the modified CPE

The CPE electrodes were electrochemically modified with α -cyclodextrin (CPE $_{\alpha\text{-CD}}$) and β -cyclodextrin (CPE $_{\beta\text{-CD}}$) immersing both CPE in the solutions respectively containing 0.01 M α -cyclodextrin or β -cyclodextrin in 1 M HClO₄. The modification was attained using a successive program of 30 potential cycles within the 1.3 to -0.85 V potential range versus Ag/AgCl at a 0.1 V s^{-1} scan rate as reported elsewhere [16].

Results and discussion

Characterization of Pb(II) and Cd(II) electrochemical behaviour in HClO₄ with the modified electrodes

CPE $_{\alpha\text{-CD}}$

Solutions of Pb(II) and Cd(II) 1×10^{-4} M in an HClO₄ 1 M medium were used with cyclic voltammetry for two working electrodes CPE and a CPE $_{\alpha\text{-CD}}$. The potential scans were in the cathodic direction from the null current potential ($E_{i=0}=0.35$) within the -1.1 to 1.05 V versus Ag/AgCl potential range at a scan rate of 0.1 V s^{-1} . Figure 1 shows typical plots of the CPE (line) and CPE $_{\alpha\text{-CD}}$ (squares) electrochemical responses: examination of both plots reveals obvious differences using the two electrodes. The CPE voltammogram has a reduction peak ($E=-0.9$ V versus Ag/AgCl) associated to the reduction of Pb(II) to Pb(0); when the potential scan was reversed there appeared a crossover at $E=-0.5$ V and a peak ($E=-0.465$ V) associated with the oxidation of Pb(0) to Pb(II). It seems that the

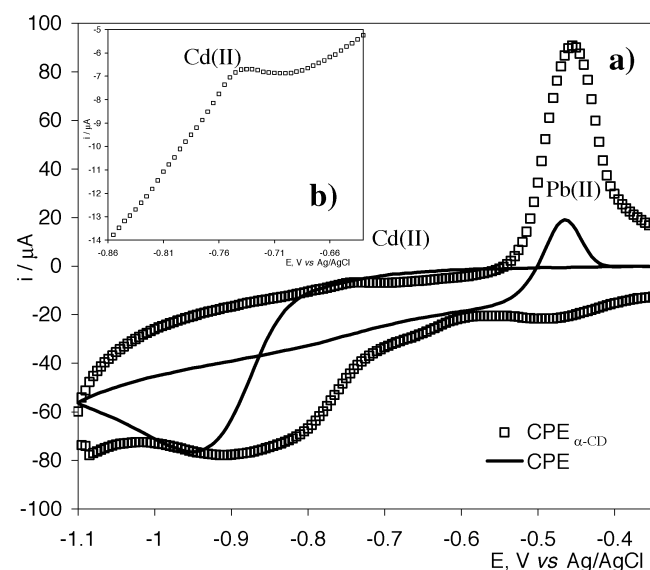


Fig. 1a,b Cyclic voltammogram for 1×10^{-4} M Pb(II) and Cd(II) solutions in HClO₄ 1 M. The cathodic scan started at $E_{i=0}=0.35$ V within the -1.1 to 1.05 V potential range versus Ag/AgCl at a 0.1 V s^{-1} rate, on **a** CPE and CPE $_{\alpha\text{-CD}}$ and **b** amplification of the Cd(II) oxidation peak on the CPE $_{\alpha\text{-CD}}$

processes associated with Cd(II) were not detected in the voltammograms, but if the sensitivity of the current scale is increased a fairly small oxidation peak becomes visible at $E=-0.74$ V versus Ag/AgCl.

The electrochemical behaviour of the $CPE_{\alpha-CD}$ shows a Pb(II) reduction peak to Pb(0) at $E=-0.9$ V, but reversing the potential scan a peak appeared at $E=-0.74$ V that is associated with Cd(0) oxidation to Cd(II) with peak current response (i_{pa}) of $1.9 \mu\text{A}$ (Fig. 1b) and a second peak at $E=-0.45$ V due to oxidation of the Pb(0) to Pb(II) without a crossover associated with an increase in the capacitive current; such behaviour is considered typical of a modified electrode, because its active surface, where the redox processes occurred, is essentially different from that of the electrode without cyclodextrins on its surface.

