Simultaneous Determination of Lead and Cadmium in the Presence of Morin by Adsorptive Stripping Voltammetry with a Nafion–Ionic Liquid–coated Mercury Film Electrode

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This work describes the use of nafion coated with the ionic liquid 1–ethyl–3–methylimidazolium trifluoromethanesulfonate ($[EMIM]F_3MSO_3$) on a mercury film electrode (NILHgFE) for simultaneous determination of Pb(II) and Cd(II) by adsorptive stripping voltammetry in the presence of morin. Morin forms complexes with a metal:ligand stoichiometry of 1:1 with Pb(II) and of 1:2 with Cd(II). Electrodes were coated with nafion and $[EMIM]F_3MSO_3$ or 1–butyl–3–methylimidazolium tetrafluoroborate or 1–butyl–3–methylimidazolium hexafluorophosphate, obtaining higher peak currents with the former. Variables like concentration of ionic liquid (C_{IL}) on the electrode, pH, morin concentration, adsorption potential (E_{ads}) and adsorption time (t_{ads}) were optimized. The best experimental parameters were: C_{IL} = 2.6 mol L^{-1}; pH = 2.9; C_{morin} = 1.1 µmol L^{-1}; E_{ads} = –0.3 V and t_{ads} = 60 s. The linear calibration curves ranged up to 16.0 µg L^{-1} for Pb(II) and Cd(II) with synthetic solutions; however, with real and certified samples linear range was up to 50.0 µg L^{-1} for Pb(II). The detection limits (3σ) were 0.12 µg L^{-1} for Pb(II) and 0.13 µg L^{-1} for Cd(II). The relative standard deviation was 2.0 % (n=7) for a solution containing 4.9 µg L^{-1} Pb(II) and Cd(II). The method was validated by determining Pb(II) and Cd(II) in reference material for measuring elements in water (TMDA–61) and waste water (SPS–WW1). Finally, the method was successfully applied to the determination of Pb(II) and Cd(II) in tap water after UV digestion.

1. INTRODUCTION

The monitoring of Pb(II) and Cd(II) in natural waters is of great importance, due to the fact that these elements tend to concentrate in all aquatic environmental matrices causing different diseases.

Lead is toxic to many organ systems of human body, such as the central and peripheral nervous system, red blood cells, kidneys, cardiovascular systems, and male and female reproduction organs [1,2]. Stripping voltammetry (AdSV) is a sensitive electrochemical technique for determination of trace metals in various biological and environmental matrices, due to high selectivity, rapid response and low cost. Mercury, as a drop (HMDE) or a thin film (HgFE) formed on an inert electrode, has been the electrode of choice for metal ion analysis for many decades, due to its high cathodic hydrogen overpotential and its ability to dissolve many metals, aiding the preconcentration process [3]. In the last ten years, reported studies indicate that bismuth film electrodes have many excellent properties similar to those of mercury electrodes and have lower toxicity. Different electrodes, such as modified multi walled carbon nanotubes (MWCNT) containing mercury or bismuth [4–8] have been explored for the voltammetric determination of Pb(II) and Cd(II). The use of MWCNT is suitable for detection of metal ions due to the fact that the composite electrodes combine the advantages of films electrodes with excellent properties of carbon nanotubes (e.g. huge specific surface area and strong adsorptive ability) [8]. On the other hand, the use of 2,2′–azinobis diammonium salt with MWCNTs on the electrode exhibits superior performance since this compound contains two sulfonic groups and several electron–donating groups that may interact with Pb(II) and Cd(II) obtaining higher sensitivity [7]. In addition when these electrodes are coated with nafion [4,5,9–11] their stability is increased and the contamination by surface active compounds such as surfactants present in environmental samples is decreased. Recently, it has been reported that modified electrodes based on incorporation of conducting polymers such as polyaniline [12,13], poly(2,5–dimercapto–1,3,4–thiadiazole) [14], poly(p–aminobenzene   sulfonic acid) [15], poly–L–lisine–poly(sodium 4–styrenesulfonate) [16], poly(sodium 4–styrenesulfonate) [17] and poly(sulfonic acid ester) [18] present high conductivity, good stability and may coordinate with heavy metal ions through sulfur atoms, increasing the accumulation of analyte on the working electrode.

However, the large majority of the published applications of simultaneous determination of Pb(II) and Cd(II) using modified electrodes utilize ASV. In adsorptive stripping voltammetry (AdSV) the metal ions must be converted into stable complexes with adequate surface–active ligands to be adsorbed on the working electrode by means of a non electrolytic process prior to the voltammetric scan, and the detection limit of AdSV is also usually better than that of ASV [19]. One possible way of enhancing the adsorptive process and the sensitivity of the method is the use of surfactants. Cationic or anionic surfactants can be adsorbed easily onto the mercury electrode by hydrophobic and electrostatic attraction. Neutral metal complexes in the solution can be attracted by the positively charged surfactant to form stable compounds and be transported consequently to the electrode surface in the accumulation step. Ionic liquid (ILs) carrying long–chain alkyl groups have similar structure and properties as those of the surfactants and could interact with the electrode increasing the peak current of analyte. In addition, ionic liquids have high conductivity, high chemical and thermal stability, almost negligible vapor pressure and wide electrochemical potential windows [20,21]. This dual nature may well be beneficial in applications of adsorptive stripping determination of metal ions. Different ionic liquids have been used in the simultaneous determination of Pb(II) and Cd(II) such as 1–butyl–3–methylimidazolium hexafluorophosphate [22], N–octylpyridium hexafluorophosphate [23,24], 1–methyl–3–[(3–triethoxysilyl) propyl] imidazolium and 1–butyl–3–methylimidazolium

tetrafluoroborate [25,26], obtaining detection limits between 0.07–8.2 µg L^{-1} for Pb(II) and 0.02–8.9 µg L^{-1} for Cd(II).

