Ex Situ Poly(3,4-ethylenedioxythiophene)-sodium Dodecyl Sulfate-Antimony Film Electrode for Anodic Stripping Voltammetry Determination of Lead and Cadmium.

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A poly(3,4-ethylenedioxythiophene)-sodium dodecyl sulfate coated antimony film electrode PEDOT-SDS-SbFE was prepared ex situ and applied to determine Pb(II) and Cd(II) by anodic stripping voltammetry (ASV). The PEDOT-SDS-SbFE exhibited well developed signals for the oxidation of Pb and Cd at −0.12 and −0.40 V respectively, with higher current compared to unmodified electrodes. The optimum parameters for PEDOT-SDS-SbFE preparation consisted in an EDOT 0.01 mol L^{-1} in KCl 0.1 mol L^{-1} with SDS 1.0 x 10^{-3} mol L^{-1} solution at scanning rate of 50 mVs^{-1} (10 cycles -0.1 a 1.6 V), 200 mg L^{-1} Sb(III) in 0.5 mol L^{-1} HCl at −1.2 V (150 s) and for the determination of Pb(II) and Cd(II) were pH = 4.0 (acetate buffer); Eacc = −1.0 V and tacc = 60 s. The electrode showed good linear behavior in concentration range from 4.5 to 140.0 μg L^{-1} for both metal ions. The limit of detection (3σ) was 0.50 and 0.80 μg L^{-1} for Pb(II) and Cd(II) respectively. The RSD for a Pb(II) a Cd(II) 47.0 μg L^{-1} was 1.5% for seven successive assays. The method was validated using model solutions with satisfactory results. The method was applied to the determination of Pb(II) and Cd(II) in commercial mineral water and river water samples.

1. INTRODUCTION

Heavy metals like lead and cadmium are toxic, are and not biodegradable, staying in ecological systems and in the food chain indefinitely, exposing predators first order in the chain to high levels of pollution [1]. The Agency for Toxic Substances and Disease Registry (ATSDR) classified lead and

cadmium among the ten most dangerous pollutants [2]. In recent years, the number of published work relating to new electroanalytical methodologies used to quantify heavy metals it has increased considerably. These reports generally are motivated entirely by the same argument, the need to develop sensitive methods necessary for determination of lead and cadmium.

Some techniques used to quantify ions metals are atomic absorption spectrometry (AAS) [3], optical emission spectrometry (OES) [4] and Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) [5]. Although these techniques provide excellent sensitivity, they need large and expensive instruments and maintenance costs [6]. On the other hand, stripping voltammetry techniques have been widely used to determine Pb and Cd, proving to be highly sensitive, reproducible and with a low cost of operation and instrumentation [7, 8]. These techniques have the advantage of allowing the use of electrodes chemically modified. This should have a reproducible and constant area, in order to improve sensitivity and selectivity. The most used supports are glassy carbon and carbon paste. These supports have been modified to quantify Pb(II) and Cd(II) using either mercury film [9], bismuth film [10] or antimony film [11-12]. with reported detection limits between 0.2 and 1.0 μgL^{-1} for Pb(II) and between 0.5 and 2.0 μgL-1 for Cd(II). Esteban et al., have reported all metal ions that have been studied antimony film electrode using AVS [13].

Polymers obtained electrochemically on the surface of a working electrode have properties that enhance the conductivity, selectivity and sensitivity of the sensors. This is mainly due to the formation of thin uniform film with a large active surface area. Moreover, the film can be deposited into small and selected areas, maintaining a uniform geometry [14]. Some polymers reported for the determination of Pb(II) and Cd(II) are poly-aniline [15, 16], Nafion [17], Poly-styrene [15] and p-amino benzene sulphonic acid [18], with detection limits below 10 μgL^{-1}.

In the above context, the interest for PEDOT has increased, because its high surface area and conductivity. PEDOT has been used for the development of biosensors [19], electrochemical determination of hydroquinone and catechol [20], cytochrome [21], acetaminophen [22], diethylstilbestrol [23], Glucose [24] and dopamine [25]. In addition, the research with PEDOT to determine the lead and cadmium have proved to be sensitive and is an evidence of that their properties allow monitoring of Pb(II) and Cd(II) in modified electrodes [14, 26, 34, 35]. The aim of this work was the development of a mercury-free electrochemical sensor suitable for the determination of lead and cadmium in water samples using a PEDOT-SDS-SbE.