When the peak current responses are compared it becomes apparent that the $CPE_{\alpha-CD}$ shows a 3.0 times bigger magnitude for lead than the CPE, while for cadmium this was only two times.

With the conditions given above, the determination of Pb(II) and Cd(II) was done with the $CPE_{\beta-CD}$.

$CPE_{\beta-CD}$

The cyclic voltammetry for Pb(II) and Cd(II) carried out with the $CPE_{\beta-CD}$ (see Fig. 2) showed that the behaviour is very similar to that observed for the $CPE_{\alpha-CD}$. The reduction wave for lead is seen at $E=-0.78$ V versus Ag/AgCl; when the scan potential was reversed there appeared an oxidation peak associated with Cd(0)/Cd(II) at $E=-0.74$ V versus Ag/AgCl with $i_{pa}=13.71 \mu\text{A}$ and another peak at $E=-0.47$ V versus Ag/AgCl for Pb(0)/Pb(II) with $i_{pa}=179.3 \mu\text{A}$.

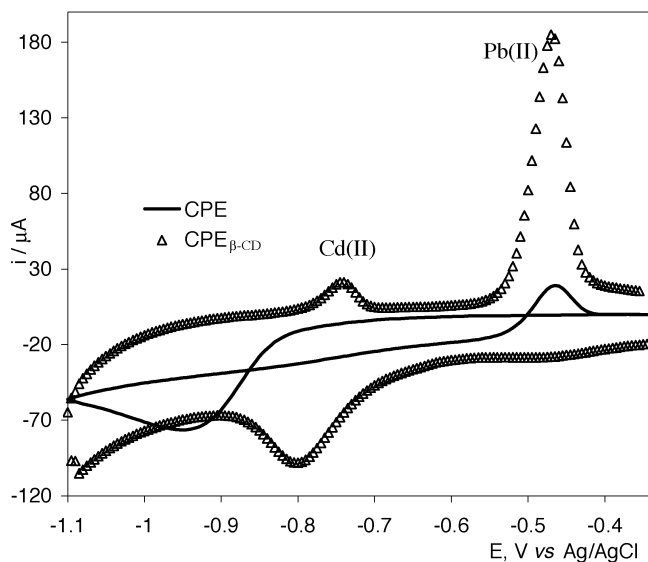


Fig. 2 Cyclic voltammogram for 1×10^{-4} M Pb(II) and Cd(II) solutions in HClO_4 1 M. Cathodic scan started at $E_{i=0}=0.3$ V within the -1.1 to 1.05 V potential range versus Ag/AgCl at a 0.1 V s^{-1} rate on CPE and $CPE_{\beta-CD}$

If the peak current responses are compared (i_p), it is plain that the $CPE_{\beta-CD}$ displays a response for lead 6 times greater than that of the CPE, while that for cadmium was 10 times greater.

It became clear that the modified electrodes presented an increment in the current response for Pb(II) and Cd(II) as compared to the CPE. In Figs. 1 and 2 it was observed that the oxidation response for Pb(II) with the $CPE_{\beta-CD}$ had an i_p 1.5 times greater than that of the $CPE_{\alpha-CD}$, while for Cd(II) the current was 7 times greater with the $CPE_{\beta-CD}$ as compared with the $CPE_{\alpha-CD}$.

With the above results it becomes simpler to select better conditions to study the ASV for the metals with both modified electrodes $CPE_{\alpha-CD}$ and $CPE_{\beta-CD}$.

Effect of deposition time and scan rate for lead and cadmium

Optimisation of working conditions

Deposition time (t_d) and potential (E_d), scan rate (ν), pulse amplitude (W_p), agitation and electrolyte's pH were some of the experimental parameters chosen to carry out the optimisation of the working conditions to perform the study with ASV. However, only two of them were actually selected during the present experimental setup as they were considered the most important ones (i.e. t_d and ν , keeping the other parameters constant, e.g. agitation=400 rpm).

