



Single and simultaneous voltammetric sensing of lead(II), cadmium(II) and zinc(II) using a bimetallic Hg-Bi supported on poly(1,2-diaminoanthraquinone)/glassy carbon modified electrode

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ABSTRACT

In this work, bimetallic film of mercury and bismuth (Hg-Bi) was incorporated with poly(1,2-diaminoanthraquinone)/glassy carbon electrode (PDAAQ/GC) using applied potential method. The obtained Hg-Bi/PDAAQ/GC electrode was characterized by square wave voltammetry (SWV), scanning electron microscope (SEM) and energy dispersive X-ray (EDX) techniques. The proposed electrode had been used as a highly sensitive sensor for both single and simultaneous determination of lead (Pb^{2+}), cadmium (Cd^{2+}) and zinc (Zn^{2+}) ions in acetate buffer solution by anodic stripping voltammetry (ASV). The adopted ASV method was achieved by optimizing different parameters such as metal deposition method (either *in-situ* or *ex-situ*), metals pre-concentration potential, pre-concentration time and different pH of values for acetate buffer solution. The prepared sensor provided a good reproducible response, high sensitivity with a linear range of 0.0–50.0 $\mu g/L$ for Cd^{2+} and Zn^{2+} with a low detection limit of 0.107 and 0.037 $\mu g/L$, respectively. The linear range of Pb^{2+} was 10.0–120.0 ng/L with a detection limit of 3.18 ng/L . Also, the sensor was used for the analysis of the analytes in water samples with satisfactory results in comparison with inductively coupled plasma – mass spectroscopy (ICP-MS).

1. Introduction

Heavy metal ions such as lead (Pb^{2+}), cadmium (Cd^{2+}) and zinc (Zn^{2+}) have been established a significant group for water contaminants. Traditional methods have been used to assess the magnitude of the environmental risk caused by heavy metal pollution, consists of chemical analysis and quantification of total metals using a classical methods such as atomic adsorption spectroscopy (AAS) [1–3] for individual determination, inductively coupled plasma- atomic emission spectroscopy (ICP-AES) [4] or mass spectroscopy (ICP-MS) [5] which has the ability for multi-elements analysis. These methods have the ability for determination of heavy metal ions in a low detection limit, but they have some limitations attributed to their high costs and the disability for using it in the field [6]. Electro-analytical methods have been widely used due to their economical cost, low detection limits either in part per billion (ppb) or in part per trillion (ppt) ranges in

some cases [7–9].

Coating of solid electrodes with conductive polymers incorporated or not with metal nanoparticles (NPs) improves their performances toward various applications. Modified electrodes present observable advantages in the water heavy metals determinations. Introducing specific binding groups such as thiol or cyano groups accelerate electron transfer rate at the electrode surface as well as increasing the efficiency of preconcentration [10–12]. In this field of environmental monitoring, the application of NPs as a functional probe for analyzing inorganic and organic pollutants in water has been extensively studied. NPs usually exhibit unique characteristics rather than bulk-sized materials, principally due to the electron confinement of the NPs [10–12].

For several decades, mercury (Hg) electrodes has been the most used working electrode for anodic stripping voltammetry (ASV) applications due to its wide cathodic ranges [13]. Also, Hg has the capability to produce amalgams with heavy metals. Bismuth (Bi) could also be

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plated due to its low toxicity and its ability to form alloys with several heavy metals [14,15].

Several modified electrodes either based on conductive polymers such as polyaniline [16], poly(1,5-diaminonaphthalene)/multi-walled carbon nanotube [17], poly(1,5-diaminonaphthalene)/graphene [18], graphene/polyaniline/polystyrene [19] and poly(1,2-diaminoanthraquinone) (PDAAQ) [20], combined both conductive polymer with bismuth such as Bi/polyaniline [21], Bi/Nafion/thiolated polyaniline [22], and Bi/poly(1,8-diaminonaphthalene) [23] or other Bi nanoparticles modified electrodes such as BiNP/NafionModifiedPGE [24], SPGE-BiNP-Nafion [25], BiNP/MWCNT/Nafion/G [26], and Bi-NCNF/GC [27] had been used for ASV of heavy metals. Moreover, preparation of bimetallic Hg-Bi modified electrode combining both the advantages of Hg and Bi increasing the sensitivity [28] and the affinity toward several metals reaching the lower detection limit compared with other published bismuth electrodes [29] or other thin films such as antimony [30], and gold [31].

In this article, determination of Pb^{2+} , Cd^{2+} and Zn^{2+} ions using ASV technique in acetate buffer solution (pH 5.3) was examined at PDAAQ/glassy carbon (PDAAQ/GC), bismuth/PDAAQ (Bi/PDAAQ/GC), mercury/PDAAQ/GC (Hg/PDAAQ/GC) and finally mercury-bismuth/PDAAQ/GC (Hg-Bi/PDAAQ/GC) modified electrodes. It is interesting for combining advantages of using bimetallic Hg-Bi and presence of conductive polymer (PDAAQ) which is characterized by its great affinity to chelate metal cations via its amino and carbonyl groups, making typical electrochemical sensor for both single and simultaneous heavy metal ions determinations.

2. Experimental

2.1. Reagents

The 1,2-DAAQ monomer, acetonitrile, lithium perchlorate ($LiClO_4$), 0.1 M acetate buffer ($CH_3COONa \cdot 3H_2O$, CH_3COOH) (NaAC/HAC), mercuric chloride ($HgCl_2$), bismuth nitrate pentahydrate ($Bi(NO_3)_3 \cdot 5H_2O$), lead nitrate ($Pb(NO_3)_2$), cadmium chloride hemipentahydrate ($CdCl_2 \cdot 3/2H_2O$), zinc sulphate heptahydrate ($ZnSO_4 \cdot 7H_2O$), sulfuric acid (H_2SO_4), alumina powder (0.05 μm) and potassium chloride (KCl 99.5%) of high purity purchased from Sigma Aldrich. Highly pure deionized water was used for reagent preparation as well as throughout experiments.