2. EXPERIMENTAL

2.1. Chemicals and reagents

Standard solutions of Cd(II) and Pb(II) were prepared by diluting commercial standards containing 1000 mg L^{-1}, Merck (Darmstadt, Germany). Water used for dilution of the standard, reagents and preparation of samples was obtained with a Milli-Q system (18.2 MΩ.cm. Millipore USA). EDOT and SDS were purchased from Aldrich (Milwaukee, USA). All other chemicals such as nitric acid, hydrochloric acid, acetic acid, ethanol, methanol, KCl etc. were analytical grade from

Merck. Buffer acetate solution (AcBS) 0.1 mol L^{-1} was prepared from CH_3COOH/CH_3COO^- and phosphate buffer solution (PBS) was prepared from $H_3PO_4/H_2PO_4^-$ adjusting to the required pH with NaOH solution. A reference water model for trace elements containing Cd, Cu, Fe, Cr, Pb, Zn and Ni 100 μg L^{-1} was used for interferences studies.

2.2. Instrumentation

The voltammograms were obtained on a Dropssens μStat400 bipotentiostat/galvanostat, using 3-mm diameter glassy carbon electrodes. The reference electrode was Ag/AgCl/KCl 3 mol L^{-1} and the auxiliary electrode was platinum wire. pH was measured with an Ohaus ST3100-F

2.3. Preparation of PEDOT-SDS coated antimony film electrode (PEDOT-SDS-SbFE)

Before measurements, the glassy carbon electrode was polished using a polishing pad with 0.05 μm Al_2O_3 slurry, rinsed with 0.3 mol L^{-1} HNO_3 and water 5 min. The electrode was placed in 10 mL of EDOT (0.01 mol L^{-1}/KCl 0.1 mol L^{-1}-SDS 3 mmolL^{-1}). The modified electrode PEDOT/SDS was prepared electrochemically as reported earlier [26], but with small changes. Deposition of polymer films on GCE by the electro-oxidation of EDOT in 0.1 M buffer phosphate pH 4.0 medium was carried out by applying the potential i of −0.3 V to +1.6 V (vs. SCE) at the scan rate of 50 mVs^{-1}. Growth of the film was controlled with the number of cycles. The PEDOT-SDS coated glassy carbon electrode modified with antimony was prepared ex situ [11]. The electrode was immersed in an electroanalytical cell containing the plating solution of Sb(III) (200 mg L^{-1}) in 0.5 mol L^{-1} HCl, and the antimony film was formed by holding the working electrode potential at −1.20 V for 150 s. The same electrode was used in a series of measurements. No deaeration of the solutions was applied in this study. The PEDOT-SDS electrode preparation is showed in figure 1.
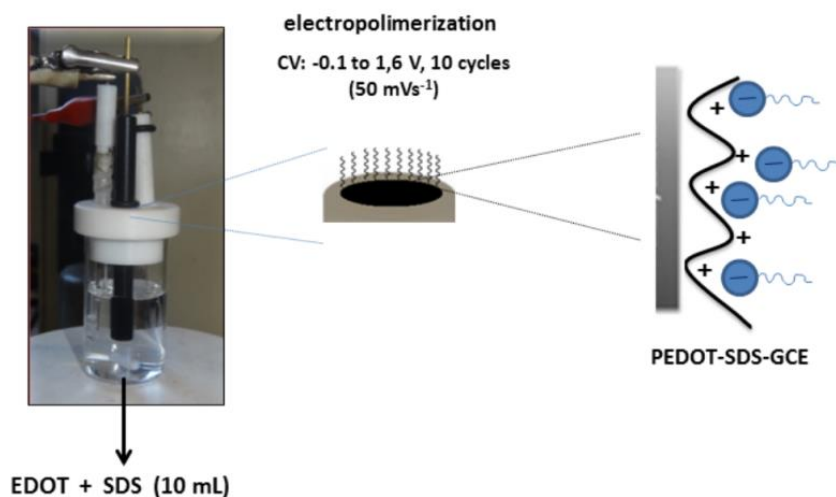

