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Carbon paste electrodes electrochemically modified with cyclodextrins

Abstract Cyclic voltammetry was used in order to obtain carbon paste electrodes (CPEs) modified with α- and β-cyclodextrins (CPE$_{\alpha\text{-CD}}$, CPE$_{\beta\text{-CD}}$) in HClO$_4$ media as electrolyte. The modified CPEs were obtained by applying 30 potential cycles, thus forming on the substrate a film with electroactive characteristics; a rise in current for the anodic and cathodic peaks became apparent as the number of cycles increased. Such behaviour confirmed the CPE modification by the species mentioned. The CPE$_{\alpha\text{-CD}}$ and CPE$_{\beta\text{-CD}}$ exhibited significant stability before various electrolytes. In order to evaluate the sort of modification attained on the CPEs, a study was conducted, varying the potential scan rate, that confirmed the CD's presence. The modified electrodes were used to determine Pb(II) ions in solution within the range from 1×10^{-5} M up to 1×10^{-3} M. The CPE$_{\alpha\text{-CD}}$ and CPE$_{\beta\text{-CD}}$ electrochemical response was studied by means of anodic stripping voltammetry of the Pb(II) ions, thereby giving a linear relation between the current for the anodic peak as a function of Pb(II) concentration with $r^2 = 0.996$ for the CPE$_{\beta\text{-CD}}$ and 0.992 for the CPE$_{\alpha\text{-CD}}$.

Keywords Cyclodextrins · Carbon paste · Cyclic voltammetry · Lead(II) · Stripping anode

Introduction

Study of electrochemically modified electrodes has gained attention during recent years owing to their sensitivity and affinity properties, which are advantageously used for the detection of electroactive species [1].

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Modification of the electrodes can be carried out through methods such as the Langmuir-Blodgett technique [2, 3], which consists of preparing single layers at water/air interfaces to transfer them later onto a solid support. Another technique widely used and improved during recent years forms self-assembled monolayers (SAMs) [4, 5, 6, 7, 8, 9, 10, 11]. The technique is based on the adsorption of an active compound on the surface of a substrate that, as a consequence of a superficial chemical reaction, results in the formation of a single organic layer having well-defined structural organization and packing.

Another relatively recent technique, the electrochemically assisted modification of carbon electrodes has been used, whereby the generation of free radicals in a solution containing chemical species with functional groups such as amines, hydroxyls, carboxylic acids, among others [12, 13, 14, 15, 16], takes place. The radicals are generated by means of a potential perturbation which is positive enough to achieve the modification of the substrate.

The chemical species that have been widely used to modify the surface of electrodes are the cyclodextrins (CDs), mainly substituted with thiol groups [4, 17], and this has contributed to the design and development of devices that use the truncated-cone molecular structure that bears a true cavity with the hydrophobic properties [18, 19, 20] that these species exhibit. However, there is no information available where the natural CDs exert superficial modifications to electrodes.

The CDs belong to the cyclic oligosaccharide family formed by D-glucopyranose units bound by $\alpha(1-4)$ glucosidic bonds [18]. The most important CDs are formed by six, seven and eight D-glucopyranose units named α, β and γ, respectively. Characteristically, they exhibit different sizes for their molecular cavities, which gives them a certain selectivity toward the inclusion of hosts, depending upon their size. The molecular structure of the CDs shows two kinds of OH groups (primary and secondary), which give it the capacity to form inclusion complexes with organic and inorganic compounds,

improving the physicochemical properties of these compounds [21, 22]. The CDs can be modified by chemical oxidation of the primary OH groups to carboxylic groups [23], because the association with the cationic substrates is increased, also improving the water solubility and their immobilization on polymeric supports. For this reason, these compounds have been widely used in different areas of chemistry, as well as in the pharmaceutical and food industries [24, 25, 26, 27]. The basis of their applicability is related to the size of the molecular cavity, which bestows them with selectivity and sensitivity increments [28].

In this work, we present the modification of a carbon paste electrode (CPE) with CDs, based on their readily usable physicochemical properties, with the aim of increasing the sensitivity and selectivity of the electrode. Electrochemical induction was used to form the modified electrode [12], applying a cyclic potential perturbation which favours the CDs oxidation and their chemical adsorption on the CPE. The capacity of the modified CPE was studied in order to detect chemical species of interest. Reports in the literature indicate that metallic electrodes become passivated with glucose oxidation products [29]; therefore we used the CPE instead, and as the CDs are also formed by glucose units they may exhibit a similar behaviour.