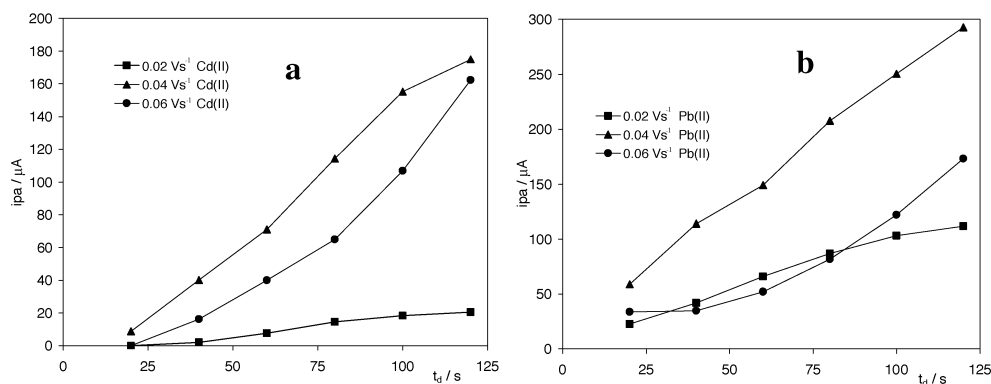
The Cd(II) and Pb(II) concentrations used for this set of experiments were 5×10^{-5} M, while the deposition potential (E_d) chosen for both electrodes was -0.9 V versus Ag/AgCl as suggested by the results obtained before. The behaviour for Pb(II) was studied using the same approach outlined.

Figure 3 shows the i_{pa} plots for Pb(II) and Cd(II) as a function of t_d at different ν using the $CPE_{\alpha-CD}$. Figure 3a presents the i_{pa} variation for Cd(II) as a function of t_d where the current increases as the latter does so due to a greater accumulation of Cd(0) on the electrode surface: this kind of behaviour was observed at all the ν studied. Even if the i_{pa} increased when the ν were 0.04 and 0.06 V s^{-1} the data points exhibited dispersion, which is associated with the shape of the stripping peaks that became wider as compared with the oxidation peaks obtained at 0.02 V s^{-1} that have quite a good definition.

Figure 3b for Pb(II) shows that the i_{pa} increased with increasing time t_d , and that when ν was 0.02 or 0.06 V s^{-1} the current increment observed was practically the same, although when ν was 0.04 V s^{-1} there was a twofold current increase as compared to other rates. However, at 0.04 and 0.06 V s^{-1} the oxidation peaks were also observed to widen. For both metals, when the t_d values were short (i.e. in the range 20 – 60 s), the shape of the peaks has been fairly well kept.

From the results of the previous study it was observed that at t_d greater than 60 s and at ν of 0.02 V s^{-1} a plateau appeared. When the ν was between 0.04 to 0.06 V s^{-1} it is clear that at t_d greater than 60 s there was a current incre-

Fig. 3a,b Plot of the i_{pa} as a function of t_d : **a** Cd(II) and **b** Pb(II) in HClO₄ 1 M using the CPE_{α-CD}



ment, which may be associated with the greater accumulation of metal in the cavities of the α -cyclodextrin [20] on the CPE, and after to Pb(II) accumulation such that the current increased.

Hence, the conditions chosen to determine Pb(II) and Cd(II) were t_d 60 s and a v of 0.02 $V s^{-1}$, with 2×10^{-7} – 1.5×10^{-5} M concentration range.

Pb(II) and Cd(II) determination using the CPE_{α-CD}

A 1 M HClO₄ solution was prepared by successive additions of Pb(II)- and Cd(II)-containing solutions to vary their concentration in the working solution. The ASV was carried out using a CPE_{α-CD} as working electrode to obtain the respective responses under the conditions chosen.

Figure 4 shows the ASV plots for Pb(II) and Cd(II). Note that for the concentrations 2×10^{-7} and 1.5×10^{-5} M Pb(II) and Cd(II) respectively, there was only Pb(0) oxidation but when the 1×10^{-5} M concentration was reached an oxidation peak appeared at $E_{pa} = -0.74$ V versus Ag/AgCl associated to Cd(II) and later at $E_{pa} = -0.460$ V versus Ag/AgCl there became apparent the Pb(II) signal, which suggests that the processes occurring are well resolved, as the peaks are sufficiently separated. Also, as the Cd(II) and Pb(II) concentrations increased the currents of the anodic peaks did so as well.

