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

Khalid Mahmoud Hassan, Seleem Elsaid Gaber, Mahmoud Fatehy Altahan, Magdi Abdel Azem

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 (Pb²⁺), cadmium (Cd²⁺) and zinc (Zn²⁺) 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 μg/L for Cd²⁺ and Zn²⁺ with a low detection limit of 0.107 and 0.037 μg/L, respectively. The linear range of Pb²⁺ 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 (Pb²⁺), cadmium (Cd²⁺) and zinc (Zn²⁺) 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
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-diaminoantriquinone) (PDAQQ) [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 nano-particles modified electrodes such as BiNPS/Nafion Modified-PG [24], SPGE-BiNPS-Nafion [25], BiNPS/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 Pb2+, Cd2+ and Zn2+ ions using ASV technique in acetate buffer solution (pH 5.3) was examined at PDAQQ/glassy carbon (PDAQQ/GC), bismuth/PDAQQ (Bi/PDAQQ/GC), mercury/PDAQQ/GC (Hg/PDAQQ/GC) and finally mercury/bismuth/PDAQQ/GC (Hg-Bi/PDAQQ/GC) modified electrodes. It is interesting for combining advantages of using bimetallic Hg-Bi and presence of conductive polymer (PDAQQ) 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 (LiClO4), 0.1 M acetate buffer (CH3COONa.3H2O, CH3COOH) (NaAC/HAC), mercuric chloride (HgCl2), bismuth nitrate pentahydrate (Bi(NO3)2.5H2O), lead nitrate (Pb(NO3)2), cadmium chloride hemi-pentahydrate (CdCl2.3/2H2O), zinc sulphate heptahydrate (ZnSO4.7H2O), sulfuric acid (H2SO4), alumina powder (0.05 μm) and potassium chloride (KCI 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 voltamograms 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/AgCl as a reference one. Ex-situ deposition, Hg and Bi were deposited initially on GC electrode and after the preconcentration step (mentioned in the experimental section), stripping peak current responses of Pb2+, Cd2+ and Zn2+ ions had been examined at bare GC electrode, PDAQQ/GC modified electrode recorded in NaAC/HAC buffer and 0.1 M KCl solution (pH 5.3) containing 0.1 M KCl at Hg-Bi/PDAQQ/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/PDAQQ/GC modified electrode

Square wave voltammetry (SWV) of Hg-Bi/PDAQQ/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 Hg2+ and Bi3+ 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/PDAQQ/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 PDAQQ film with a percent of 12.16% and 1.77%, respectively.

3.2. Simultaneous determination of Pb2+, Cd2+ and Zn2+ 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 Pb2+, Cd2+ and Zn2+ 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 Pb2+, Cd2+ and Zn2+ ions had been examined at bare GC electrode, PDAQQ/GC, Hg-Bi/GC, Bi/PDAQQ/GC, Hg/PDAQQ/GC and Hg-Bi/PDAQQ/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 Pb2+, Cd2+ and Zn2+ 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 Pb2+ and Cd2+, respectively were observed at PDAQQ/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 Pb2+, Cd2+ and Zn2+, respectively with low anodic peak currents (Fig. 2A, curve c). Remarkably enhanced stripping peak
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 Pb$^{2+}$, Cd$^{2+}$ and Zn$^{2+}$ 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 Pb$^{2+}$, Cd$^{2+}$ and Zn$^{2+}$, 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 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 Pb$^{2+}$, Cd$^{2+}$ and Zn$^{2+}$ 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 Pb$^{2+}$, Cd$^{2+}$ and Zn$^{2+}$ using Hg-Bi electrodeposited onto PDAQQ/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 Zn$^{2+}$ and Pb$^{2+}$ (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 Cd$^{2+}$ in “ex-situ” mode at
−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 Pb²⁺, Cd²⁺ and Zn²⁺ ions, respectively (Fig. 3B).