2.2. Instruments

Electrochemical measurements were carried out using an Epsilon-EC voltammetric analyzer instrument from BASi (USA). All voltammograms were achieved in a conventional three-electrode cell having a 3.0 mm diameter GC electrode as a working electrode, platinum wire as an auxiliary electrode and Ag/Ag⁺ or Ag/AgCl as a reference one. BRANDSTEAD SMART2PURE from Thermo Scientific Co. was used for deionized water. Scan electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDX) measurements were conducted at the National Research Center, Cairo, Egypt, using SEM model QUANTA FEG 250. Inductively coupled plasma – mass spectroscopy (ICP-MS) model NexION 300, PerkinElmer was used for real sample analysis.

2.3. Preparation of Hg-Bi/PDAAQ/GC modified electrodes

At first, GC electrode was polished with alumina paste using a polishing kit followed by rinsing with water to ensure removing any traces from the alumina. The polished electrode had been applied to a constant potential (+ 0.30 V) in 0.50 M H_2SO_4 solution for 5 min. The electrode was placed in acetonitrile containing 0.10 M $LiClO_4$ and 1.0 mM DAAQ monomer. Repetitive cyclic voltammetry (CV) had been applied in the potential range from +0.2 to +1.4 V at a sweep rate of 0.05 V/s for 5 cycles to prepare the modified electrode PDAAQ/GC

[20]. Then, PDAAQ/GC modified electrode was placed under stirring in a solution of 0.1 M NaAC/HAC (pH 4.5) containing 100 mg/L of a mixture of Hg and Bi salts (4: 1 by weight) for 4 min. The co-deposition of Hg and Bi was achieved at –1.0 V for two minutes with continuous stirring [28]. For single metal-electrode, Hg or Bi was deposited individually from 100 mg/L of each metal salt using the same manner followed for the co-deposition. For *in-situ* deposition, both Hg and Bi ions were presented in the solution together with Cd^{2+} , Pb^{2+} and Zn^{2+} ions, while for *ex-situ* deposition, Hg and Bi were deposited initially on PDAAQ/GC modified electrode, and then applied for anodic stripping of the target metal cations.

2.4. ASV of Pb^{2+} , Cd^{2+} and Zn^{2+}

The ASV was conducted in two steps in a solution of Pb^{2+} , Cd^{2+} and Zn^{2+} ions in 0.1 M NaAC/HAC (pH 5.3) containing 0.1 M KCl at Hg-Bi/PDAAQ/GC electrode. Ions preconcentration was achieved at –1.7 V for 5 min under magnetic stirring, followed by SWV at frequency 15 Hz, pulse height 25.0 mV and step height 4.0 mV applied with a potential limit from –1.7 V to –0.3 V. After each measurement, the electrode was cleaned at applied potential of - 0.30 V for 2 min in the same solution to assure the complete elimination of deposited Zn, Cd and Pb.

3. Results and discussion

3.1. Electrochemical characterization and morphology of Hg-Bi/PDAAQ/GC modified electrode

Square wave voltammetry (SWV) of Hg-Bi/PDAAQ/GC electrode recorded in NaAC/HAC buffer and 0.1 M KCl solution (pH 5.3) in the potential range from –1.30 to 1.00 V is displayed in Fig. 1A. It could be seen that Hg^{2+} and Bi^{3+} stripping were detected at peak potentials 0.20 and –0.15 V, respectively giving the potential window available for metal ions detection to be at lower potential between –0.15 and –1.30 V.

Since the electrochemical response of the modified electrode is related to its physical morphology, the surface topographies of Hg-Bi/PDAAQ/GC modified electrode was analyzed using SEM (Fig. 1B). The figure demonstrates the presence of Hg and Bi nanoparticles as small light-grey dots ranging from 159.0 to 308.7 nm. This was confirmed by EDX analysis (Fig. 1C) showing the presence of both Hg and Bi nanoparticles dispersed in PDAAQ film with a percent of 12.16% and 1.77%, respectively.

3.2. Simultaneous determination of Pb^{2+} , Cd^{2+} and Zn^{2+} ions at different electrodes

ASV is a well identified sensitive technique in electrochemistry for trace heavy metals detection. It consists of two steps for the determination of Pb^{2+} , Cd^{2+} and Zn^{2+} ions. First step; preconcentration of three metal ions at a pretested potential for a definite period of time. Second step; stripping of accumulated metals. Stripping peaks are used to observe their concentration in the solution. Determinations of Pb^{2+} , Cd^{2+} and Zn^{2+} ions had been examined at bare GC electrode, PDAAQ/GC, Hg-Bi/GC, Bi/PDAAQ/GC, Hg/PDAAQ/GC and Hg-Bi/PDAAQ/GC modified electrodes in NaAC/HAC buffer (pH 5.3) containing 0.1 M KCl. At GC electrode and after the preconcentration step (mentioned in the experimental section), stripping peak current responses of Pb^{2+} , Cd^{2+} and Zn^{2+} ions got relatively low anodic current values at –0.55 V, –0.76 V and –0.98 V, respectively (Fig. 2A, curve a). Only two peaks, at –0.42 V and –0.64 V due to Pb^{2+} and Cd^{2+} , respectively were observed at PDAAQ/GC (Fig. 2A, curve b). At Hg-Bi/GC modified electrode, three anodic peaks appeared at –0.52 V, –0.70 V and –1.13 V for Pb^{2+} , Cd^{2+} and Zn^{2+} , respectively with low anodic peak currents (Fig. 2A, curve c). Remarkably enhanced stripping peak