Experimental

Reagents and electronic equipment

All solutions were prepared using analytical grade reagents prepared with deionized water (18.2 MΩ). The solubility studies for the α- and β-CDs (Sigma) were carried out in different support electrolytes, in order to enable adequate selection of the working conditions for this work. The best electrolytic media was 1 M $HClO_4$. The α- and β-CDs were dissolved in the acid until a 0.01 M concentration was achieved. The lead solutions were prepared from $Pb(NO_3)_2$ (Baker) to a 0.1 M concentration; thereafter the necessary volume was taken to prepare different concentration solutions in the range 1×10^{-5} to 1×10^{-3} M.

The carbon paste electrode (CPE) was prepared from a mixture of graphite powder single-crystal (99.99%, Alfa AESAR) and nujol oil (Fluka) in a 1:1 proportion, to ensure easy manipulation.

The electrochemical studies were carried out using a BAS-100W potentiostat, coupled to a traditional three-electrode cell, with the CPE as the working electrode, a graphite rod as counter electrode and mercury(II) sulfate (MSE) as reference.

Results and discussion

Electrochemical modification of the CPE using the α- and β-CDs in acid media

The working solutions were prepared by adding the 0.01 M CD solution to the 1 M $HClO_4$ media. The electrochemical modification was attained using a successive program of 30 potential cycles within the range from 0.9 V to –1.3 V at 0.1 V/s scan rate, starting at the null current potential $(E_{i=0}) = 0.041$ V/MSE in the anodic direction,

inverting the scan potential when the oxidation limit was reached, to begin then with the cathodic sweep.

Figure 1 shows the cyclic voltammogram evolution during the application of a potential which was positive enough to induce adsorption of the β-CD on the CPE surface. A rather small oxidation peak can be observed at (a) –0.025 V, as a function of the applied number of cycles. The resulting reduction wave in the cathodic zone (b), at a potential of –0.9 V, grows with the number of cycles. The voltammograms in Fig. 1 reveal the existence of processes associated with the modifications of the electrochemical double layer. The peak current (i_p) increment obtained upon applying the successive cycle program can be attributed to the formation of a coating of adsorbed species due to the production of cationic radicals of the β-CD exhibiting redox properties on the surface of the CPE.

In the anodic potential region can be observed the presence of two small oxidation shoulders, one at a 0.38 V potential (c) and the other one at 0.6 V (c'), which is very close to the oxidation wall. Upon reversing the potential scan, a broad reduction band can be observed (d), this being attributed to adsorption on the surface of the electrode.

Using the same procedure outlined above, a CPE was modified with α-CD. Figure 2 shows a series of cyclic voltammograms for the CPE/α-CD. The i vs. E response was recorded using the same potential range as before for the β-CD. It can be observed that the voltammogram exhibits oxidation and reduction waves (a and b) at 0.78 V and –0.9 V, respectively. The redox process appears somewhat near potential values close to those obtained for the previous case with the β-CD (see Fig. 1). Also, the presence can be observed of a well-defined oxidation peak (c'), with the pre-wave (c) and reduction (d) bands at potential values of 0.55, 0.35 and 0.22 V, respectively. The cathodic and anodic i_p values reveal an increment of the peak height with an increasing
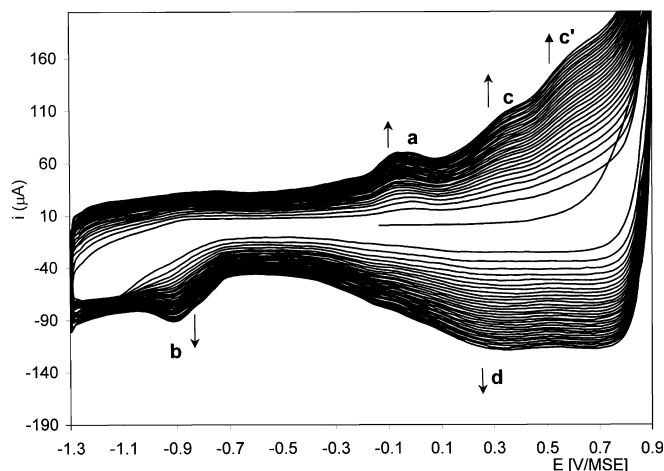