Figure 1. Preparation the modified electrode

2.4. Sample preparation

Commercial mineral water was purchased in a supermarket. Five river water samples from the river surface were collected in February 20, 2016 at three points of the Ambala river, which is close to Ibagué University (Ibagué, Colombia). The samples were collected in high-density polyethylene bottles which had been acid-washed and rinsed with Milli-Q water. The collected river water samples were filtered through a polycarbonate 0.45 μm membrane filter and stored frozen until analysis. Before the analysis, all the samples were digested with H_2SO_4 for 90 min at 90 °C in the presence of H_2O_2 to decompose organic substances.

2.5. Voltammetric procedure

Deionized water (10 mL) (or water samples), 200-μL of acetate buffer solution (0.1 mol L^{-1}) and aliquots (10-20 μL) of Pb(II) and Cd(II) solutions (5.0 mg L^{-1}) were pipetted into the voltammetric cell. Then, the pre-concentration step was initiated for a given tacc and Eacc at a stirring speed of 500 rpm. After an equilibration time of 3 s, anodic voltammograms were recorded, while the potential was scanned from −1.0 to 0.2 V using square wave modulation with 10 mV step amplitude, 100 mV pulse amplitude and a frequency of 20 Hz. Each voltammogram was repeated three times. The calibration curves were obtained and linear regression and detection limits (LoD) were calculated. The LoD was calculated from $y_{DL} = a + 3S_{x/y}$ and $y_{DL} = a + bx_{DL}$, where a is the intercept, $S_{x/y}$ is the random error in x and y, and b is the slope [27]. The modified electrode was applied to the determination of Pb(II) and Cd(II) in commercial mineral water and river 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 PEDOT-SDS modified electrode.

Electro-polymerizing of monomer in the presence and absence of SDS was done and studied using hydroquinone as a model solution. Fig. 2 shows the cyclic voltammograms of hydroquinone (HQ) (0.01mol L^{-1}) in acetate buffer solution (AcBS) at pH 4.0 (0.1 mol L^{-1}), using an glassy carbon electrode (GCE, curve a), PEDOT coated glassy carbon electrode (PEDOT-GCE, curve b) and a PEDOT-SDS coated glassy carbon (PEDOT-SDS-GCE, curve c). With the electrode without PEDOT and SDS (curve a) the redox peak of HQ reaction ($C_6O_2H_2 \rightarrow C_6O_2^{2-} + H_2^+ + 2e^-$) [20] at 1.05 V anodic current and 0.266 V cathodic current were seen clearly, whereas with the PEDOT-GCE (curve b) the peak currents decreased almost 90%. The electron transfer was affected by the polymeric film. PEDOT on the electrode surface possibly acts as a screen that blocks electron transfer of organic molecules. Two well-developed peaks appear with the PEDOT-SDS-GCE (curve c). Although the oxidation current is slightly lower compared with the electrode unmodified (curve a), is evident the SDS effects. SDS is below micellar concentration and this allows be a medium more organized for

EDOT electro-polymerization [28]. It is possible that the SDS remains immersed in the polymer chain through EDOT positive charge and the negative side of the SDS group head allowing charge transfer.
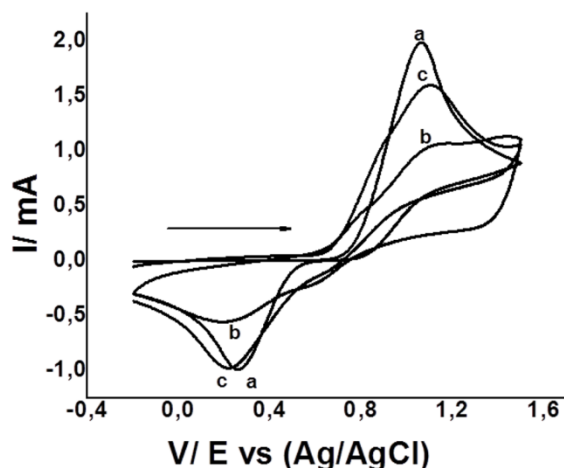

Figure 2. Cyclic voltammograms of GCE (a), GC-PEDOT modified electrode (b) and GC-PEDOT-SDS (c) modified electrode in AcBS pH 4.0 containing 0.01 mol L^{-1} HQ. Scan rate: 0.1 mVs^{-1}.