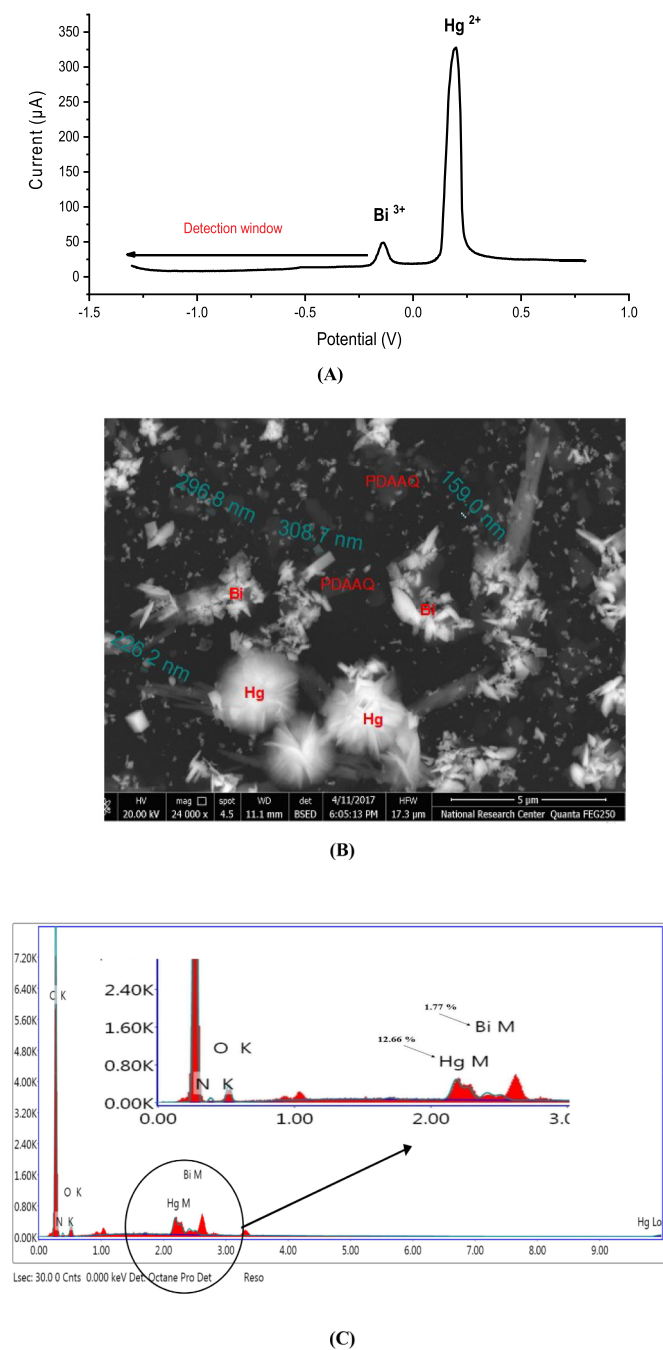


Fig. 1. (A) Square wave voltammetry of Hg-Bi/PDAAQ/GC electrode in NaAC/HAC buffer and 0.1 M KCl (pH 5.3), (B) SEM image of Hg-Bi/PDAAQ/GC and (C) EDX for the surface of Hg-Bi/PDAAQ/GC electrode.

currents were detected at Hg/PDAAQ/GC, Bi/PDAAQ/GC and Hg-Bi/PDAAQ/GC electrodes giving priority for the last one as indicated in Fig. 2B. Results showed that peak current values of Pb²⁺, Cd²⁺ and Zn²⁺ at Hg/PDAAQ/GC electrode were about 5.00, 4.90 and 6.70 times, respectively, as high as those obtained at GC electrode as presented in Fig. 2B curve a. At Bi/PDAAQ/GC electrode, peak current values were 2.54, 2.34 and 2.15 as higher as those detected at GC electrode for Pb²⁺, Cd²⁺ and Zn²⁺, respectively as shown in Fig. 2B curve b. On the other hand, Hg-Bi/PDAAQ/GC electrode improved peak current values about 6.80, 6.70 and 8.26 times for the three ions, respectively as compared with GC electrode (Fig. 2B curve b). The peak currents enhancement could be attributed to the high contact surface area, high electrical conductivity and the capability of metal double