Fig. 1 Cyclic voltammograms for the system 0.01 M β-CD on a CPE in 1 M $HClO_4$ media. Successive potential cycles in the range of 0.9 to –1.3 V starting at $E_{i=0} = 0.041$ V/MSE at a scan rate of 0.1 V/s
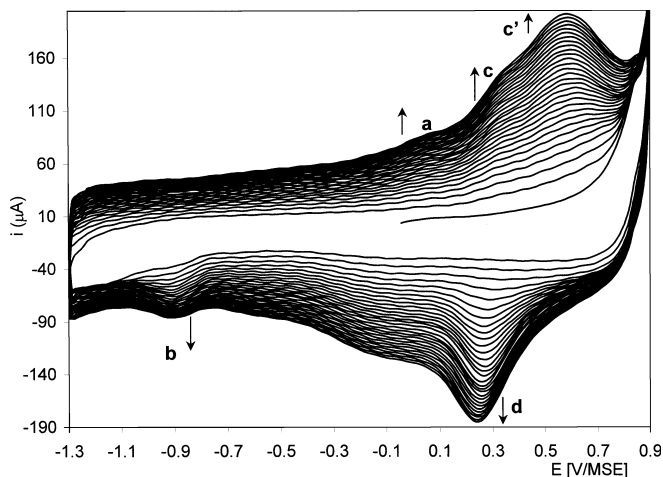
Fig. 2 Cyclic voltammograms for the system 0.01 M α-CD on a CPE in 1 M HClO₄ media, with a successive scan program in the range of 0.9 to –1.3 V at a 0.1 V/s potential scan rate starting at $E_{i=0} = 0.041$ V/MSE

Fig. 3 Plot of q_c as a function of the number of cycles for both α-CD and β-CD

number of cycles, thus indicating that an electroactive species is being deposited on the surface of the CPE.

The potential difference (ΔE_p) indicates that the processes observed in these systems are characteristically irreversible, given that ΔE_p for the first pair was 0.33 V/MSE (c and d in Fig. 2), while that for the processes associated with both waves at a and b (same figure) was 0.822 V/MSE.

Figures 1 and 2 exhibit common redox processes (peaks a and b), as the potential values where both appear may well show the same redox process that favours adsorption of the CD on the CPE, whereas peaks c′ and d from the α-CD possibly correspond to some other type of arrangement, such as formation of a surface coating where the oxidized CDs interact among themselves, thus giving rise to a polymeric arrangement.

Figure 3 is the result from the study of the cathodic charge variation (q_c) as a function of the number of cycles in the voltammograms presented in the two previous figures. From the graph, two linear regions associated with an accumulation of both the CDs on the CPE are observed. However, the β-CD exhibits a larger experimental data dispersion as compared to the α-CD one, but nevertheless both are functions of the number of cycles for the potential applied.
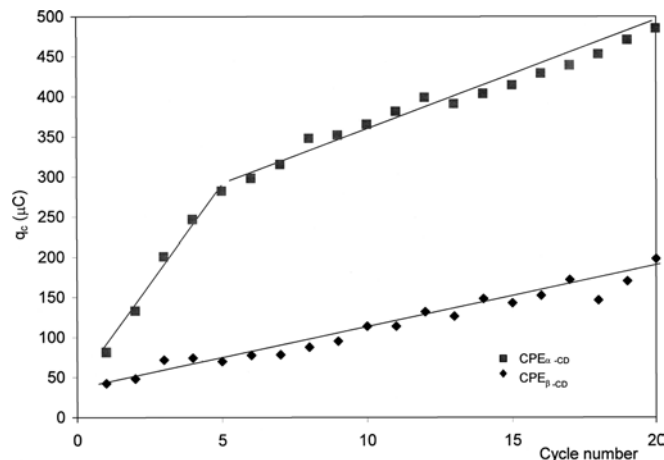
The behaviour depicted can be associated with a change in the kinetic mechanism governing the growth of the CD film on the CPE. This work aims at explaining the two stages observed during the modification of the electrode as a function of the number of cycles.