3.2. Characterization of the PEDOT-SDS-SbF modified electrode

The electroanalytical performance of the PEDOT-SDS-SbF modified electrode was examined using Cd(II) and Pb(II) as model ions. Fig. 3 shows the square wave anodic voltammograms of Pb(II) and Cd(II) (47.0 µg L^{-1}) in AcBS pH 4.0 (0.002 mol L^{-1}), using a glassy carbon electrode (GCE, dash line) PEDOT-SDS coated glassy carbon electrode (PEDOT-SDS-GCE, dot line), PEDOT-coated antimony film electrode (PEDOT-SbFE, dash-dot line) and PEDOT-SDS-coated antimony film electrode (PEDOT-SDS-SbFE, solid line). With the GC electrode two signal of Pb(II) at −0.11 V and Cd at -0.32 V were seen, whereas with the PEDOT-SDS and PEDOT-SbF electrodes one well-developed stripping peak at −0.39 for Cd(II) was observed whereas a less-developed stripping peak at -0.11 V for Pb(II) was observed. On the other hand, on a PEDOT-SDS-SbFE, showed two best and well-developed stripping peaks at −0.39 V and -0.12 for Cd(II) and Pb(II), respectively. With respect to the position of the signals, Hocevar et al. and Arancibia et al., [11-29] reported values of −0.53; -0.73 V for Pb (II) and -0.78; -0.92 V for Cd(II), respectively, using antimony film. Yasri et al., [35] reported value of -0.36 V for Pb(II) using PEDOT. In our measurements the oxidation potentials were more positive because the desorption of Cd and Pb requires more energy. Probably, Cd (II) and Pb (II) Disseminates more internally in the crystal structure of Sb film. Moreover, presence of SDS improvement the electron transfers. The ex situ prepared PEDOT-SDS-SbFE revealed higher sensitivity for Pb(II) and Cd(II).
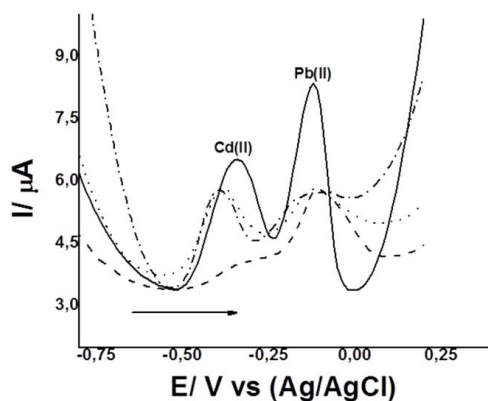
Figure 3. Square wave anodic stripping voltammograms of Pb(II) and Cd(II) (47.0 µg L^{-1}) using a glassy carbon electrode (GCE, dash line) PEDOT-SDS coated glassy carbon electrode (PEDOT-SDS-GCE, dot line), PEDOT-coated antimony film electrode (PEDOT-SbFE, dash-dot line) and PEDOT-SDS-coated antimony film electrode (PEDOT-SDS-SbFE, solid line). Conditions: AcBS pH 4.0; Eacc: −1.0 V; tacc: 60 s. step amplitude: 10 mV; pulse amplitude: 100 mV, and frequency: 20 Hz.