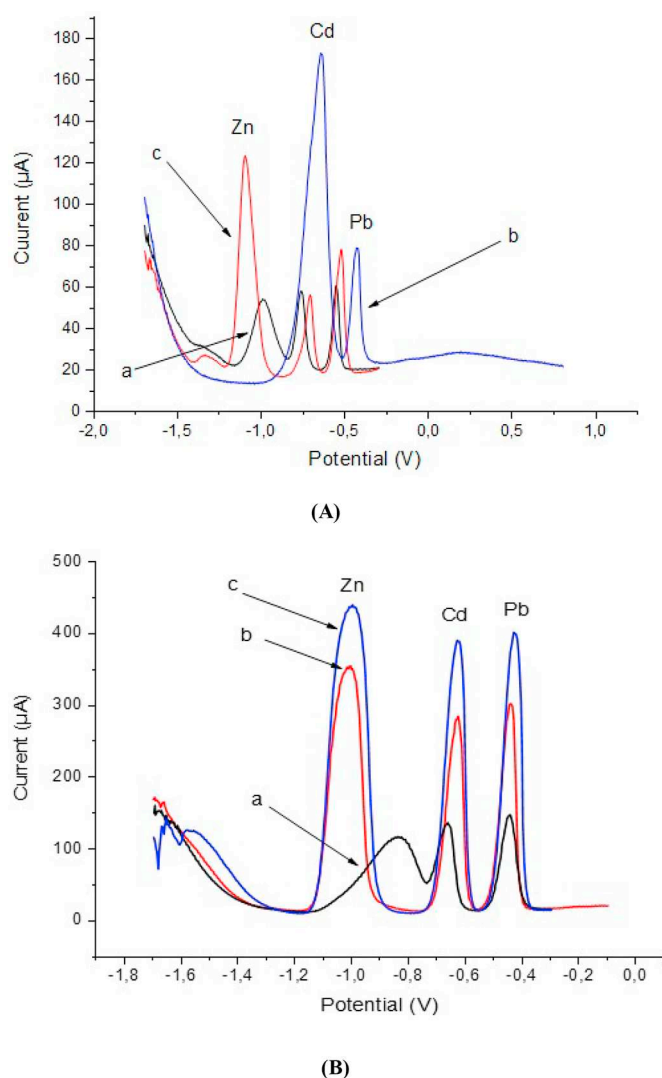


Fig. 2. Anodic stripping voltammograms of 100 μg/L Pb²⁺, Cd²⁺ and Zn²⁺ at: A) (a) bare GC, (b) PDAAQ/GC, (c) Hg-Bi/GC modified electrodes, and B) (a) Hg/PDAAQ/GC, (b) Bi/PDAAQ/GC, (c) Hg-Bi/PDAAQ/GC modified electrodes in 0.1 M NaAC/HAC buffer (pH 5.3) containing 0.1 M KCl (frequency 15 Hz, pulse height 25.0 mV and step height 4.0 mV).

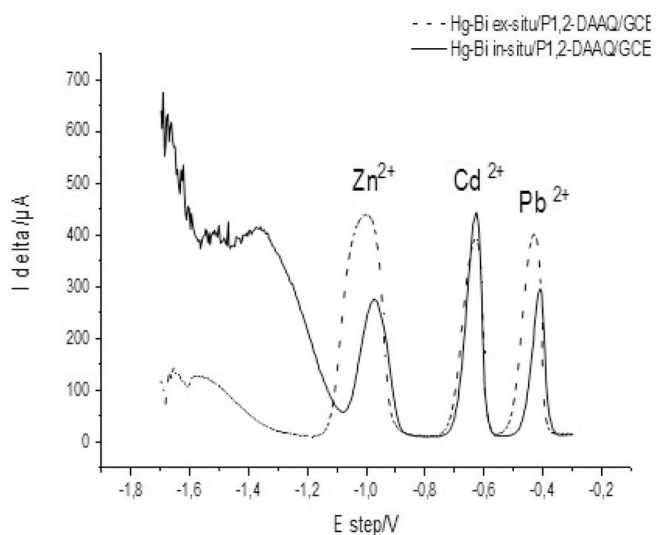
layer as well as the presence of PDAAQ film to chelate metal ions through amino and carbonyl groups in the polymer chain [20]. These results agreed with the obtained morphology results showing the role that metal nanoparticles play.

3.3. Optimization of analytical studies

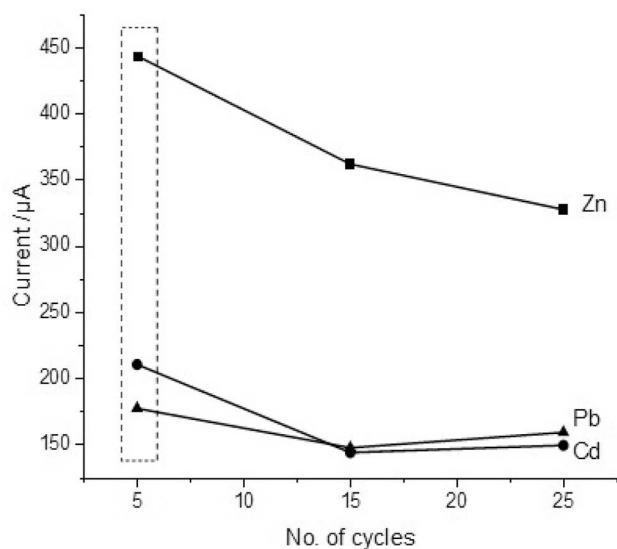
To achieve better voltammetric performance toward Pb²⁺, Cd²⁺ and Zn²⁺ detection, several parameters including methods of electrochemical deposition of bimetallic Hg-Bi film, thickness of PDAAQ film, metal preconcentration potential, preconcentration time and finally pH measurements of NaAC/HAC buffer were examined in details.

3.3.1. Method of electrochemical deposition of bimetallic Hg-Bi

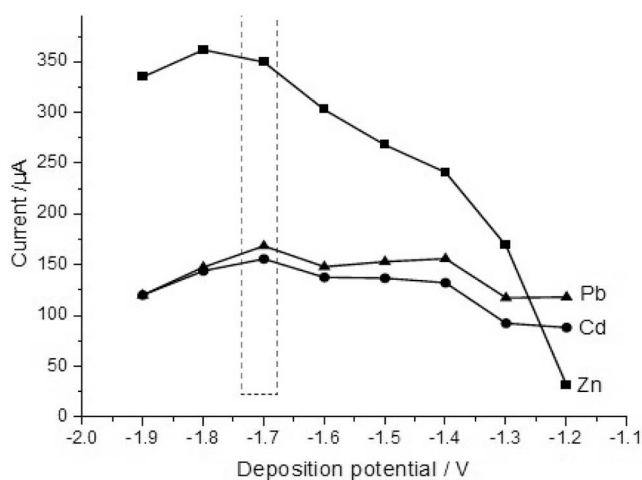
The analytical determination of Pb²⁺, Cd²⁺ and Zn²⁺ using Hg-Bi electrodeposited onto PDAAQ/GC modified electrode was studied with both “*in-situ*” and “*ex-situ*” modes (Fig. 3A). It is clear that “*ex-situ*” electrodeposition coating gave better performances for Zn²⁺ and Pb²⁺ (Fig. 3A, solid lines) with enhanced peak currents at -1.00 V and -0.42 V, respectively compared with “*in-situ*” method. On the other hand, stripping peak got a lower value for Cd²⁺ in “*ex-situ*” mode at



(A)



(B)



(C)

Fig. 3. Effect of A) method of electrochemical deposition of bimetallic Hg-Bi layer (“*in-situ*” and “*ex-situ*” modes), B) PDAAQ film relative thickness, C) pre-concentration potential of Pb^{2+} , Cd^{2+} , Zn^{2+} ions, D) pre-concentration time of Pb^{2+} , Cd^{2+} , Zn^{2+} ions and E) pH value of the NaAC/HAC buffer on the stripping peak current values of 100 $\mu\text{g/L}$ of Pb^{2+} , Cd^{2+} and Zn^{2+} at Hg-Bi/PDAAQ/GC electrode.