Stage 1. The CPE modification with the CD is linked to the polar group interactions, mainly the primary OH groups of the CD with the surface of the substrate, which appear to be favoured by the cyclic potential perturbation. It has been reported in the literature that when an applied potential is sufficiently anodic it is possible to partially oxidize the CD [30], not just to provoke the polarization of the molecule, thus generating radicals from the species that can adhere to the surface of the CPE. Figure 4 suggests a possible mechanism whereby the modification of the electrode surface can be carried out, at least during an initial stage. The size of the α-CD is smaller than the β-CD, and thus more capable of being polarized and strongly adsorbed on the substrate, which can be an explanation for the better α-CD voltammograms definition.

Stage 2. The formation of oligomers occurs such that they may precipitate on the CPE, forming an electroactive film. It can be considered to happen as follows: as the CD can be oxidized and the primary OH groups from the CD are more susceptible toward oxidation, this gives rise to the formation of an aldehyde and/or carboxylic acid [23, 30]. Also, the species' radicals, formed by

Fig. 4 Scheme for the initial stage of the CPE surface modification mechanism with β-CD and/or α-CD
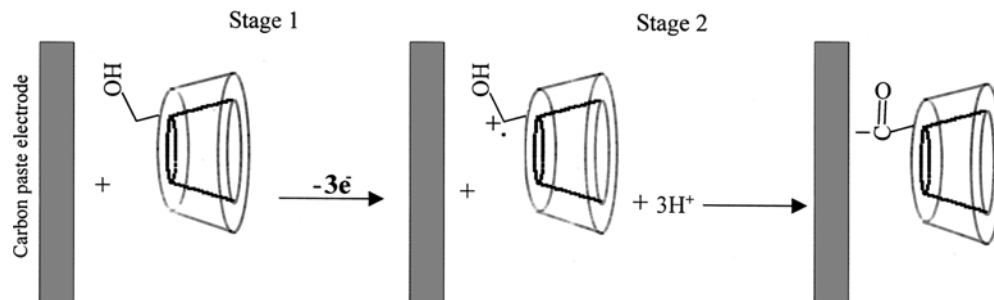
electrochemical stimulation during the application of oxidation potentials in successive cycles, can react with another CD molecule and form a dimer with subsequent liberation of water, due to repetition of the process during *n* cycles (see Fig. 5).

A CPE-β-CD$_{ads}$ was obtained by immersion of a CPE in a β-CD solution for 20 min with open current, with β-CD adsorbed only physically. In order to justify the superficial modification on the electrochemically obtained CPEs, the voltammograms of the CPE$_{\beta\text{-CD}}$ and CPE-β-CD$_{ads}$ are compared in Fig. 6. It can be considered from both plots that the electrochemically active species are adsorbed on the CPE$_{\beta\text{-CD}}$, this being a possible indication of CD polymerization.

These results show that the two electrodes, as modified by preconcentration and by electrochemical induction, exhibit different behaviour. As far as the magnitude of the capacitive current is concerned, the aforementioned holds as correct, apart from the redox processes (a, b, c, c′ and d) which the modified CPE exhibits as a result of electrochemical induction. Other experiments were carried out after the electrode was modified so that further characterization could be pursued.

Characterization of the CPE modified with CD

Electrochemical properties

As previously indicated, the support electrolyte used was 1 M HClO$_4$ to carry out the experiments concerning the modification of CPE by electrochemical induction (CPE$_{\beta\text{-CD}}$ and CPE$_{\alpha\text{-CD}}$). From Fig. 7 it can be observed that the curves of current (*i*) as a function of the applied potential (*E*) obtained are identical to those recorded previously during the last potential cycle applied during their formation. It is relevant to underline that the redox processes (a, b, c, c′ and d) observed during formation of the electrodes persist in the cyclic voltammogram used as control in a solution free of CD.