3.3. Effect of EDOT, SDS and Sb(III) concentration and electrolysis time.

Important parameters that influence the quality and thickness of the PEDOT-SDS and antimony film are the concentration and electrolysis time of EDOT, SDS and Sb(III). Deposition of poly-EDOT-SDS films on GCE by electro-oxidation of EDOT in buffer phosphate 0.1 mol L^{-1} pH 6.0 medium was carried out by electro-deposited. The potential range of −0.3 V to +1.6 V (vs. SCE), scan rate of 50 mVs^{-1}. The growth of the film was controlled with the number of cycles. The EDOT and SDS concentration and number of cycles were was examined using a solution containing 24.0 µg L^{-1} of Pb(II) and Cd(II), and pH 4.0 (acetate buffer) (Eacc = −1.0 V, tacc = 60 s) (not shown). The effect of accumulation time on the peak current of Pb(II) and Cd(II) increased up to10 cycles and then decreased sharply for higher cycles. With respect to the numbers cycles, Manisankar et al. [30] report 15 cycles with 0.1 µm thick the films. In our measurements 15 cycles decreased the peak current of Pb(II) and Cd(II). Thick films less 0.1 µm (10 cycles) was chosen as the optimum. The plating potential, and the time used for the electrode preparation. Sb(III) concentration were varied in the 50–200 mg L−1 range (0.5 mol L^{-1} HCl; Edep = −1.20 V; tdep = 150 s) and the effect was examined using a solution containing 47 µg L^{-1} of Pb(II) and Cd(II), and pH 4.0 (acetate buffer) (Eacc = −1.0 V, tacc = 60 s) (not shown). Increasing concentration of Sb(III) (200 mg L^{-1}) in the solution, the peaks currents of Pb(II) and Cd(II) increased compared with lower concentrations . Therefore, the optimum Sb(III) concentration was 200 mg L^{-1}. On the other hand, the effect of accumulation time on the peak current of Pb(II) and Cd(II) was studied between 50 to 150 s. On the basis of this study, we decided to use a deposition time of 150 s in all further electrode preparations. The *ex situ* prepared PEDOT-SDS-SbFE revealed higher sensitivity for Pb(II) and Cd(II) with EDOT 10 mmol L^{-1} and SDS 1.0 mmol L^{-1}. Similar works report same concentrations [30]. *In-situ* preparation of antimony film, Hoceval et al., reported 1.0 mg L-1 of Sb(III) [11]. In our measurements we used 200 times more, but 100 mL of antimony solution was used for all the full study

3.4. Effect of operational parameters

3.4.1. Influence of pH

The electrochemical oxidation of the reduced Pb(II) and Cd(II) deposited   on the PEDOT-SDS coated antimony film electrode was studied in acid phosphate/phosphate and acetic acid/acetate solutions in the 2.0–5.0 pH range, as depicted in Fig. 4. The experimental conditions were: Pb(II), Cd(II) 47.0 µg L^{-1}; Eacc = −1.0 V and tacc = 60 s. The peak potentials of the Pb(II) and Cd(II) shifted toward more positive values with increasing pH, and maximum peak current was obtained at pH 4.0 for both metal ions. With respect to the pH value,   Manisankar et al. report similar pH value [26]. Formation of metal hydroxide complexes can decrease the peak current at pH values higher of 4.0 [31].

3.4.2. Effect of accumulation potential (Eacc)

The effect of the accumulative potential on the anodic stripping peak current of the Pb(II) and Cd(II) were studied in the -0.7 to −1.2 V range. The experimental conditions were: Pb(II), Cd(II) 47.0 µg L^{-1}; pH 4.0 (AcBS) and tacc = 60 s. (Fig. not shown). The peak current increases when the potential is changed from −0.7 to −1.0 V, and at more negative values it decreased sharply. An anodic potential of −1.0 V gives the best sensitivity and was selected for further measurements.
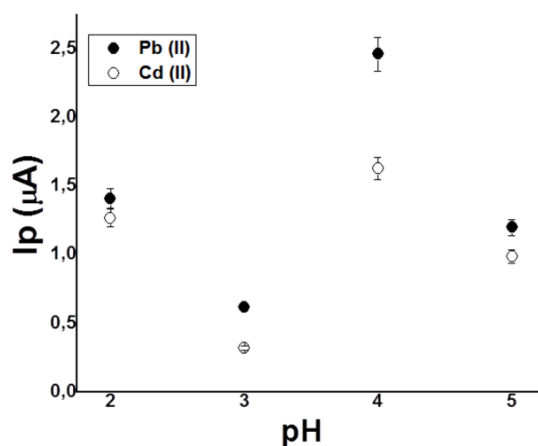

Figure 4. Effect of pH on the peak current of the Pb(II) and Cd(II) . Conditions: Pb(II), Cd(II) 47 µg L^{-1}; Eacc: −1.0 V; tacc: 60 s. Other conditions as in Fig. 3.