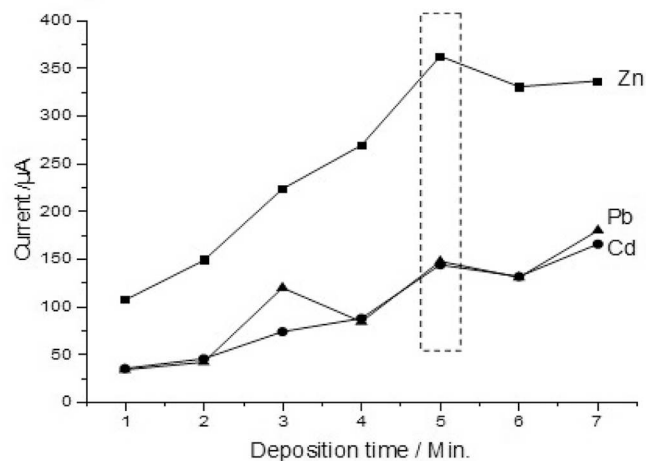
–0.62 V compared with in “*in-situ*” one.

3.3.2. Effect of PDAAQ film thickness

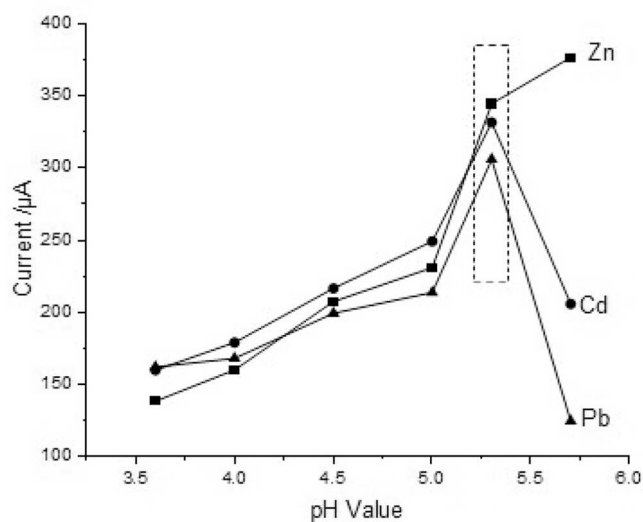
Relative PDAAQ film thickness depends on both DAAQ monomer concentration and number of polymerization cycles. Different numbers of polymerization cycles (2, 5, 15 and 25 cycles) were used for films formations. Optimum stripping peaks currents were obtained with PDAAQ film formed by 5 scanning cycles with values of 215.0, 180.0 and 445 μA for Pb^{2+} , Cd^{2+} and Zn^{2+} ions, respectively (Fig. 3B).

3.3.3. Effect of pre-concentration potential of Pb^{2+} , Cd^{2+} and Zn^{2+} ions

Fig. 3C has illustrates the effect of different pre-concentration potentials of Pb^{2+} , Cd^{2+} and Zn^{2+} deposition from –1.90 V to –1.20 V on the stripping currents. The optimum potential chosen was around –1.7 V depending on the related anodic stripping current values which



(D)



(E)

Fig. 3. (continued)