As can be observed from Figs. 1 and 2, a and b waves are present in both cases, which is interpreted as a possible response to CD adsorption over the CPE, while
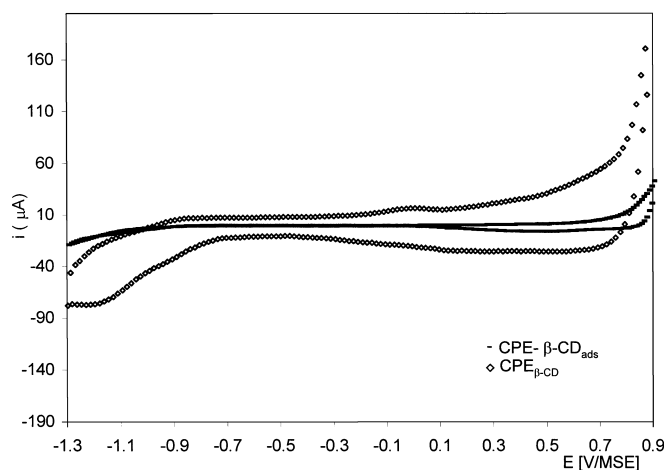
Fig. 6 Cyclic voltammograms obtained for two modified electrodes, one in 1 M HClO$_4$ media using a preconcentrated CPE-β-CD$_{ads}$ in a solution of 0.01 M β-CD during 20 min, and the other for CPE$_{\beta\text{-CD}}$ obtained by electrochemical induction, with the scan sweep starting at $E_{i=0} = -0.05$ V at a scan rate of 0.1 V/s
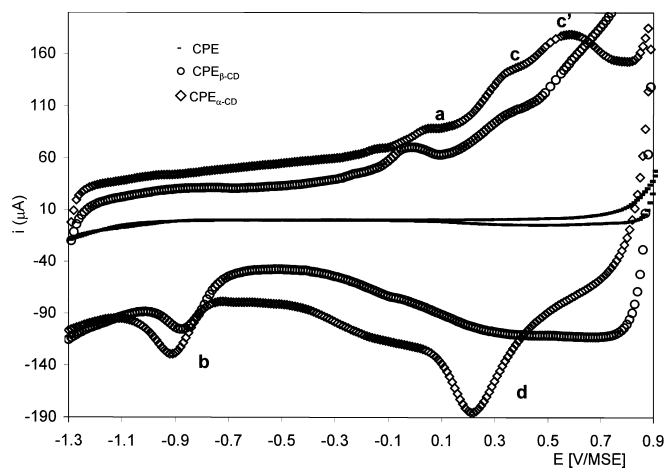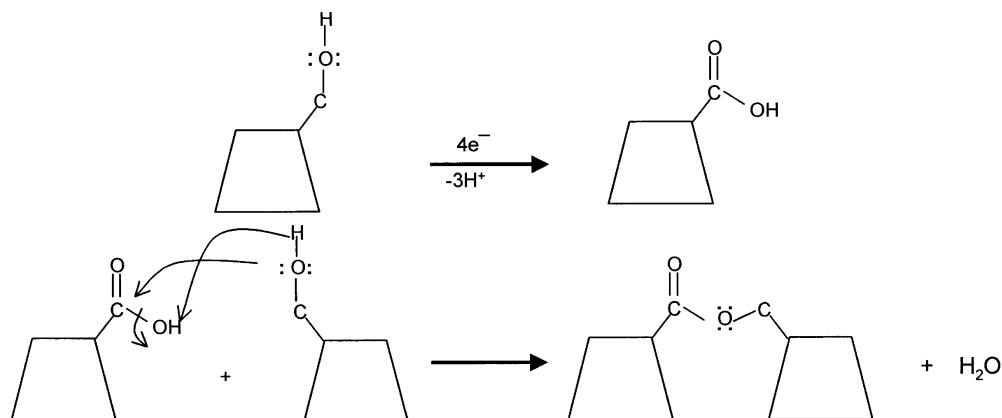
Fig. 7 Cyclic voltammograms for control of a CPE, CPE$_{\beta\text{-CD}}$ and CPE$_{\alpha\text{-CD}}$ in a CD-free electrolyte solution, obtained with scan sweeps beginning at $E_{i=0} = -0.1$ V at a scan rate of 0.1 V/s

Fig. 5 Second stage for the schematic mechanism proposed for the propagation of the polymer of α-CD over the CPE

for the c, c′ and d peaks it becomes possible to relate them to other electrochemical process associated with the formation of a polymeric coating. The fact that the voltammogram in a CD-free solution is quite similar to that of the last cycle constitutes an indication of the system coating stability.