With the data from ASV in Fig. 4 two i_{pa} plots were built as a function of Pb(II) and Cd(II) concentration, where a linear relationship among the data points is clearly apparent for the variables i_p and [Pb(II)] with a linear correlation coefficient (r^2) of 0.9946, while for [Cd(II)] r^2 was 0.9840.

The detection limits were obtained from the statistic results for Pb(II) and Cd(II) [31, 32] having the following values 6.3×10^{-7} M (0.208 ppm) and 2.51×10^{-6} M (0.505 ppm), respectively. The corresponding expressions for the straight lines are as follows:

$$Cd(II) \quad i_{pa} = -3.4(\pm 0.35) \mu A + 4.2 \times 10^5 (\pm 2.7 \times 10^4) \mu A M^{-1} \\ r^2 = 0.9840$$

$$Pb(II) \quad i_{pa} = -5.2(\pm 1.1) \mu A + 5.28 \times 10^6 (\pm 1.4 \times 10^5) \mu A M^{-1} \\ r^2 = 0.9946$$

The slope obtained for Pb(II) was 5 times larger than that for Cd(II); the difference in slopes indicates the sensitivity

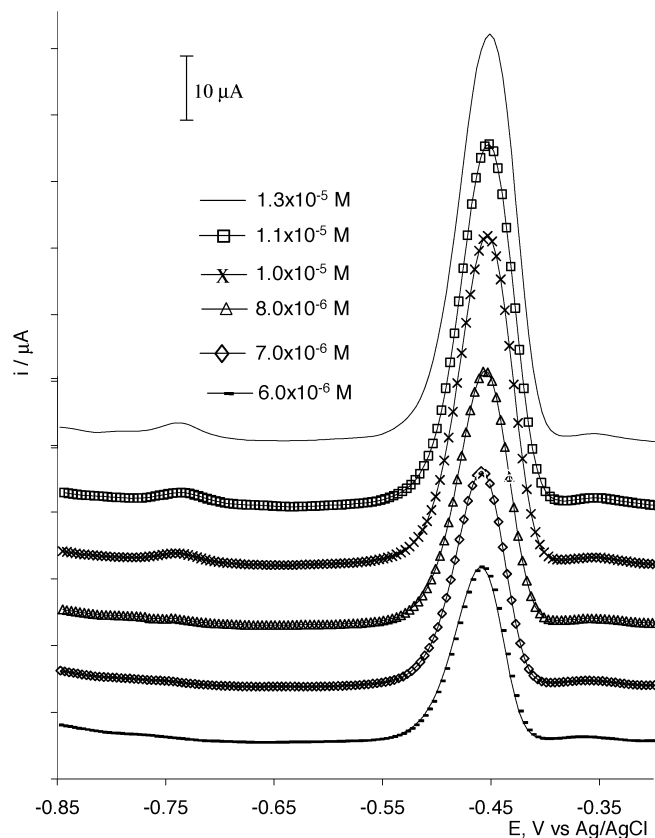
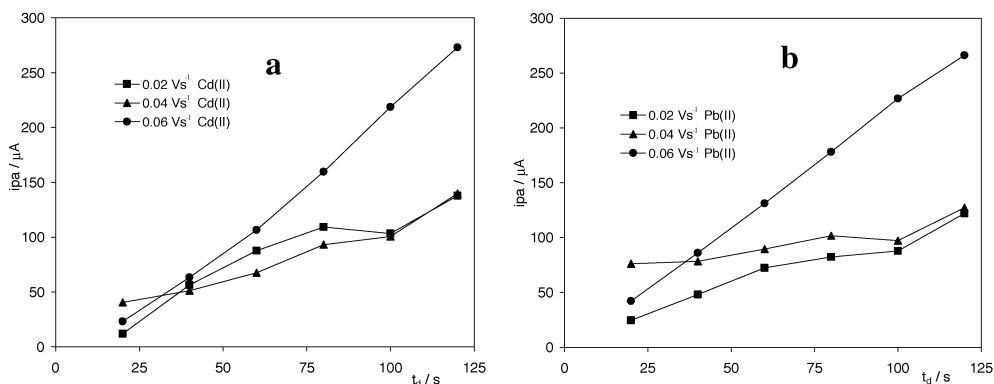


Fig. 4 ASV plots for Pb(II) and Cd(II) in different concentrations in 1 M HClO₄ medium, using a CPE_{α-CD}. The conditions working are to $E_d = -0.9$ V, $t_d = 60$ s and $v = 0.02$ $V s^{-1}$

of the CPE_{α-CD} toward the metals studied; thus when the slope is large there are significant changes taking place in the chemical response for small changes in concentration.