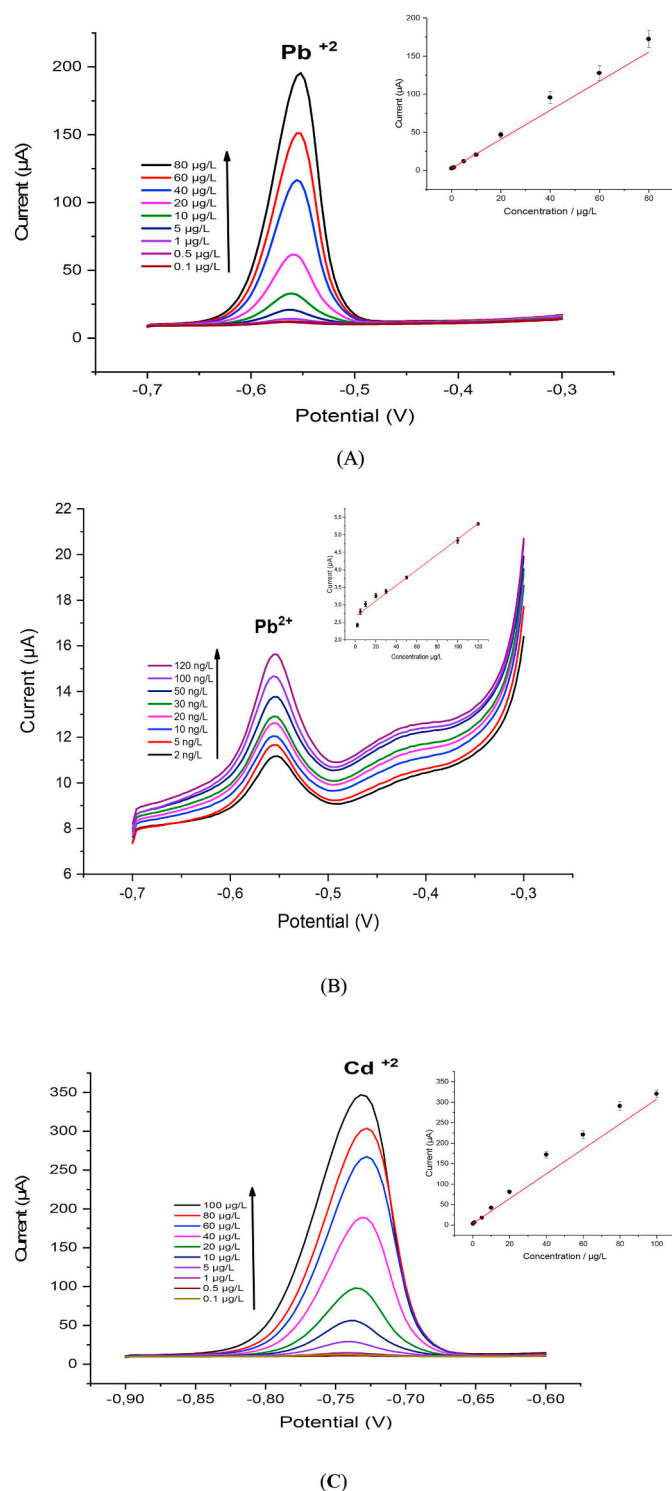


Fig. 4. Stripping performances and calibration curves of A) Pb²⁺ from 0.10 to 80.0 μg/L B) Pb²⁺ from 10.0 to 120 ng/L, C) Cd²⁺ from 0.10 to 100.0 μg/L, D) Zn²⁺ from 0.02 to 60 μg/L and E) Pb²⁺, Cd²⁺ and Zn²⁺ at different concentrations (1.0, 2.0, 5.0, 10.0, 25.0, 50.0 μg/L) in NaAC/HAC buffer (pH 5.3) at Hg-Bi/PDAAQ/GC electrode. Deposition time 120 s, deposition potential −1.70 V, error bar (± 16) (n = 3).

were 170.0, 155.0 and 350 μA, respectively, noting that the anodic peak current of Zn²⁺ had a higher value at −1.8 V.

3.3.4. Effect of preconcentration time of Pb²⁺, Cd²⁺ and Zn²⁺

The effect of Pb²⁺, Cd²⁺ and Zn²⁺ preconcentration time from 1 to

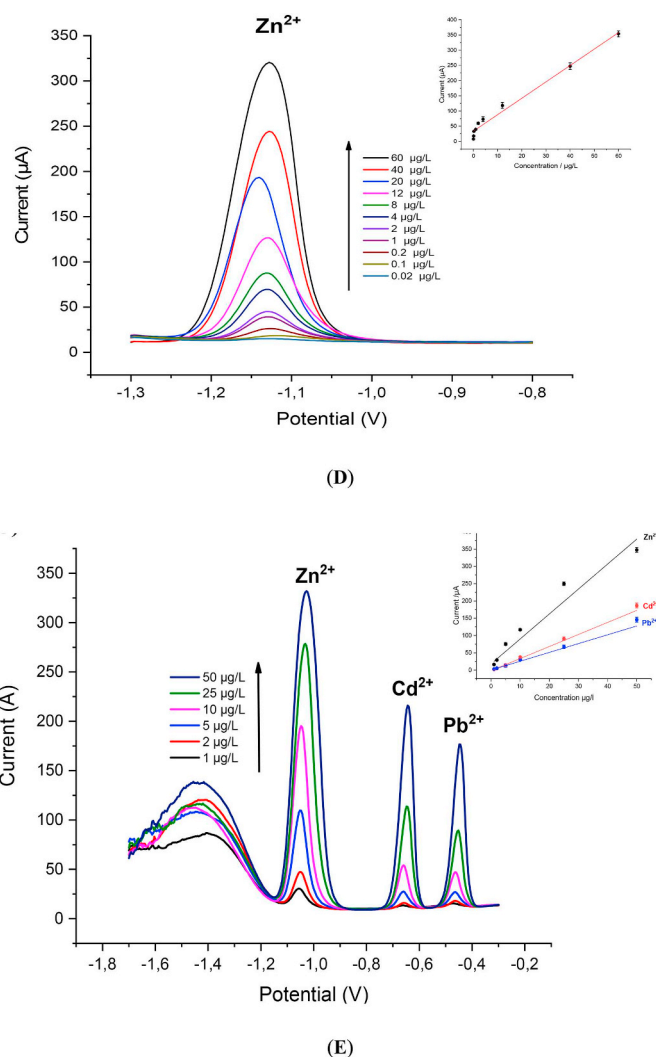


Fig. 4. (continued)

7 min on the stripping peak currents of the studied metal ions (Fig. 3D) were detected. Values revealed that preconcentration time of 7 min got the preferred values of 187.5 μA and 173.0 μA for both Pb²⁺ and Cd²⁺, respectively. On the other hand, 362.5 μA was recorded for Zn²⁺ at 5 min for which no enhancement was detected ongoing further which could be due to the saturation of the modified electrode surface with Zn metal during preconcentration step, hence 5 min had been chosen for overall experiments.

3.3.5. Effect of pH

The effect of pH values of the NaAC/HAC buffer solution containing target Pb²⁺, Cd²⁺ and Zn²⁺ metals ions on their stripping currents (Fig. 3E) showed that the optimum stripping currents of Pb²⁺ and Cd²⁺ observed at pH 5.3 with current values of 300.0 μA and 330 μA, respectively, while Zn²⁺ had 370 μA at pH 5.7. For all experiments, pH value of 5.3 had been chosen [16].

3.4. Analytical performance

Under the optimized experimental conditions, analytical performances of Hg-Bi/PDAAQ/GC electrode as a sensor for single and simultaneous determination of Pb²⁺, Cd²⁺ and Zn²⁺ ions were examined. Single determinations were carried out by increasing each metal ion concentration from 0.10 to 80.0 μg/L for Pb²⁺, 0.02 to 60.0 μg/L for Cd²⁺ and 0.10 to 100.0 μg/L for Zn²⁺ (Fig. 4A, C and D).

Table 1Analytical parameters of ASV for single and simultaneous determination of Pb^{2+} , Cd^{2+} and Zn^{2+} at Hg-Bi/PDAAQ/GC electrode.