The aim of this study is to optimize the adsorptive stripping voltammetry technique to determine Pb(II) and Cd(II) simultaneously using morin (3,5,7,2′,4′–pentahydroxyflavone) as complexing and adsorbing ligand. This ligand has been used in AdSV with HMDE as a chelating agent for molybdenum [27,28], antimony [29], indium [30], aluminum and iron [31], bismuth and copper [32], copper, zinc and lead [33], but its use for the simultaneous determination of Pb(II) and Cd(II) using glassy carbon electrode, modified with Hg–nafion–ionic liquid, has not been reported yet.

2. EXPERIMENTAL PART

2.1. Apparatus

The voltammograms were obtained on a BASi CV50W in a three–electrode configuration. The modified glassy carbon electrode (NILHgFE, disc diameter of 3 mm), was used as working electrode with a 3 mol L^{-1} Ag/AgCl/KCl reference electrode, and a platinum wire auxiliary electrode. The pH measurements were carried out with an Orion–430 digital pH/mV meter equipped with combined pH glass electrode. UV–irradiation of water samples was carried out in quartz tubes using a 705 UV–digester (Metrohm).

2.2. Reagents and solutions

Water used for sample preparation, dilution of the reagents, and rinsing purposes was obtained with a Milli–Q system (18.2 Ohm. Millipore, USA). All chemicals (nitric acid, hydrochloric acid, boric acid, acetic acid, ethanol, methanol, etc.) were analytical grade from Merck. Standard stock solutions of 1.0 mg L^{-1} Pb(II) and Cd(II) and 200 mg L^{-1} Hg(II) were prepared from standards of 1000 mg L^{-1} Pb(II), Cd(II) and Hg(II) solutions (Merck). The stock solution of morin was prepared by dissolving the reagent in methanol (0.25 mmol L^{-1}). 1–Ethyl–3–methylimidazolium trifluoromethanesulfonate ([EMIM]F$_3$MSO$_3$), 1–butyl–3–methylimidazolium tetrafluoroborate ([BMIM]BF$_4$) and 1–butyl–3–methylimidazolium hexafluorophosphate ([BMIM]PF$_6$) were purchased from Merck. Nafion (5% w/v solution in a mixture of water and lower alcohols) was purchased from Aldrich (Milwaukee, WI). Britton Robinson (BR) buffer solutions were used to investigate pH in the 2.2–3.6 range. These buffers were prepared by mixing equal volumes of orthophosphoric acid, acetic acid, and boric acid, adjusting to the required pH with 2.0 mol L^{-1} NaOH solution (0.4 mol L^{-1}). Certified reference water (TMDA–61.2, Environment Canada) containing Al 57.9; As 34.4; Cd 58; Co 63; Cu 63.5; Fe 79.7; Mn 75.7; Ni 57.5; Pb 61.4; V 71.1; Zn 71.3 µg L^{-1} and certified waste water level 1 (SPS–WW1, Norway) containing Al 2.0; As 0.1; Cd 0.02; Co 0.06; Cr 0.2; Cu 0.4; Fe 1.0; Mn 0.4; Ni 1.0; P 1.0; Pb 0.1; V 0.1, Zn 0.6 mg L^{-1} were used for validation measurements.

2.3. Procedure for preparation of NILHgFE

Before measurement, the glassy carbon substrate electrode was thoroughly polished using a polishing pad with 0.3 and 0.05 μm Al_2O_3 slurry, rinsed with 0.3 mol L^{-1} HNO_3, water and methanol for five minutes in an ultrasonic bath and dried with N_2. 1–Ethyl–3–methylimidazolium trifluoromethanesulfonate; 1–butyl–3–methylimidazolium tetrafluoroborate and 1–butyl–3–methylimidazolium hexafluorophosphate composites were prepared by mixing 100 μL of 5% Nafion solution with 100 μL of ionic liquids and sonicated por five minutes. 10–μL of nafion solution or 10–μL of nafion–ionic liquid solution was placed on the electrode surface and the solvents were evaporated off at room temperature for 60 min. The electrode was then transferred into the plating solution containing 200 mg L^{-1} Hg(II) and the Hg film was formed by holding the working electrode potential at −1.30 V for 150 s. The same electrode was used in a series of measurements.

2.4. Sample preparation

Domestic tap water samples were collected in our laboratory. Before the analysis all the samples were digested under UV radiation for 90 min at 90 °C in the presence of H_2O_2 (10.0 mL of sample with 100 μL of 30 % H_2O_2) to decompose organic substances. To make sure of the reliability of the method the samples were analyzed by ICP–AES.