On the basis of the aforementioned results, the CPE_{α-CD} has better sensitivity to detect Pb(II) ions than Cd(II); nevertheless, it is possible to carry out the simultaneous determination of both metals in view of the good resolution obtained. As the CPE_{β-CD} showed a larger response increase for the metal ions, it seems relevant to study the CPE_{β-CD}-modified electrode.

Fig. 5a,b Plots of i_{pa} as a function of t_d **a** Cd(II) and **b** Pb(II) in HClO₄ 1 M using CPE_{β-CD}



Study of the CPE_{β-CD} electrode

Considering the response obtained with the CPE_{β-CD} as related to the CPE_{α-CD}, it is fit to undertake analytic studies to determine Pb(II) and Cd(II) on this electrode. Figure 5 shows the i_{pa} plots for Pb(II) and Cd(II) as a function of t_d at various v , using the CPE_{β-CD}. It is noted that the current tends to increase as a function of increasing t_d suggesting that for all the scan rates used, there was increasing accumulation of Cd(0) and Pb(0) on the electrode surface. Particularly, when the scan rates were 0.02 and 0.04 V s⁻¹ the i_p responses for both metals are similar, namely the i_{pa} variation is practically the same, but at a t_d greater than 80 s a plateau was observed thus indicating a surface saturation on the electrode. Similarly, when the rate was 0.06 V s⁻¹ the i_{pa} variation with respect to t_d was quite linear; however, the stripping peaks became wider as compared to those obtained at 0.02 V s⁻¹ where well-defined oxidation peaks appeared for both metals.

This modified electrode at a t_d greater than 60 s and at $v=0.02$ V s⁻¹ presented a behaviour like that of the CPE_{α-CD}. However, the i_p was larger on the CPE_{β-CD} than for the CPE_{α-CD}; such current difference can be associated with the size of the cavity of the β-cyclodextrin, which is larger than that of the α-cyclodextrin.

With the results above it is possible to choose the desired conditions to study the determination of Pb(II) and Cd(II) as: a t_d of 60 s and $v=0.02$ V s⁻¹, and 2×10^{-7} – 1.5×10^{-5} M as concentration range.

Pb(II) and Cd(II) determination using the CPE_{β-CD}

The approach used was the same to determine both metals using ASV with the CPE_{α-CD}. Figure 6 shows the ASV plots of the determination of Pb(II) and Cd(II) using the CPE_{β-CD}. With a concentration of 2×10^{-7} M first for Pb(II) and Cd(II) respectively, only the Pb(0) oxidation peak at $E=-0.48$ V versus Ag/AgCl became apparent, but when the concentration increased to 1×10^{-5} M there appeared first a Cd(0) oxidation peak at $E=-0.75$ V versus Ag/AgCl and after that, at $E_{pa}=-0.48$ V versus Ag/AgCl there was the Pb(II) peak. As the oxidation peaks for both metals are sufficiently separated, this suggests a good working resolution between the peaks. The anodic peak currents