	Metal	Linear range	Regression equation	R^{2a}	Sensitivity ($\mu\text{A.L}/\mu\text{g}$)	LOD ($\mu\text{g/L}$)	LOQ ($\mu\text{g/L}$)
Simultaneous	Pb^{2+}	0–50 $\mu\text{g/L}$	$I_{\text{p}}(\mu\text{g/L}) = 2.8905C_{(\mu\text{g/L})} - 0.5743$	0.998	2.8905	0.105	0.349
	Cd^{2+}	0–50 $\mu\text{g/L}$	$I_{\text{p}}(\mu\text{g/L}) = 3.763C_{(\mu\text{g/L})} - 1.8513$	0.999	3.763	0.107	0.358
	Zn^{2+}	0–50 $\mu\text{g/L}$	$I_{\text{p}}(\mu\text{g/L}) = 6.6683C_{(\mu\text{g/L})} - 27.936$	0.956	6.6683	0.037	0.123
Single	Pb^{2+}	0.1–80 $\mu\text{g/L}$	$I_{\text{p}}(\mu\text{g/L}) = 2.1464C_{(\mu\text{g/L})} - 2.0019$	0.997	2.1464	0.069	0.232
		10–120 ng/L	$I_{\text{p}}(\text{ng/L}) = 0.0206C_{(\text{ng/L})} - 2.7956$	0.997	0.0206 ($\mu\text{A.L}/\text{ng}$)	3.18 (ng/L)	10.6 (ng/L)
	Cd^{2+}	0.02–60 $\mu\text{g/L}$	$I_{\text{p}}(\mu\text{g/L}) = 3.9861C_{(\mu\text{g/L})} - 2.8113$	0.992	3.9861	0.195	0.652
	Zn^{2+}	0.1–100 $\mu\text{g/L}$	$I_{\text{p}}(\mu\text{g/L}) = 7.3427C_{(\mu\text{g/L})} - 39.625$	0.980	7.3427	0.169	0.563

^a R^2 = Coefficient of detection.**Table 2**

Performance of the proposed sensor in a comparison with other Hg, Bi and Sb modified electrodes.

Electrode material	Method	Linear Range ($\mu\text{g/L}$)			LOD ($\mu\text{g/L}$)			Ref
		Pb^{2+}	Cd^{2+}	Zn^{2+}	Pb^{2+}	Cd^{2+}	Zn^{2+}	
Hg/GCE	SWASV	4144–20,700	2248–11,241	–	600	520	–	[33]
Bi/PANI/GC	ASV	0–120	0–120	–	1.03	1.48	–	[21]
Bi/poly(p-ABSA)/GC	DPASV	1.0–130	1.0–110.0	1.0–110.0	0.80	0.63	0.62	[34]
Bi/poly(PCV)/MWCNT/GC	DPASV	1.0–300	1.0–300	–	0.4	0.2	–	[35]
Bi/Poly(1,8-DAN)/CPE	SWASV	0.5–50	–	–	0.3	–	–	[23]
In-situ BiSPCE	DPASV	0.83–23.3	1.35–14.5	–	0.25	0.40	–	[36]
Ex-situ BiSPCE	DPASV	0.48–19.6	0.80–17.2	–	0.14	0.24	–	[36]
Bi _{ox} SPCE	DPASV	0.52–12.0	0.33–9.0	–	0.16	0.1	–	[36]
Bi _{sp} SPE	DPASV	0.53–19.8	0.33–12.3	–	0.16	0.1	–	[36]
Hg-Bi/SWCNTs/GC	SWASV	5–1100 (ng/L)	0.5–11	0.5–11	0.12 (ng/L)	0.076	0.23	[37]
SbSPCE	DPASV	17.5–100.9	9.5–100.3	–	5.3	2.8	–	[30]
SbSPCE-GPH	DPASV	28.8–100.9	13.2–100.3	–	8.6	4.0	–	[30]
SbSPCE-MWCNT	DPASV	14.7–100.9	8.6–100.3	–	4.4	2.6	–	[30]
SbSPCE-CNF	DPASV	6.9–100.9	3.7–100.3	–	2.1	1.1	–	[30]
Bi oxycarbide /GC	DPASV	10–50	10–50	–	3.97	4.24	–	[29]
2D bismuthene-graphene/GC	SWASV	1–30	1–30	–	0.3	0.3	–	[38]
BiOCl-MWCNT/GC	SWASV	–	–	2.5–80	–	–	0.75	[39]
Hg-Bi/PDAAQ/GC	SWASV	12–120 (ng/L)	0–50	0–50	7.18 (ng/L)	0.107	0.037	This work

Table 3Determination of Zn^{2+} , Cd^{2+} and Pb^{2+} ions in tap water ($n = 3$) using ICP-MS and ASV techniques.

Sample	Added ($\mu\text{g/L}$)			Founded by ICP-MS \pm SD ^a ($\mu\text{g/L}$)			Founded by ASV \pm SD ($\mu\text{g/L}$)			Recovery %		
	Pb^{2+}	Cd^{2+}	Zn^{2+}	Pb^{2+}	Cd^{2+}	Zn^{2+}	Pb^{2+}	Cd^{2+}	Zn^{2+}	Pb^{2+}	Cd^{2+}	Zn^{2+}
Tap water	5.0	5.0	5.0	4.98 ± 0.035	5.05 ± 0.02	5.05 ± 0.13	4.6 ± 0.05	5.05 ± 0.3	5.05 ± 0.9	93	103	107
	10.0	10.0	10.0	10 ± 0.088	9.92 ± 0.073	10.02 ± 0.036	9.8 ± 0.03	8.7 ± 0.29	9.51 ± 0.05	98	88	97
	15.0	15.0	15.0	15.01 ± 0.08	15.02 ± 0.066	15.03 ± 0.046	15.3 ± 0.072	14.54 ± 0.01	14.87 ± 0.02	102	97	99

^a SD: standard deviation.