3.3.3. Effect of preconcentration potential of Pb²⁺, Cd²⁺ and Zn²⁺ ions
Fig. 3C illustrates the effect of different preconcentration potentials of Pb²⁺, Cd²⁺ and Zn²⁺ 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
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 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.

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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).
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 μg/L and 0.232, 0.652 and 0.169 μg/L for Pb2+, Cd2+ and Zn2+, respectively. Moreover, to prove the high sensitivity of the prepared electrode, a lower linear range of Pb2+ 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 μg/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 μg/L, and 0.349, 0.358, 0.123 μg/L for Pb2+, Cd2+ and Zn2+, respectively. Obtained regression equations and coefficients of detection are collected in Table 1.

The performance of the proposed sensor in a comparison with other Hg, Bi and 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 Pb2+ and Cd2+, 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.

**Table 1**

Analytical parameters of ASV for single and simultaneous determination of Pb2+, Cd2+ and Zn2+ at Hg-Bi/PDAAQ/GC electrode.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Linear range (μg/L)</th>
<th>Regression equation</th>
<th>R²</th>
<th>Sensitivity (μA.L/μg)</th>
<th>LOD (μg/L)</th>
<th>LOQ (μg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb2+</td>
<td>0–50 μg/L</td>
<td>I_{peak} = 2.8905C_{Pb2+} -0.5743</td>
<td>0.998</td>
<td>2.8905</td>
<td>0.105</td>
<td>0.349</td>
</tr>
<tr>
<td>Cd2+</td>
<td>0–50 μg/L</td>
<td>I_{peak} = 3.763C_{Cd2+} -1.8513</td>
<td>0.999</td>
<td>3.763</td>
<td>0.107</td>
<td>0.358</td>
</tr>
<tr>
<td>Zn2+</td>
<td>0–50 μg/L</td>
<td>I_{peak} = 6.6683C_{Zn2+} -27.936</td>
<td>0.956</td>
<td>6.6683</td>
<td>0.037</td>
<td>0.123</td>
</tr>
<tr>
<td>Single</td>
<td>Pb2+ 0.1–80 μg/L</td>
<td>I_{peak} = 2.1646C_{Pb2+} -2.0019</td>
<td>0.997</td>
<td>2.1646</td>
<td>0.069</td>
<td>0.232</td>
</tr>
<tr>
<td>Cd2+</td>
<td>0.02–60 μg/L</td>
<td>I_{peak} = 3.9661C_{Cd2+} -2.8113</td>
<td>0.992</td>
<td>3.9661</td>
<td>0.195</td>
<td>0.652</td>
</tr>
<tr>
<td>Zn2+</td>
<td>0.1–100 μg/L</td>
<td>I_{peak} = 7.3427C_{Zn2+} -39.625</td>
<td>0.980</td>
<td>7.3427</td>
<td>0.169</td>
<td>0.563</td>
</tr>
</tbody>
</table>

*a* R² = Coefficient of detection.

**Table 2**

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

<table>
<thead>
<tr>
<th>Electrode material</th>
<th>Method</th>
<th>Linear Range (μg/L)</th>
<th>LOD (μg/L)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb2+</td>
<td>ASV</td>
<td>0–120</td>
<td>1.03</td>
<td>[21]</td>
</tr>
<tr>
<td>Bi/poly(p-ABSA)/GC</td>
<td>DPASV</td>
<td>1.0–130</td>
<td>0.80</td>
<td>[34]</td>
</tr>
<tr>
<td>Bi/poly(PCV)/MWCNT/GC</td>
<td>DPASV</td>
<td>1.0–300</td>
<td>0.40</td>
<td>[35]</td>
</tr>
<tr>
<td>Bi/Poly1,8-DAN/CPE</td>
<td>SWASV</td>
<td>0.5–50</td>
<td>0.3</td>
<td>[23]</td>
</tr>
<tr>
<td>In-situ BiSPCE</td>
<td>DPASV</td>
<td>0.83–23.3</td>
<td>0.25</td>
<td>[36]</td>
</tr>
<tr>
<td>Ex-situ BiSPCE</td>
<td>DPASV</td>
<td>0.48–19.6</td>
<td>0.14</td>
<td>[36]</td>
</tr>
<tr>
<td>Bi,SPCE</td>
<td>DPASV</td>
<td>0.52–12.0</td>
<td>0.16</td>
<td>[36]</td>
</tr>
<tr>
<td>Bi, SPE</td>
<td>DPASV</td>
<td>0.53–19.8</td>
<td>0.16</td>
<td>[36]</td>
</tr>
<tr>
<td>Hg-Bi/SWCNTs/GC</td>
<td>SWASV</td>
<td>5–1100</td>
<td>0.12</td>
<td>[37]</td>
</tr>
</tbody>
</table>

