

Carbon Nanotube Paste Electrode with a Bismuth Film in Anodic Stripping Voltammetry for the Determination of Heavy Metals

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Abstract: In this article, a new type of metal-based non-mercury electrode based on carbon nanotubes (both multi-walled and single-walled) paste electrode is introduced and examined for electrochemical stripping analysis of selected heavy metals. All important parameters have been optimized by using Cd(II) and Pb(II) as the model ions by square-wave anodic stripping voltammetry, as well as the role of bismuth concentration. It was found that bismuth coated multi-walled carbon nanotubes paste electrode had exhibited a fine linear response at the μg -per-litre concentration level of cadmium and lead.

Keywords: Carbon nanotubes paste electrode, Carbon nanotubes, Bismuth film, Electrochemical stripping analysis, Heavy metals, Lead, Cadmium.

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Introduction

Carbon paste electrodes (CPEs) have attracted attention due to their unique properties such a very easy surface renewing or applicability in inorganic, organic and biological analysis. When compared with traditional carbon powder, carbon nanotubes (CNTs) provide better physicochemical properties, such as ordered structure with high aspect ratio, very good mechanical stability, or high electrical and thermal conductivity, and mainly distinct electrocatalytical properties [1,2].

Due to the attractive properties mentioned, the CNTs are in recent years used for preparation of new configurations carbon-based electrodes. The first approach for preparation of CNTs electrodes (CNTE) is identical to preparation of classical carbon paste electrode. Instead of carbon powder CNTs (multi-walled or single-walled) are used and mixed in appropriate ration with binding liquid [1-12]. The second type could be prepared by enrichment of carbon powder with small amount of CNTs and this solid mixture subsequently mixed in appropriate ration with binding liquid [13-22]. Last but not least, the third type of CNTE could be prepared by modification of the electrode surface itself (e.g. glassy carbon or carbon paste) when a small volume of CNTs suspension is dropped on the electrode surface and dried in the air [23-27]. Behaviour and properties of CNTE are very similar to classic CPE with wide range of application in inorganic, organic and biological analysis. Utilization of CNTE in inorganic applications is mainly focus on trace analysis of heavy metals: lead [4,5,13,23,24,28,29], cadmium [3,5,17,23,24,28,29], zinc [5,24,28], mercury [3,14,15], bismuth [16], copper [18], antimony [19] and molybdenum [25]. In the area of organic and biological analysis CNTE are used for determination of homocysteine [6], N-acetylcysteine [7], guanine [8], pentoxifylline [9], quercetin [10], ascorbic acid, norepinephrine, epinephrine [12], ricin [20], tryptophan [21], and dopamine [26]. More or less, carbon nanotube paste electrodes (CNTPE) are from the same “family” as classical carbon paste electrodes, which allow us to implement selected CPE configurations into the CNTPE form.

Concerning bismuth-modified variants, *i.e.* BiF-CNTPEs or Bi-CNTPEs resp., several examples were already demonstrated [14, 17, 27-29]. For instance, recently, Juo et al prepared carbon paste modified with multi-walled CNTs with *in-situ* coated bismuth film for determination of cadmium in tap water at the $\mu\text{g-per-litre}$ level [17]. This type of electrode configuration belongs to the second type of CNTE when carbon paste is modified with certain amount of CNTs. In this way, the above mentioned electrode configuration should be considered as CPE modified or doped with CNTs rather than “pure” CNTE. The preparation of carbon paste doped with nano-carbon material is not only limited to CNTs but also currently studied graphene based materials are in centre of interest [29]. In this particular study graphene modified CPE with *in situ* deposited bismuth film (Bi/Gr/CPE) was used in automated flow system for the determination of lead and cadmium in low- (tap water) and high-complex (sea bass fish and undulated surf clam tissues) matrix samples at the concentration level under $1 \mu\text{g}\cdot\text{L}^{-1}$. Regarding to the third type of CNTE (small volume of CNTs suspension is dropped on the electrode surface and dried in the air), the novel type of electrode configuration was prepared by suspension coating of bismuth oxide nanoparticles

and multi-walled CNTs on the glassy carbon electrode (Bi₂O₃-MWCNTs/GCE) and subsequently firmly anchored horseradish peroxidase by the aim of Nafion[®] (NF/HRP/Bi₂O₃-MWCNTs/GCE) [27]. This sandwich-like electrode configuration lowers the overpotential of H₂O₂ reduction rather than MWCNTs, Bi₂O₃-MWCNTs or unmodified GCEs, making it very promising for further biosensing applications. Screen printed carbon nanotube electrode with *in situ* plated bismuth film (BiF-CNT/SPE) [28], as well as the screen printed bismuth electrode modified with MWCNTs (MWCNTs/BiF-SPE) [14] offer a planar electrode configuration easily compatible with flow system which were tested for simultaneous determination lead, cadmium and zinc [28] or mercury [14] in model samples.