3.4.3. Effect of accumulative time (tacc)

The effect of accumulation time (tacc) was examined in the 10–80 s range. The experimental conditions were: Pb(II), Cd(II) 47.0 µg L^{-1}; pH 4.0 (AcBS) and Eacc = −1.0 V. As seen in Fig. 5, initially, after 10 s the peak current increase only to Pb(II), but after 20 s increases both for Pb (II) and Cd (II). However, when accumulative times were over 60 s, the peaks heights decreased slightly and

then reached a constant value, Hocevar et al., reports 120 s accumulative times [11]. Possibly due to the saturation of the antimony film surface, the modified electrode needed less accumulation time. On the basis of this study, we decided to use an accumulation time of 60 s for all further measurements.
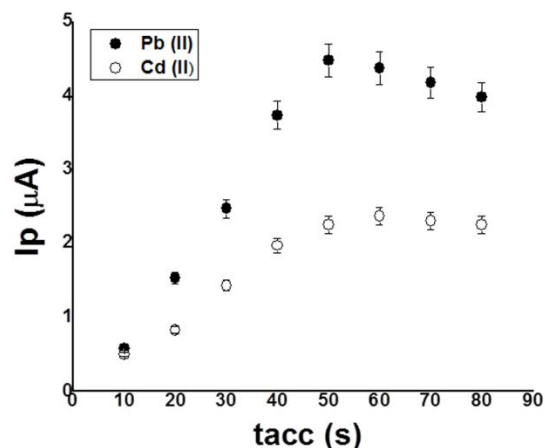

Figure 5. Effect of tacc on the peak current of the Pb(II) and Cd(II). Conditions: Pb(II), Cd(II): 47.0 µg L^{-1}; AcBS pH 4.0 ; Eads: −1.0 V. Others conditions as in Fig. 3.

3.4.4. Effect of frequency, step potential and pulse amplitude

Peaks currents of Pb (II) and Cd(II) increased at frequency to 20 Hz, step potential to 10 mV and pulse amplitude to 100 mV. With respect to step potential and pulse amplitude, values of 10 and 100 mV, respectively, were chosen as the optimum.

3.5. Analytical performance of PEDOT-SDS-SbFE

The best conditions related to the sensitivity were: pH 4.0 (200-µL AcBS 0.1 mol L^{-1}), an Eacc of −1.0 V, and a tacc of 60 s. Anodic stripping voltammograms with the corresponding calibration plots (insets) are presented in Fig. 6. Two well-developed and separate peaks at −0.19 and −0.40 V for Pb(II) and Cd(II), respectively, were seen, and the calibration plots exhibited good linearity with increasing concentration between 4.5 and 140.0 µg L^{-1}, with LoDs (3σ) of 0.50 and 0.80 µg L^{-1} for Pb(II) and Cd(II), respectively. The calibration curves and correlation coefficients were y = −0.1334 + 0.01716x, r = 0.9976 and y = 0.2014 + 0.01341x, r = 0.9971 for Pb(II) and Cd(II), respectively (n = 12). However, when the concentration was about 140.0 µg L^{-1} the peak current of the Pb(II) and Cd(II) were almost constant. On the others hand, the peak current of the Pb(II) shifted to less negative potentials. relative standard deviations were 1.5% at the 10.0 µg L^{-1} level of Pb(II) and Cd(II) with 60 s of accumulation (n = 7). With respect to sensibility, Hocevar et al., and Estaban et al., reported values between 0.7 - 0.15 µg L^{-1} for Pb (II) and 0.9 - 0.3 µg L^{-1} for Cd(II), respectively [11-13] using antimony film on glassy carbon electrode . Moreover, Hocevar et al., reported values of 0.2 and 0.8