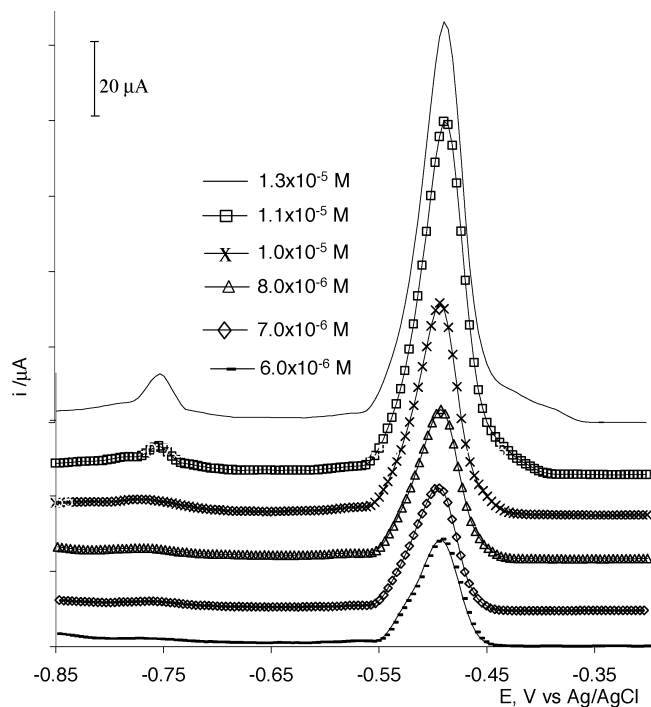


Fig. 6 ASV of Cd(II) and Pb(II) with different concentrations in 1 M HClO₄ medium using the CPE_{β-CD}. The working conditions are to $t_d=60$ s, $E_d=-0.9$ V and $v=0.02$ V s⁻¹

increased with increasing Cd(II) and Pb(II) concentrations.

From the results shown in Fig. 6, a plot of i_{pa} (μA) as a function of Cd(II) and Pb(II) concentration, it becomes plain that a linear relationship exists between the variables for Cd(II) and Pb(II), as indicated by the linear correlation coefficients (r^2), which were 0.991 and 0.993 respectively.

The detection limits for Pb(II) and Cd(II) were 7.14×10^{-7} M (0.236 ppm) and 2.03×10^{-6} M (0.41 ppm), respectively. The expressions of the straight lines are as follows:

$$Cd(II) \quad i_{pa} = -26(\pm 1.95) \mu A + 2.8 \times 10^6(\pm 1.6 \times 10^5) \mu A M^{-1} \\ r^2 = 0.9908$$

$$Pb(II) \quad i_{pa} = -12(\pm 1.6) \mu A + 6.6 \times 10^6(\pm 2.2 \times 10^5) \mu A M^{-1} \\ r^2 = 0.9930$$

For both modified electrodes the response to Pb(II) was obtained at lower concentrations (3×10^{-6} M) than for Cd(II)

Table 1 Variation of i_{pa} of 1×10^{-5} M solutions of Pb(II) and Cd(II) containing other ions at 1×10^{-5} M

CPE $_{\alpha-CD}$			CPE $_{\beta-CD}$		
Contribution (%)			Contribution (%)		
Cation	i_p Cd(II)=100%	i_p Pb(II)=100%	Cation	i_p Cd(II)=100%	i_p Pb(II)=100%
Cu(II)	-71.6	-10.2	Cu(II)	1.3	18.9
Zn(II)	114.3	12.8	Zn(II)	<1	<1
Ni(II)	*	<1	Ni(II)	<1	-7.4
Mg(II)	*	<1	Mg(II)	<1	1.2
Mn(II)	<1	-19.2	Mn(II)	<1	-4.8
Na(I)	<1	-13.7	Na(I)	<1	-22.0
Fe(II)	<1	<1	Fe(II)	<1	-9.8
Ba(II)	*	6.4	Ba(II)	<1	-2.9
K(I)	*	6.6	K(I)	-1.3	-14.0
Li(I)	*	<1	Li(I)	<1	-3.3
Ca(II)	*	16.5	Ca(II)	<1	-11.0
Tl(III)	+28.6	-20.5	Tl(III)	50.0	-11.5

*The peak disappears

(1×10^{-5} M) and with a better sensitivity toward Pb(II). With all the results obtained for the said electrodes, it is straightforward that the CPE $_{\beta-CD}$ displays a better analytical response toward both metals studied (Pb(II) and Cd(II)) as the slopes obtained were greater (1.2 times for Pb(II) and 6.8 times for Cd(II)) compared to the slopes of the CPE $_{\alpha-CD}$.

The allowable limits stated in the Mexican official standards (NOM) for river waters are 0.5–1 ppm Pb(II) and 0.2–0.4 ppm for Cd(II). Considering the water for public consumption, the ranges are 0.2–0.4 ppm for Pb(II) and 0.1–0.2 ppm for Cd(II). The limits for agricultural land are 5–10 ppm for Pb(II) and 0.05–1.0 ppm for Cd(II). In agreement with the aforementioned results the method suggested is applicable to determine Pb(II) preferably.

Effects of other ions

The aim in obtaining a modified electrode is to get better sensitivity and selectivity to determine species of interest; therefore, it is necessary to know the analytical response variation as a function of the presence of other ions. For the present case various cations were considered like Ca(II), K(I), Fe(III) in food stuffs, or Mg(II), Ca(II), Cu(II) and Zn(II) in residual waters.