**Table 3**

Determination of Zn2+, Cd2+ and Pb2+ ions in tap water (n = 3) using ICP-MS and ASV techniques.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Added (μg/L)</th>
<th>Found by ICP-MS ± SD (μg/L)</th>
<th>Found by ASV ± SD (μg/L)</th>
<th>Recovery %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb2+</td>
<td>5.0</td>
<td>5.0 ± 0.035</td>
<td>5.05 ± 0.02</td>
<td>102</td>
</tr>
<tr>
<td>Cd2+</td>
<td>10.0</td>
<td>10.0 ± 0.088</td>
<td>10.02 ± 0.036</td>
<td>100</td>
</tr>
<tr>
<td>Zn2+</td>
<td>15.0</td>
<td>15.0 ± 0.08</td>
<td>15.02 ± 0.066</td>
<td>100</td>
</tr>
</tbody>
</table>

*a* SD: standard deviation.

The precision 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 μg/L and 0.232, 0.652 and 0.169 μg/L for Pb2+, Cd2+ and Zn2+, respectively. Moreover, to prove the high sensitivity of the prepared electrode, a lower linear range of Pb2+ 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 μg/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 μg/L, and 0.349, 0.358, 0.123 μg/L for Pb2+, Cd2+ and Zn2+, respectively. Obtained regression equations and coefficients of detection are collected in Table 1.

LOD and LOQ could be obtained using the following equations:

\[
LOD = 3 \times SD/Slope \\
LOQ = 10 \times SD/Slope
\]
3.5. Effect of ions interferences

To study the effect of ions interferences with solution containing target metal ions (Pb²⁺, Cd²⁺ and Zn²⁺) on their stripping peak currents, a 1.0 mg/L of a foreign metal ions (Na⁺, Ca²⁺, Mg²⁺ and Al³⁺, Ag⁺, Mn²⁺, Ni²⁺, Cu²⁺, Fe²⁺ or Cr⁶⁺) were added to a solution containing 50.0 μg/L of Pb²⁺, Cd²⁺ and Zn²⁺ (figure not shown). At higher concentration of Na⁺, Ca²⁺, Mg²⁺ or Al³⁺ interfering ions found in real samples (like real water samples), no significant changes were observed. However, the presence of Ag⁺, Mn²⁺, Ni²⁺, Cu²⁺, Fe²⁺ or Cr⁶⁺ 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 Cu²⁺, 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 Pb²⁺, Cd²⁺ and Zn²⁺ 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 μg/L of Zn²⁺, Cd²⁺ and Pb²⁺ 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 Zn²⁺, Cd²⁺ and Pb²⁺, 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 μg/L of Zn²⁺, Cd²⁺ and Pb²⁺, respectively for three replicate measurements using Hg-Bi/PDA AQ/GC electrode and ICP-MS methods [42]. Hg-Bi/PDA AQ/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 composite polymer PDA Q and used as an interesting sensor for anodic stripping voltammetry of Zn²⁺, Cd²⁺ and Pb²⁺ 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 μg/L and 0.037 μg/L for simultaneous determination of Cd²⁺ and Zn²⁺, respectively, while reached 3.18 ng/L for Pb²⁺. 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/PDA AQ/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.

Acknowledgement

Authors would like to thank Alexander von Humboldt Foundation for the scientific donation of some electrochemical equipment.

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