In this work, a new type of carbon nanotube paste electrode with *in situ* coated bismuth film (Bi/CNTPE) is described and used for the determination of selected heavy metals by anodic stripping voltammetry. It can be stated that this study follows up the recently published author's report concerning the preparation and characterization of CNTPE with the respect to the best ratio of CNTs and binding liquid [11].

Experimental

Chemicals, Reagents, Stock and Standard Solutions

All chemicals used for the preparation of stock solutions were analytical grade and purchased from Merck, Sigma-Aldrich and Lachema (Brno, Czech Republic). The stock solutions of acetate buffer, ammonia buffer, phosphate buffer, NaOH, H₂SO₄, HClO₄, and HCl were prepared as 1 M in concentration from the respective chemicals by using doubly distilled water and diluted as required for experiments. The AAS-standard solution of Cd(II), Pb(II), were used and diluted as required. Water used throughout the experimental work was obtained by double distillation of deionised water through a laboratory made distillation unit. All the measurements were carried out at room temperature (24±1 °C).

Electrochemical Apparatus and Other Instrumentation

A modular electrochemical system AUTOLAB equipped with PGSTAT-12 (Metrohm / Autolab B.V., Utrecht, The Netherlands) was used in combination with NOVA 1.7 software of the same manufacturer.

This assembly was connected to an external electrode stand incorporating the three-electrode cell with the working electrode, Ag/AgCl/3M KCl reference, and Pt-plate auxiliary electrodes. Stirring was carried out with magnetic bars rotated at *ca.* 400 rpm.

Electrode Preparation

Carbon Paste. The proper mixture was prepared by thoroughly hand-mixing of 75% (w/w) graphite powder (“CR-5”, Maziva Týn, Czech Republic) and 25% (w/w) paraffin oil (Merck) using a pestle and mortar.

Carbon Nanotube Paste. Two types of nanotubes were used: SW-CNTs (single-walled; diameter 2 nm) and MW-CNTs 1030 (multi-walled, diameter 10–30 nm) both purchased from Shenzhen Nanotech Port Co., China. The nanotube paste was prepared by hand-mixing of 60% (w/w) carbon nanotubes and 40% (w/w) paraffin oil according to previous results [11].

Carbon Paste electrode (CPE) and Carbon Nanotube Paste Electrode (CNTPE) Substrates. Freshly made carbon paste mixtures were checked with respect to their ohmic resistance; all values being within an interval of 7 – 35 Ω . After that all the pastes were packed into piston driven carbon paste holders. The carbon paste electrode surfaces were renewed by extruding approx. 0.5 mm of carbon paste out from the holder with subsequently smoothing on wet filter paper. Typically, this mechanical renewal was made before starting a new set of experiments or, eventually, prior to analysis of each sample.

Voltammetric Measurements

Anodic stripping voltammetry measurements were carried out in the square-wave mode (SWV). Typical experiments consisted of three conventional steps: (i) time-controlled electrochemical deposition, (ii) the rest period and (iii) the positive going voltammetric stripping scan under conditions chosen, ended with fourth electrochemical conditioning (cleaning) step. The individual experimental conditions and instrumental parameters are then specified later – in the legend of each figure.

Results and Discussion

Behaviour and Basic Characteristics of CNTPE in Dependence of the Types of CNTs

Fig. 1 shows square-wave voltammograms with respective peaks of cadmium and lead for different types carbon-based paste electrodes: (i) classical CPE; (ii) multi-walled CNTPE (MW-CNTPE) and (iii) single-walled CNTPE (SW-CNTPE). Experiments were done on the bare electrode surface (Fig.1, dash lines) and with coated bismuth film (Fig. 1 full line). Electrode prepared from the SW-CNTs did not provide satisfactory current response for bare neither bismuth coated SW-CNTPE. On the basis of this results SW-CNTPE were not used for further experiments. The current responses of the bare MWCNTPE and CPE did not differ significantly, but for the bismuth film coated BiF-MW-CNTPE (when compared to the BiF-CPE) higher responses were obtained. The respective peaks heights were: 23.8 μA for Pb(II); 11.51 μA for Cd(II) on the Bi-MWCNTPE and 15.9 μA for Pb(II); 9.08 μA for Cd(II) on the Bi-CPE which means 49% increase of signal for lead and 26% increase for cadmium.