µg L^{-1} for Pb (II) and Cd(II), respectively [33], using antimony film on carbon paste. In our measurements the sensibility of Pb (II) and Cd (II) were equally satisfactory.
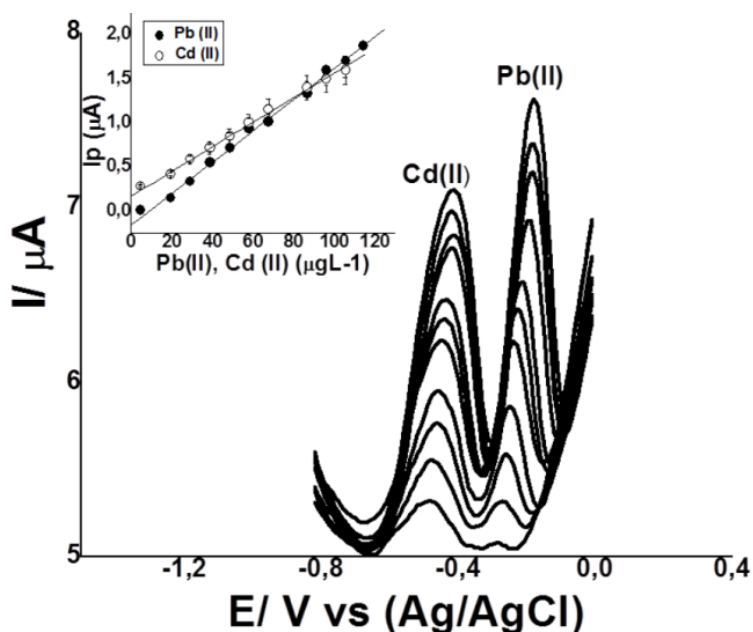

Figure 6. Square wave anodic stripping voltammograms and calibration curves (insert) by increasing concentrations of Pb(II) and Cd(II). (4.0 – 120 µgL^{-1}) Conditions: pH 4.0 (acetate buffer); Eacc: −1.0 V; tacc: 60 s. Other conditions as in Fig. 3.

3.6. Validation of the method and interference study.

The accuracy of the reported method was assessed by determining Pb(II) and Cd(II). Two samples were prepared in model solutions with ultrapure water for HPLC where added 25.0 µgL^{-1} of Pb(II) - Cd(II) and 9.7 µgL^{-1} of Pb(II) - Cd(II). This analysis was carried out with 9.0 mL of deionized water, 1 mL of sample, 200 µL of AcBS pH 4.0 (0.1 mol L^{-1}) . To quantify these metal ions contents the applied Eacc was −1.0 V during 60 s. The Pb(II) and Cd(II) concentrations in the sample were found to be 24.57 ± 0.5 and 30.91 ± 0.7 µg L^{-1} to Pb(II) and Cd(II) (−1.72% and 23.6% RE) and 10.59 ± 0.7 and 5.93 ± 0.6 µg L^{-1} to Pb(II) and Cd(II) (9.17% and 38.6% RE) respectively. Fig. 7 shows Anodic voltammograms together with the corresponding calibration plots (insets) to model solutions with 25.0 µgL^{-1} of Pb(II) and Cd(II). The values Pb(II) were satisfactory agreement. The values Cd(II) were less accurate. It is possible that the lead and cadmium have a competition in the accumulation time. The lead was reduced to less potential and allows its early accumulation. The interference study was performed by adding various metals cations such as Cu, Mo, Bi, Ni and Zn in 10 fold excess into a standard solution containing Pb (II) and Cd (II) 47 µg L^{-1}. None of these cations interferes with the signals of Pb (II) and Cd (II). Values are summarized in table 1.
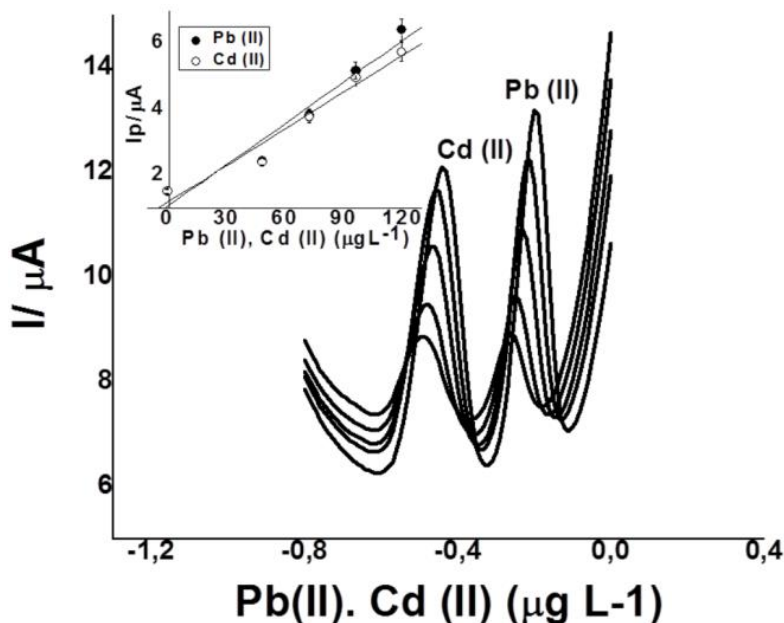
Figure 7. Square wave anodic stripping voltammograms and calibration curves (insert) with model solution of Pb(II) and Cd(II)   25.0 µgL^{-1}. Conditions: pH 4.0 (acetate buffer); Eacc: −1.0 V; tacc: 60 s. Other conditions as in Fig. 3.