2.5. Measurement Procedure

10–mL of deionized water (or tap water samples), 0.5 mL of Britton–Robinson buffer solution (0.4 mol L^{-1}), 1.0–100.0 μL of morin solution (0.1 mmol L^{-1}), and aliquots of Pb(II) and Cd(II) solution (1.0 mg L^{-1}) were pipetted into the voltammetric cell. The solution was purged with argon (saturated with water vapor) for 5 minutes in the first cycle and for 60 s for each successive cycle. Then, the preconcentration step was initiated for a given t_{ads} and E_{ads} at a stirring speed of 500 rpm. After an equilibration time of 10 s, adsorptive voltammograms were recorded, while the potential was scanned from −0.2 to −0.9 V using square wave modulation with 10 mV step amplitude, 10 mV pulse amplitude, and a frequency of 25 Hz. Each voltammogram was repeated three times. The calibration curves were obtained and linear regression and detection limits were calculated. The proposed method was applied to the determination of Pb(II) and Cd(II) in tap water. To eliminate matrix effects the standard addition method was used. All data were obtained at room temperature (~25 °C).

3. RESULTS AND DISCUSSION

3.1. Characterization of the NILHgFE

Preliminary experiments were carried out to identify the general features that characterize the behavior of Pb(II) and Cd(II) with morin as chelating agent. Morin, whose pK_a values are: $pK_1 = 4.99$

$\pm$ 0.09; pK_2 = 8.29 $\pm$ 0.08 and pK_3 = 10.33 $\pm$ 0.11 [34], forms complexes with a metal:ligand stoichiometry of 1:1 with Pb(II) and of 1:2 with Cd(II). Figure 1 shows adsorptive voltammograms of Pb(II) and Cd(II) (4.9 μg L^{-1}) in the presence of morin (0.8 μmol L^{-1}) in acetate buffer solution at pH 4.1, using a nafion coated glassy carbon electrode (curve a), nafion coated mercury film electrode (curve b) and ionic liquid–nafion coated mercury film electrode (curve c). Two almost imperceptible signals were observed for Pb(II)–morin and Cd–morin complexes using a nafion coated glassy carbon electrode. When a film of mercury was added to the electrode two small signals were observed at –0.6 and –0.8 V with peak current of 0.04 and 0.02 μA for the reduction of Pb(II) and Cd(II) complexes respectively. Finally, when the electrode was coated with a mixture of nafion and 1–ethyl–3–methylimidazolium trifluoromethanesulfonate (NILHgFE) the electrochemical reduction of the Pb–morin and Cd–morin complexes ocurred at–0.5 and –0.6 V with peak currents of –0.38 and –0.14 μA, respectively. The presence of ionic liquid increased the peak current of the complexes and the sensitivity of the method was better.
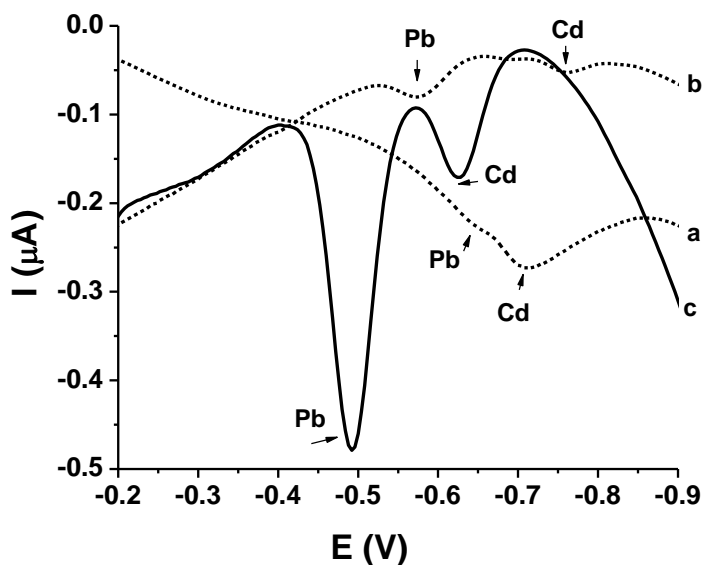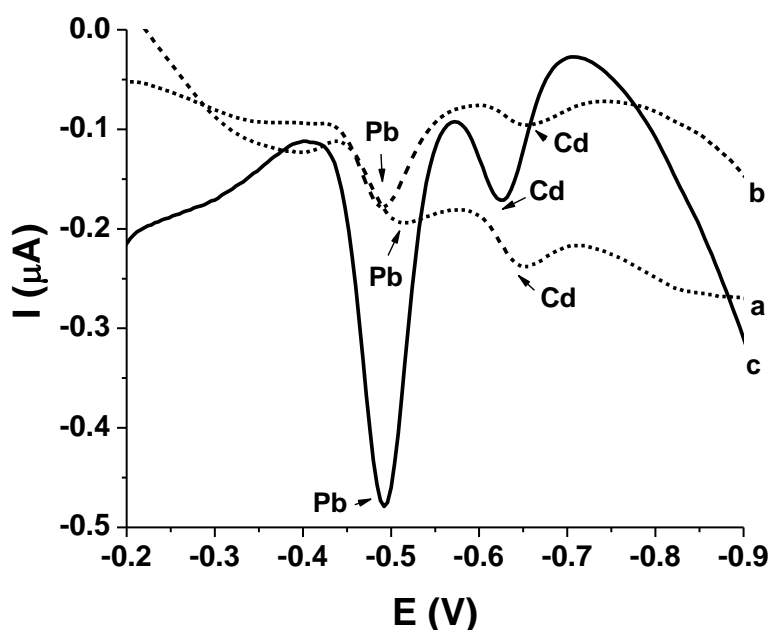