Cyclic voltammograms at different scanning rates were performed to analyse the properties of the coatings on CPE$_{\beta\text{-CD}}$ and CPE$_{\alpha\text{-CD}}$. Taking as reference the (a) peak, a statistical analysis was performed using the relation of i_{pa} as a function of the scan rate. The data obtained are reported in Table ble 1. In accordance with the data obtained, it can be considered that during modification of the electrode the electrochemical process is not controlled by diffusion [31], that is the α-CD and the β-CD can be found on the CPE.

The CPE$_{\alpha\text{-CD}}$ and CPE$_{\beta\text{-CD}}$ were advantageously used, owing to the affinity displayed by the CD to encapsulate species compatible with the hydrophobic characteristics in the cavity. As can be expected, we also took advantage of the ClO$_4^-$ ions' ability to modify the hydrophobic properties of the β-CD cavity, in order to favour its interaction with metal ions to produce inclusion complexes [32]. Therefore, it was desirable to test the efficiency of the modified electrodes with respect to Pb(II) ions, as its analytical determination was the subject to be studied.

Analytical application: calibration of the CPE$_{\beta\text{-CD}}$ as a function of Pb(II) concentration

The analytical response capacity of the CPE$_{\beta\text{-CD}}$ and CPE$_{\alpha\text{-CD}}$ was studied as a function of varying concentrations of Pb(II). For such a study, the 1 M HClO$_4$

Table 1 Results for the statistical analysis of the i_{pa} study as a function of the potential scan rate

Electrode	b (μA)	Slope (μA s/V)	r^2
EPC$_{\beta\text{-CD}}$	9.0 ($\pm$2.8)	0.9616 ($\pm$0.011)	0.998
EPC$_{\alpha\text{-CD}}$	−1.0723 ($\pm$1.25)	1.0072 ($\pm$0.005)	0.9998
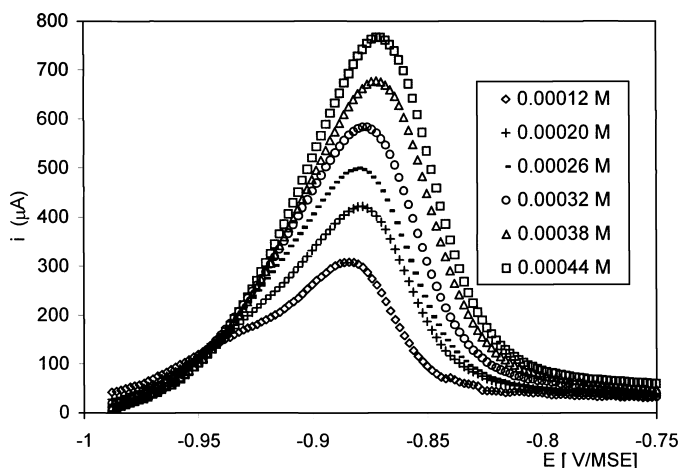
support electrolyte was used with successive Pb(II) additions in the range 1×10^{-5} to 1×10^{-3} M. The analytical response from the two electrodes (CPE$_{\beta\text{-CD}}$ and CPE$_{\alpha\text{-CD}}$) was monitored via anodic stripping voltammetry. The applied electrodeposition potential (E_d) was –1.3 V and lasted for 30 s; the Pb(II) stripping was recorded in the range from –1.3 to –0.6 V at a scan rate of 0.1 V/s. Figure 8 shows the general shape and the peaks obtained during the anodic stripping in the system. It can be observed that the anodic peak currents increase proportionally with increasing Pb(II) concentration.

The resulting data from the figure were used to plot the peak anodic current as a function of Pb(II) concentration. Figure 9 shows the plot; it can be observed that a linear relationship becomes apparent for both modified electrodes. Table ble 2 presents the results of the statistical analysis of the date plotted in Fig. 9.

In agreement with the statistical analysis of the calibration curve, and comparing both slopes in the figure above, the slope of the curve corresponding to the CPE$_{\beta\text{-CD}}$ is larger (by one unit); therefore it would appear that the response of the CPE$_{\beta\text{-CD}}$ towards Pb(II) is more sensitive than that of the CPE$_{\alpha\text{-CD}}$. Nevertheless, both modified electrodes can be used in Pb(II) ion determination.