The vision of these curves with their insets revealed that peak currents are directly proportional to each metal ion concentration (Fig. 4A, C and D insets). Limit of detection values (LODs) and limit of quantification values (LOQs) were found to be 0.069, 0.195 and 0.169 $\mu\text{g/L}$ and 0.232, 0.652 and [$\mu\text{g/L}$ for Pb^{2+} , Cd^{2+} and Zn^{2+} , respectively. Moreover, to prove the high sensitivity of the prepared electrode, a lower linear range of Pb^{2+} from 10 to 120 ng/L was achieved with LOD and LOQ values of 3.18 ng/L and 10.6 ng/L , respectively as presented in Fig. 4B and inset. Meanwhile, simultaneous determinations of the three targets were performed by increasing each metal ion concentration in an ascending protocol with a linear range of 0–50 $\mu\text{g/L}$. Fig. 4E (and inset) represents direct proportionality of peak current values with different concentrations of each metal ion. LODs and LOQs values were 0.105, 0.107, 0.037 $\mu\text{g/L}$, and 0.349, 0.358, 0.123 $\mu\text{g/L}$ for Pb^{2+} , Cd^{2+} and Zn^{2+} , respectively. Obtained regression equations and coefficients of detection are collected in Table 1.

LOD and LOQ could be obtained using the following equations:

$$\text{LOD} = 3 \times \text{SD}/\text{Slope} \quad (1)$$

$$\text{LOQ} = 10 \times \text{SD}/\text{Slope} \quad (2)$$

where (SD) is the standard deviation of blank response in μA (obtained from 20 blank signals) divided by the slope of the calibration curve in $\mu\text{A.L}/\mu\text{g}$ (sensitivity of the method) [32].

It is noticed from Table 1, that Hg-Bi/PDAAQ/GC sensor is more sensitive to Pb^{2+} determination in single system, while more sensitive to Cd^{2+} and Zn^{2+} determination in simultaneous one.

The performance of the proposed sensor in a comparison with other recent Hg, Bi or antimony (Sb) modified electrodes is presented in Table 2. Regarding analytical parameters, evidences provided that the present sensor has an extremely lower LOD values when compared with other electrodes except that of Hg-Bi/SWCNTs/GC especially for Pb^{2+} and Cd^{2+} , as the bimetallic film of Hg-Bi supported on the single walled carbon nanotubes provides a great surface. The low cost of our proposed sensor gives an additional economic advantage with a good analytical performance.

3.5. Effect of ions interferences

To study the effect of ions interferences with solution containing target metal ions (Pb^{2+} , Cd^{2+} and Zn^{2+}) on their stripping peak currents, a 1.0 mg/L of a foreign metal ions (Na^+ , Ca^{2+} , Mg^{2+} and Al^{3+} , Ag^+ , Mn^{2+} , Ni^{2+} , Cu^{2+} , Fe^{2+} or Cr^{6+}) were added to a solution containing 50.0 $\mu\text{g/L}$ of Pb^{2+} , Cd^{2+} and Zn^{2+} (figure not shown). At higher concentration of Na^+ , Ca^{2+} , Mg^{2+} or Al^{3+} interfering ions found in real samples (like real water samples), no significant changes were observed. However, the presence of Ag^+ , Mn^{2+} , Ni^{2+} , Cu^{2+} , Fe^{2+} or Cr^{6+} ions causes a significant effect on the stripping peak currents of the three target metal ions which could be diminished by the addition of complexing agent beside the ASV analysis [40], as for example in case Cu^{2+} , the addition of 0.10 mM ferrocyanide to the sample could decrease this effect, in which an insoluble and stable copper-ferrocyanide complex have been formed with the help of a ligand [41].

3.6. Repeatability performance and stability

Depending on current responses, the electrode showed a good reproducibility toward the target metal ions at the same modified electrode with anodic peak current of approximately 45.0 μA , 30.0 μA and from about 62.0 to 75.0 μA for Pb^{2+} , Cd^{2+} and Zn^{2+} , respectively, giving a relative standard deviation (RSD) equals to 4.97%, 1.87% and 4.74% for them, respectively (RSD < 5%). Long term stability was also studied by eight repetitive measurements of 50.0 $\mu\text{g/L}$ of Zn^{2+} , Cd^{2+} and Pb^{2+} each every seven days along with two months at different prepared modified electrodes. The electrode showed a good stability for the preparation of the modified electrode with RSD values of 0.67%, 1.33% and 1.05% for Zn^{2+} , Cd^{2+} and Pb^{2+} , respectively.

3.7. Sample analysis

Table 3 illustrates results obtained for heavy metal ions determination for spiked tap water with 5.0, 10.0 and 15.0 $\mu\text{g/L}$ of Zn^{2+} , Cd^{2+} and Pb^{2+} , respectively for three replicate measurements using Hg-Bi/PDAAQ/GC electrode and ICP-MS methods [42]. Hg-Bi/PDAAQ/GC electrode showed favorable recovery ranged from 88.0 to 107.0% in comparison with very complicated technique (ICP-MS).

4. Conclusion

In summary, the bimetallic film of Hg-Bi was successfully incorporated into the conductive polymer PDAAQ and used as an interesting sensor for anodic stripping voltammetry of Zn^{2+} , Cd^{2+} and Pb^{2+} ions in NaAC/HAC buffer (pH 5.3). Under the pre-optimized conditions, the proposed sensor showed an excellent analytical performance with LOD values of 0.107 $\mu\text{g/L}$ and 0.037 $\mu\text{g/L}$ for simultaneous determination of Cd^{2+} and Zn^{2+} , respectively, while reached 3.18 ng/L for Pb^{2+} . The reproducibility of the sensor has good RSD values for the target heavy metal ions. The effect of different interfering ions was examined. The sensor analytical performance of real water samples was examined and compared with ICP-MS technique giving priority to Hg-Bi/PDAAQ/GC electrode.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper

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