Figure 1. AdSV of Pb(II) and Cd(II) (4.9 μg L^{-1}) in the presence of morin (0.8 μmol L^{-1}) in acetate buffer solution at pH 4.1 using a nafion coated glassy carbon electrode (curve a), nafion coated mercury film electrode (curve b) and [EMIM]F$_3$MSO$_3$–nafion coated mercury film electrode (curve c) (NILHgFE). E_{ads}: −0.20 V; t_{ads}: 60 s; step amplitude: 10 mV; pulse amplitude: 10 mV and frequency: 25 Hz.

3.2. Study of the influence of ionic liquid types

Figure 2 presents adsorptive voltammograms of 4.9 μg L^{-1} Pb(II) and Cd(II) in the presence of 0.8 μmol L^{-1} morin at pH 4.1 (buffer acetate) with nafion coated mercury film electrodes containing different ionic liquids: 1–butyl–3–methylimidazolium hexafluorophosphate ([BMIM]PF$_6$) (curve a), 1–butyl–3–methylimidazolium tetrafluoroborate ([BMIM]BF$_4$) (curve b) and 1–ethyl–3–

methylimidazolium trifluoromethanesulfonate ([EMIM]F$_3$MSO$_3$) (curve c). A poor peak at −0.5 V for Pb(II) and at –0,6 V for Cd(II) are observed in the presence of [BMIM]PF$_6$ and [BMIM]BF$_4$, whereas a sensitive peak current is obtained in the presence of [EMIM]F$_3$MSO$_3$, indicating the strong preconcentration of Pb(II) and Cd(II) as complexes with morin at the modified electrode. The sensibility of the method is greatly affected by the anion component of the ionic liquid in the electrode (PF$_6^-$, BF$_4^-$ and F$_3$MSO$_3^-$), and the peak current is significantly increased in the presence of [EMIM]F$_3$MSO$_3$. It could facilitate the electron transference rate between the electron surface and the electroactives Pb-morin and Cd-morin complexes. Gey et al [35] showed that the glassy carbon electrode modified with this ionic liquid and thiol-functionalized mesoporous molecular sieve was very effective in the determination of Cd(II) in water samples. However, Lan et al [36] used screen-printed antimony film electrodes modified with multiwalled carbon nanotubes for the determination of Hg(II) obtaining the largest stripping current in the presence of [BMIM]BF$_4$. On the other hand, Fuchigami et al [37] reported that the imidazolium ionic liquid having F$_3$MSO$_3^-$ was much superior electrolyte for the electrooxidative polymerization of pyrrole to those having either the BF$_4^-$ or PF$_6^-$ anions because [EMIM]F$_3$MSO$_3$ has a higher viscosity than the others. Huang et al [38] studied the effect of cation (ethyl, butyl, hexyl) of ionic liquid in the electrochemistry and bioelectrocatalysis of horseradish peroxidase (HRP) in Nafion films at glassy carbon electrode. The three ionic liquid were: [EMIM]BF$_4$, [BMIM]BF$_4$ and [HMIM]BF$_4$. They reported that the presence of a small amount of water was crucial for the electroactivity of HRP and the optimum water content and electrocatalytic reduction decreases with the increase of alkyl chain length on imidazole ring, which is due to the difference of the hydrophilicity of the ionic liquid.

Figure 2. AdSV of Pb(II) and Cd(II) (4.9 µg L^{-1}) in the presence of morin (0.8 µmol L^{-1}) in acetate buffer solution at pH 4.1 using a NILHgFE containing the following ionic liquids: [BMIM]PF$_6$ (curve a), [BMIM]BF$_4$ (curve b) and [EMIM]F$_3$MSO$_3$ (curve c). E$_{ads}$: −0.2 V; t$_{ads}$: 60 s. Other conditions as in Fig.1