Conclusions

This work reported, for the first time, experimental evidence related to the formation of a polymeric coating of α- and β-CDs on CPEs as well as the electrochemical characterization of the modified electrode by cyclic voltammetry. The voltammograms revealed that the electrochemical behaviour for both systems is quite similar, particularly as the peaks (a and b) in stage 1 are related to the response of the CD-OH primary groups, and with the species generated during the electrochemical perturbation

Fig. 8 Anodic stripping voltammograms for various Pb(II) concentrations in 1 M HClO$_4$, using both CPE$_{\beta\text{-CD}}$ and CPE$_{\alpha\text{-CD}}$ at a $E_d = -1.3$ V applied during 30 s, stripping at a potential of –0.6 V
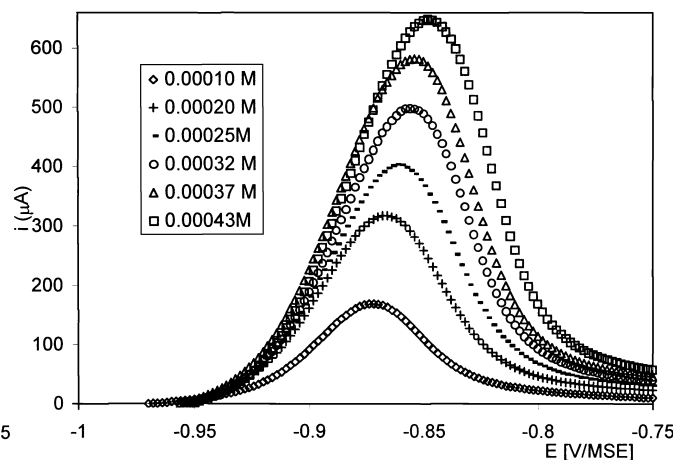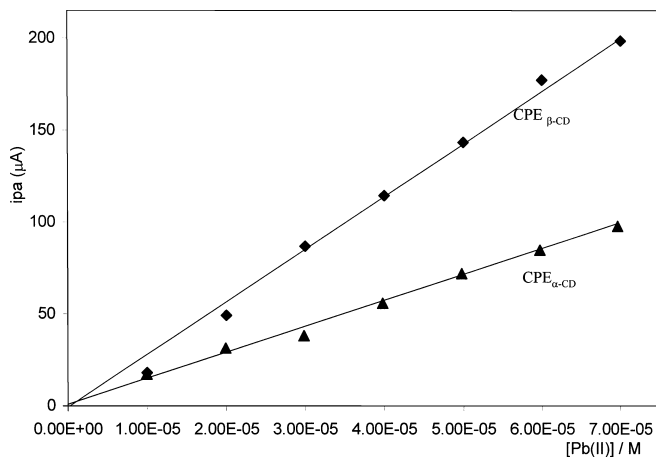
Fig. 9 Plot of the linear relationship between the peak anodic current (i_{pa}) and the lead Pb(II) concentration obtained with CPE$_{\beta\text{-CD}}$ and CPE$_{\alpha\text{-CD}}$

Table 2 Results for the statistical analysis of the i_{pa} data as a function of [Pb(II)]

Electrode	b (μA)	Slope ($\mu A\ M^{-1}$)	r^2
EPC$_{\beta\text{-CD}}$	−9.6 (± 3.5)	3.05×10^6 ($\pm 78{,}132$)	0.996
EPC$_{\alpha\text{-CD}}$	1.8 (± 2.2)	1.37×10^6 ($\pm 49{,}602$)	0.992

which interact with the surface of the CPE, giving rise to the superficial modification associated with the increment in capacitive current and peak broadening.

The peak heights are associated with the surface concentration of the adsorbed species according to the CD type, which is quite clear from the CPE$_{\alpha\text{-CD}}$ c′ and d peaks. The CPE$_{\alpha\text{-CD}}$ associated charge shows a two-step growth, with the first rate constant greater than the second one. The former effect is associated with the different α-CD conformations on the electrode surface. On the other hand, the CPE$_{\beta\text{-CD}}$ shows a single growing step.

The modified electrodes obtained were used to determine Pb(II) concentration, with a linear relation between the stripping peak anodic current and the ion concentration for both the systems studied. The results show that the Pb(II)-β-CD system shows more chemical affinity and sensitivity than the Pb(II)-α-CD one. Finally, it must be mentioned that the work is the first evidence of using CPEs coated by CDs applied in heavy metal [Pb(II)] analytical determinations.

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