The Pb(II) and Cd(II) solutions to be used contained 1×10^{-5} M each; the same ASV conditions of work were as before, while the concentration for all the ions in the problem solutions was 1×10^{-5} M. Table 1 presents the results obtained for the modified electrodes used to determine Cd(II) and Pb(II) in the presence of other ions.

To determine whether the changes in the current of the peaks corresponding to Pb(II) and Cd(II) with the modified electrodes in the presence of other ions are associated to them, it was necessary to carry out a statistical analysis using the F test, in which the standard deviations from the experimental data are compared. The critical F (F_{crit}) obtained from tables must be bigger than the calculated F (F_{cal}) in order to consider that there is no interference.

As indicated in Table 1 there were interferences to the CPE $_{\alpha-CD}$ during Cd(II) determination from Ni(II), Mg(II), Ba(I), K(I), Li(I) and Ca(II), because the oxidation peak disappeared thus making it impossible to apply the F test. This can be ascribed to the interfering ions occupying the cavities in the α -cyclodextrin on the CPE, as their ionic size effectively blocks Cd(II) ions from entering the polymeric network on the modified electrode. After performing the F test it was found that Cu(II) interferes because of the significant decrease of the peak current while Tl(III) and Zn(II) increase it. For Pb(II) the signal was observed in all cases with significant interferences from Tl(III), Cu(II), Zn(II), Mg(II), Na(I), Ba(I) and K(I). Cd(II) did not exhibit significant interferences with the CPE $_{\beta-CD}$ for all the metals except Ta(III), this being ascribed to the size of the cavity of β -cyclodextrin which is bigger than that of α -cyclodextrin. For Pb(II) there were significant interferences from Tl(III), Cu(II), Ni(II), Fe(II), K(I) and Ca(II).

It is important to underline that there are cations such as Cu(II) that interfere with the Pb(II) signal in both modified electrodes; however, there is also an increment in the peak current for the CPE $_{\beta-CD}$ while a decrease occurs for the CPE $_{\alpha-CD}$. A comparison of the results obtained with Ca(II) and K(I) shows that the behaviour was the inverse to that given by Cu(II). Such changes can be associated to the type of modification that is produced in the cyclodextrins during the preparation of the CPE [20] and because of the cavity sizes in the cyclodextrin's networks. The interferences can be eliminated by performing a sample pretreatment.

Conclusions

The modified electrodes have better sensitivity in their electrochemical responses to the system Pb(II) 1×10^{-4} M compared to a CPE, as shown by cyclic voltammetry. The CPE $_{\alpha-CD}$ and the CPE $_{\beta-CD}$ exhibited good analytical response in determining Pb(II) by means of ASV, as evidenced by the statistical analysis: a 3×10^{-6} M detection limit

comparable to that exhibited by other modified electrodes. However, the modifications studied present the added advantage that the experiments performed used 60-s deposition times, which are undoubtedly lower compared to other works (namely 6 min) [16, 17, 18, 19]. The slope obtained for Cd(II) was smaller compared to that of Pb(II) with both electrodes, while for the CPE $_{\alpha\text{-CD}}$ the Cd(II) did not exhibit a good analytic response.

The CPE $_{\beta\text{-CD}}$ displayed better sensitivity for the detection of both metals compared to the CPE $_{\alpha\text{-CD}}$ because the slopes were greater in both cases. From interference studies and the statistical *F* test, it was possible to determine which ions really affect the determination of Pb(II) and Cd(II) obtained with both modified electrodes. The use of a standard statistical tool such as the *F* test permitted us to sort out the interference effects from other ions in solution during the determination of Pb(II) and Cd(II). Such interferences are closely related to the polymeric network of the modified CPE, which suggests that the system can be made more selective in relation to the size of the cavity of the respective cyclodextrins.

The modified electrodes certainly are an effective choice for the simultaneous determination of Pb(II) and Cd(II), mainly with the CPE $_{\beta\text{-CD}}$, as its resolution is good for the cations studied, and may be an alternative to substitute the HDME, because its base metal is associated with severe health and environmental risks, while the electrodes studied are biodegradable and non-contaminating.

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