3.3. Study of the influence of [EMIM]F₃MSO₃ concentration

The effect of the [EMIM]F$_3$MSO$_3$ concentration on the peak current of the Pb(II) and Cd(II) complexes was investigated in the 0.0–5.0 mol L^{-1} range. The experimental conditions were: pH 4.1 (acetate buffer), 4.9 µg L^{-1} Pb(II) and Cd(II), C$_{morin}$ 0.8 µmol L^{-1}; E$_{ads}$ = –0.2 V and t$_{ads}$ = 60 s. The peak current increased with increasing [EMIM]F$_3$MSO$_3$ concentration up to 2.6 mol L^{-1} and then decreased slightly, probably due to saturation of the electrode (Fig.3). An optimum ionic liquid concentration of 2.6 mol L^{-1} was used for further experiments (IL:nafion 1:1. w:w)
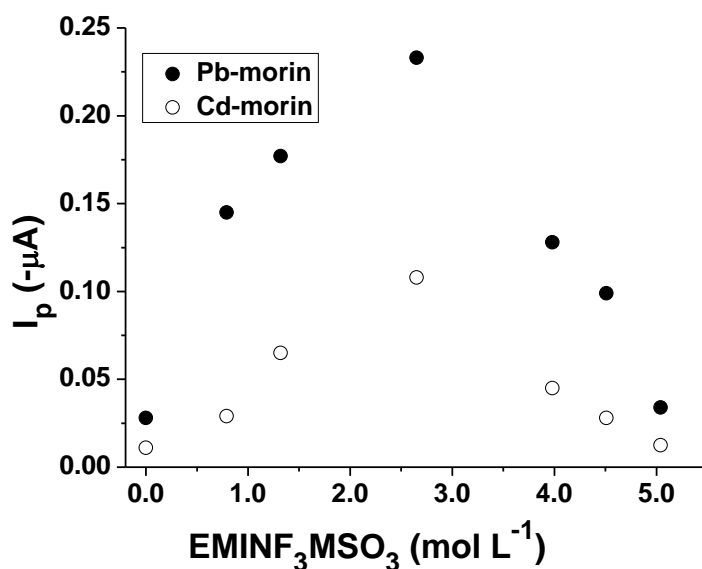
Figure 3. Effect of [EMIM]F$_3$MSO$_3$ concentration on the peak current at pH 4.1. Conditions: Pb(II), Cd(II); 4.9 µg L^{-1}; C$_{morin}$: 0.8 µmol L^{-1}; t$_{ads}$: 60 s; E$_{ads}$: −0.2 V. Other conditions as in Fig. 1.

3.4. Effect of pH variation

The influence of pH on the adsorptive peak currents of the Pb(II) and Cd(II) complexes were studied in the 2.3–4.0 pH range (Fig. 4). In order to keep the composition of the buffer constant when studying the effect of pH, Britton–Robinson (BR) buffers were used. The experimental conditions were: Pb(II), Cd(II) 4.9 µgL^{-1}; C$_{morin}$ 0.8 µmol L^{-1}; E$_{ads}$ = –0.2 V and t$_{ads}$ = 60 s. It was found that with increasing pH up 2.6 – 2.9 the peak current increased. However, at higher pH values the peak current decreased with increasing pH probably due it changes the net charge of the complexes and the adsorption on the electrode are less effective. The ionic liquid could interact with morin or morin complexes yielding ion pairs and have an effect on the dissociation constant. pH of 2.9 was used for further experiments.
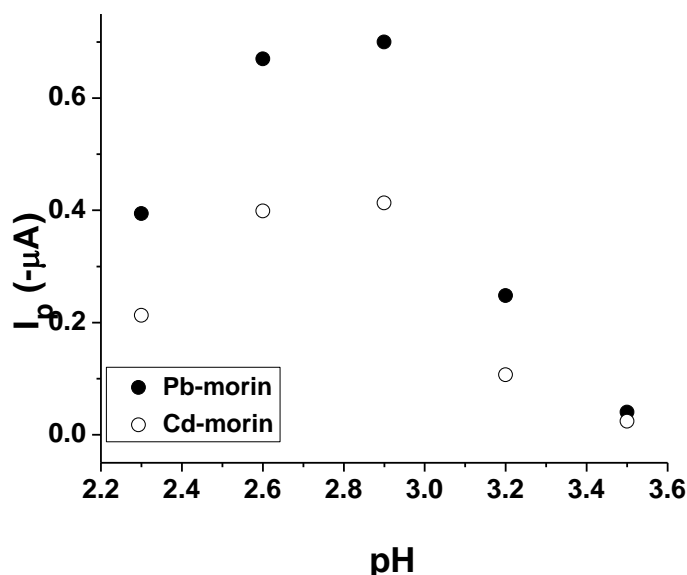
Figure 4. Effect of pH on the peak current of the Pb–morin and Cd–morin complexes. Conditions: Pb(II), Cd(II) 4.9 μgL^{-1}; C_{morin}: 0.8 $\mu mol\ L^{-1}$; E_{ads}: −0.2 V; t_{ads}: 60 s. Other conditions as Fig. 1.

3.5. Comparison between of ASV and AdSV techniques for Pb(II) and Cd(II) determination.

Figure 5 shows the anodic and adsorptive stripping voltammograms obtained with the same Pb(II) and Cd(II) solution at pH 2.9. In anodic voltammograms ($E_{dep} = −1.0$ V) the oxidation peaks of the Pb(0) and Cd(0) are observed at –0.4 and –0.6 V, respectively, whereas in adsorptive voltammograms ($E_{ads} = −0.2$ V) the reduction peak of the Pd(II)–morin and Cd(II)–morin complexes are observed at –0.5 and –0.7 V, respectively. The reduction peaks of the complexes shift to more negative potentials, which is indicative of the stability of the complexes with morin. The peak currents obtained with the AdSV technique are higher than those obtained with the ASV technique.
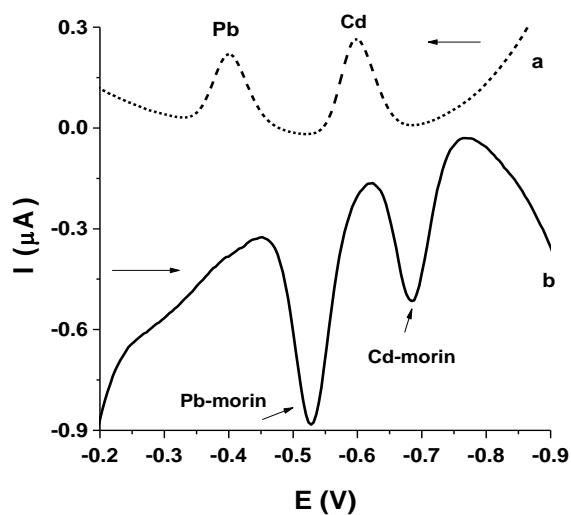