Table 1. Summary of values detected for lead and cadmium.

Waters samples	Added (µg L^{-1})		Found (µg L^{-1})		% RE	
	Pb	*Cd*	*Pb*	*Cd*	*Pb*	*Cd*
Standard 1	25.0	25.0	24.57±0.5	30.91±0.7	-1.74	23.62
Standard 2	9.70	9.70	10.59±0.7	5.93±0.6	9.17	-38.6
River	-	-	-	0.98±0.1	-	-
Mineral	-	-	0.90±0.1	-	-	-

3.7. Analysis of Pb(II) and Cd(II) in river water and mineral water samples.

The proposed method was applied to the determination of Pb(II) and Cd(II) in river water and commercial mineral water previously digested. These analyses were carried out with 10.0 mL of water samples, 0.2 mL of AcBS pH 4.0 (0.1 mol L^{-1}) by standard addition method. . Samples were analyzed three times. The Cd(II) average content was 0.98 ± 0.1 in river water (Ambala, Fig. 8), Pb(II) was not detected,   possibly the lead concentration is lower than the detecting limit. The Pb(II) average content was   0.90 ± 0.2 µg L^{-1} in commercial mineral water, Cd(II) was not detected,   possibly the cadmium   concentration is lower than the detecting limit. However the levels are below the limit proposed by the EPA [32]. Values are summarized in table 1.
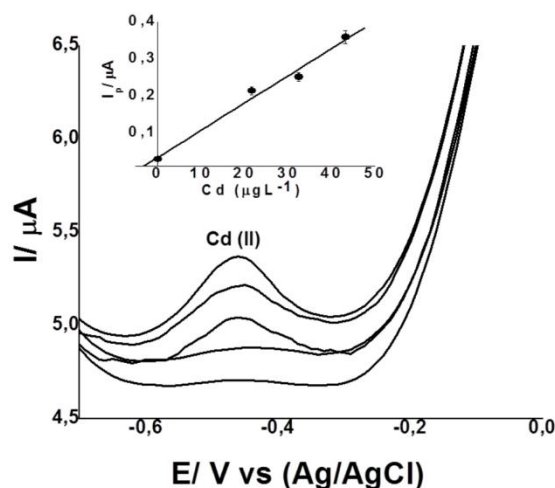
Figure 8. Square wave anodic stripping voltammograms of river water (Ambala) and calibration curve of Cd(II) (insert). Conditions: pH 4.0 (acetate buffer); Eacc: −1.0 V; tacc: 60 s. Other conditions as in Fig. 3.

4. CONCLUSIONS

The PEDOT-SDS-coated antimony film electrode was investigated for the first time in the anodic stripping voltammetry of Pb(II) and Cd(II), providing high sensitivity, selectivity, low limits of detection, and satisfactory repeatability. We clearly demonstrated that with PEDOT-SDS-SbF electrode deposited ex situ, is more sensitive than the PEDOT, PEDOT-SDS and PEDOT-SbF modified electrodes. The sensitivity improved dramatically with the cycles number, concentration of EDOT-SDS and Sb(III) concentration and the electrode position time used in the preparation of the electrode.

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