Figure 5. Anodic (curve a) and adsorptive (curve b) stripping voltammograms at pH 2.9. Conditions: Pb(II), Cd(II) 4.9 μgL^{-1}; C_{morin}: 0.8 $\mu mol\ L^{-1}$; E_{ads}: −0.2 V; E_{dep}: −1.0 V; t_{ads}: 60 s. Other conditions as Fig. in 1.

3.6. Effect of morin concentration (C$_{morin}$)

Figure 6 shows the effect of the variation of C$_{morin}$ on the peak current of Pb(II) and Cd(II) at pH 2.9. The experimental conditions were: Pb(II), Cd(II) 4.9 µg L^{-1}; E$_{ads}$ = −0.2 V and t$_{ads}$ = 60 s. The peak current increased with increasing C$_{morin}$ up to 1.1 µmol L^{-1} for Pb(II) (M:L ratio 1:48) and Cd(II) (M:L ratio 1:26). At concentrations higher than 1.8 µmol L^{-1} the peak current decreased slightly with increasing concentration of free morin, probably due to the competition of morin with complexes for adsorption on the electrode. An optimum ligand concentration of 1.1 µmol L^{-1} was used for further experiments, however with the real samples a higher concentration of morin could be necessary.
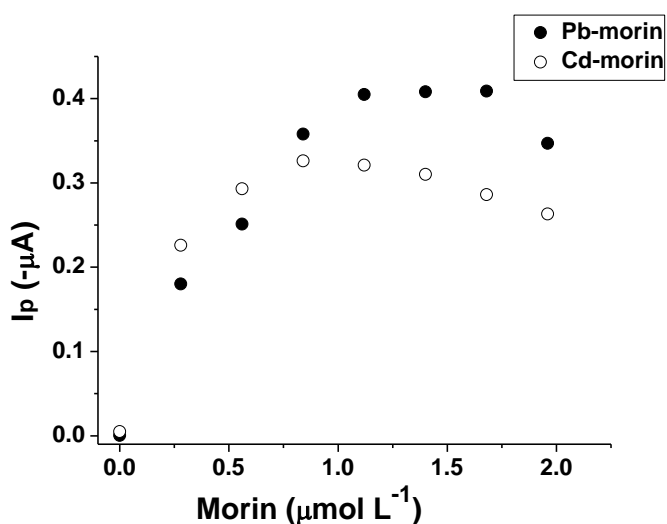
Figure 6. Effect of morin concentration on the peak current at pH 2.9. Conditions: Pb(II), Cd(II) 4.9 µg L^{-1}; t$_{ads}$: 60 s; E$_{ads}$: −0.2 V. Others conditions as in Fig. 1.

3.7. Effect of accumulation potential (E$_{ads}$)
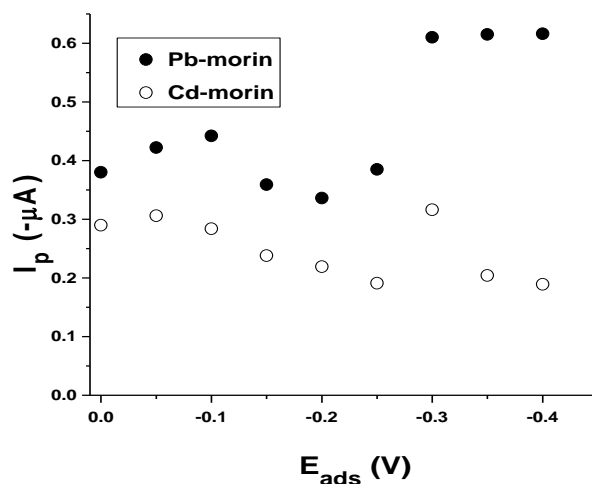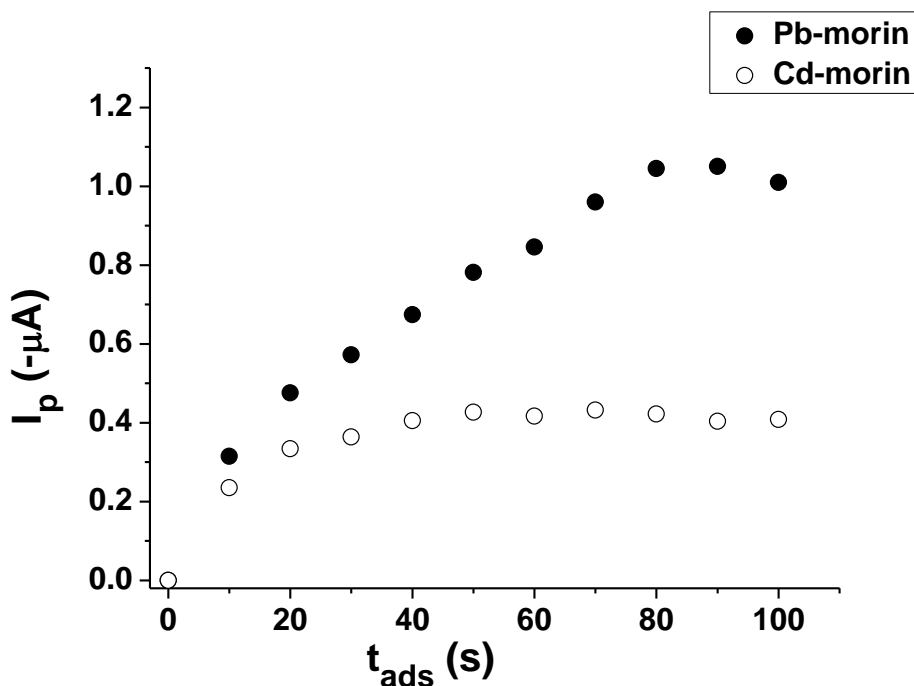

Figure 7. Effect of accumulation potential on the peak current at pH 2.9. Conditions: Pb(II), Cd(II) 4.9 µgL^{-1}; C$_{morin}$: 1.1 µmol L^{-1}; t$_{ads}$: 60 s. Others conditions as in Fig. 1.

The effect of the accumulation potential on the stripping peak current of the Pb–morin and Cd–morin complexes at pH 2.9 were studied from 0.0 to –0.4 V range. The experimental conditions were: Pb(II), Cd(II) 4.9 µg L^{-1}; C$_{morin}$: 1.1 µmol L^{-1} and t$_{ads}$ = 60 s. As shown in Fig. 7, the peak current of the complexes decreases when the potential is changed from –0.10 to –0.25 V, and then the peak current of Pb–morin complex increases whereas that of Cd–morin complex is maintained almost constant. The experimental electrocapillary curve shows that the mercury electrode surface has a negative excess charge at more negative potentials of $\approx$ –0.58 V and it can cause repulsion with the Cd(II)–morin complex [Cd(morin)$_2$]$^-$. An accumulation potential of −0.3 V gives the best sensitivity and was selected for further measurements with both complexes.

3.8. Effect of accumulation time (t$_{ads}$)

Figure 8 shows the effect of accumulation time on the stripping peak current of the Pb–morin and Cd–morin complexes at pH 2.9, over the 0–100 s range. The experimental conditions were: Pb(II), Cd(II) 4.9 µgL^{-1}; C$_{morin}$ = 1.1 µmol L^{-1} and E$_{ads}$ = –0.3 V. Peak current increases with increasing accumulation prior to the potential scan, indicating that the Pb(II) and Cd(II) complexes are readily adsorbed on the modified electrode surface. Peak current of Pb–morin complex increased with time up to 80 s, whereas peak current of Cd–morin complex is almost constant. Considering the speed of the measurement, a t$_{ads}$ of 60 s was used for further studies, but in the analysis of real samples higher times can be used to achieve good sensitivity.

**Figure 8**. Effect of accumulation time on the peak current of Pb(II) and Cd(II) complexes at pH 2.9. Conditions: Pb(II), Cd(II) 4.9 µgL^{-1}; C$_{morin}$: 1.1 µmol L^{-1}; E$_{ads}$: –0.3 V. Others conditions as in Fig. 1.

3.9. Effect of instrumental variables (frequency, step potential and amplitude)

The peak current of the Pb–morin and Cd–morin complexes increased as the frequency increased from 10 to 30 Hz. However, at frequencies of 30 Hz there was a deterioration of the peak shape and the background, so 25 Hz was adopted as optimum. Peak current increased linearly with step potential variations from 1 to 10 mV and pulse amplitude from 5 to 20 mV, so 10 mV and 15 mV were adopted as optimum for step potential and pulse amplitude, respectively

3.10. Analytical parameters

The calibration graphs for the simultaneous determination of Pb(II) and Cd(II) were obtained under the optimized conditions: pH 2.9; (200 μL of 0.4 mol L^{-1} BR buffer); C_{morin} 1.1 μmol L^{-1}; E_{ads} − 0.3 V; t_{ads} 60 s. The peak currents of Pb–morin and Cd–morin increased proportionally with increasing concentration between 0.97–16.0 μg L^{-1} for Pb(II) and Cd(II). However, when the concentration was up to 20 μg L^{-1} the peak current was almost constant probably due to saturation of the surface electrode. The limits of detection (3σ) were 0.12 and 0.13 μg L^{-1} for Pb(II) and Cd(II), respectively. The relative standard deviations were 3.0 and 2.0 % at the 4.9 μg L^{-1} level of Pb(II) and Cd(II) with 60 s of accumulation (n=7). Figure 9 shows the adsorptive voltammograms and the calibration curve. Similar detection limits for Pb(II) and Cd(II) (0.12 and 0.11 μg L^{-1}) with ASV were obtained for Wu et al [39], who used a carbon paste electrode modified with bismuth and octylpyridinium hexafluorophosphate. In our work the peak currents obtained with the AdSV technique are higher than those obtained with the ASV technique.
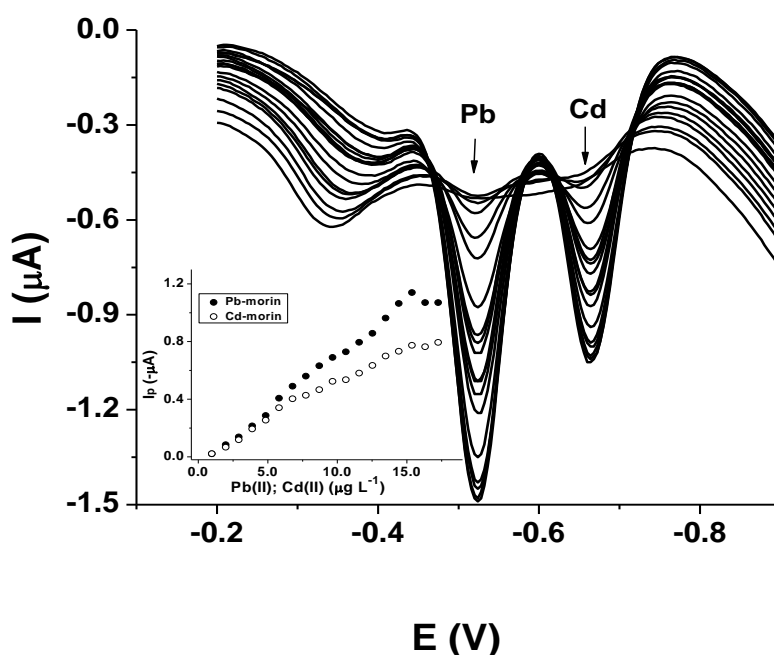
Figure 9. Adsorptive voltammograms and calibration curve at pH 2.9. Conditions: C_{morin}: 1.1 μmol L^{-1}; E_{ads}: –0.3 V; t_{ads}: 60 s. Other conditions as in Fig. 1.

3.11. Interference studies and validation of the method

The present method was validated by analysis of Pb(II) and Cd(II) in certified reference waste water (SPS–WW1) containing 0.10 mg L^{-1} of Pb and 0.02 mg L^{-1} of Cd. This analysis was carried out with 10.0 mL of deionized water, 1.4 mL of sample, 0.5 mL of BR buffer (0.4 mol L^{-1}) and 100 µL of morin (0.25 mmol L^{-1}. t_{ads}: 60 s; E_{ads}: –0.3 V). The value obtained for Pb(II) was 9.9 ± 0.2 µg L^{-1} (real value 11.7 µg L^{-1}. –15,4 % RE) and for Cd(II) was 2.2 ± 0.1 µgL^{-1} (real value 2.3 µg L^{-1}. –4,3 % RE). The plot was linear up to 50.0 and 10 µg L^{-1} for Pb(II) and Cd(II), respectively. The usefulness of the present method was also evaluated by analysis of Pb(II) and Cd(II) with a certified water less contaminated: TMDA–61 containing 61.4 µg L^{-1} of Pb and 58 µgL^{-1} of Cd. The experimental conditions were: 10.0 mL of deionized water, 400 µL of sample, 0.5 mL of BR buffer (0.4 mol L^{-1}) and 100 µL of morin (0.3 mmol L^{-1}. t_{ads}: 60 s; E_{ads}: –0.3 V). The value obtained for Pb(II) was 2.3 ± 0.1 µg L^{-1} (real value 2.2 µg L^{-1}. 4.5 % RE) and for Cd(II) was 2.0 ± 0.1 µgL^{-1} (real value 2.1 µg L^{-1}. –4,8 % RE). Three replicate analyses were performed for each sample. In these analyses morin concentration was higher than the optimized value (2.0 instead 1.1 µmol L^{-1}) because the certified samples contained many metal ions that form complexes with morin.

3.12. Analysis of Pb(II) and Cd(II) in tap water

The proposed method was applied to the determination of Pb(II) and Cd(II) in domestic tap water previously digested with UV radiation in the presence of H_2O_2 solution. Pb(II) concentration was 7.0 ± 0.3 µg L^{-1} and Cd(II) was not detected (five samples). To check the reliability of the method the samples were analyzed by ICP–AES. However, the results obtained with this technique were below 10 µg L^{-1}, which is the detection limit of this procedure.

4. CONCLUSIONS

The simultaneous determination of Pb(II) and Cd(II) was carried out by forming Pb–morin and Cd–morin complexes which are adsorbed on Nafion–ionic liquid–mercury glassy carbon electrodes (NHgFE). Normally the Pb(II) and Cd(II) determination reported were carried out by ASV. However, with our system the peak currents obtained with AdSV technique are higher than those obtained with ASV technique. We demonstrate that the sensitivity of this novel electrode is improved dramatically in the presence of [EMIM]F_3MSO_3. This reveals some advantages of ionic liquids, which increase the accumulation of the complexes in the working electrode and/or increase the peak current on the stripping step due their conductivity and fast electron transfer.

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