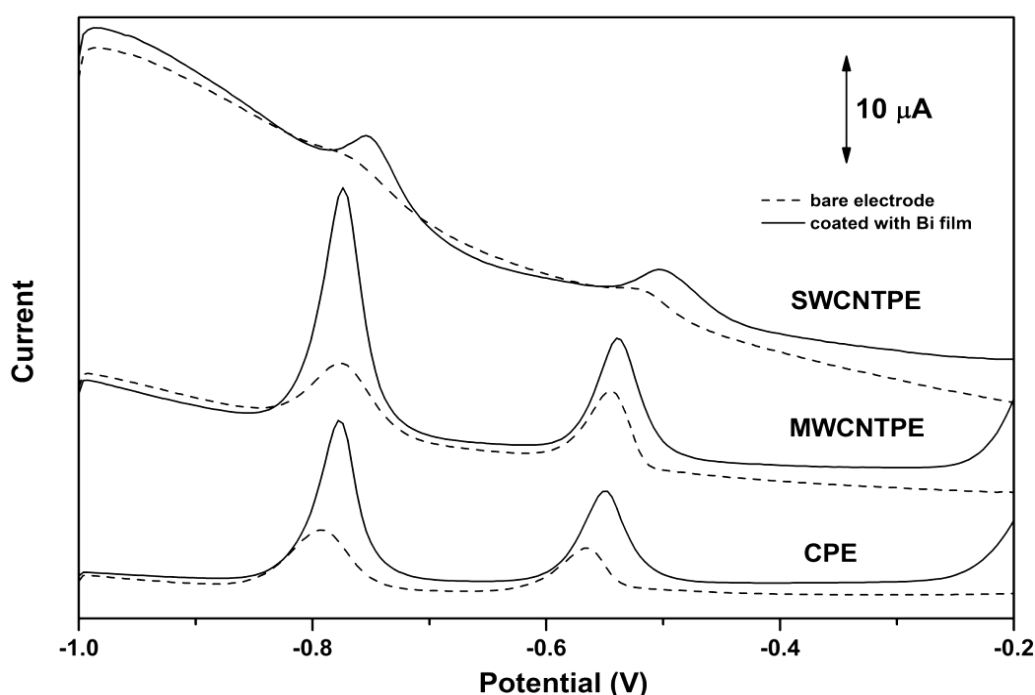


Fig. 1: Influence of carbon-based paste type on response of Cd(II) and Pb(II).

Legend: Solution: 0.2 M acetate buffer, $c_{\text{Cd}} = c_{\text{Pb}} = 100 \mu\text{g}\cdot\text{L}^{-1}$, $c_{\text{Bi}} = 1 \text{ mg}\cdot\text{L}^{-1}$. SWASV condition: deposition potential, $E_{\text{dep}} = -1 \text{ V}$; final potential, $E_{\text{fin}} = 0.1 \text{ V}$; deposition time, $t_{\text{dep}} = 90 \text{ s}$; equilibrium period, $t_{\text{eq}} = 15 \text{ s}$; frequency, $f_{\text{sw}} = 25 \text{ Hz}$; pulse height, $\Delta E = 20 \text{ mV}$; increment = 4 mV.

The Composition of Supporting Electrolyte and Its Effect on the Responses of Heavy Metals in Electrochemical Stripping Analysis with the Bi/CNTPE

It could be noticed that in electrochemical stripping analysis with bismuth-film based electrodes acetate buffer is almost dogmatically used as a supporting electrolyte. In order to avoid this dogma the current responses of cadmium and lead were investigated in several supporting electrolytes. In neutral and mild alkaline electrolytes (namely: phosphate buffer, ammonia buffer, and sodium hydroxide) were obtained insignificant current responses if there were any (not shown). As expected, the acid media seems to be more appropriate (see Fig. 2). The electrolytes based on HClO_4 and H_2SO_4 provide small current responses whereas in acetate buffer and HCl were these signals significantly higher. When one looks at the voltammograms carried out in acetate buffer and HCl it could be noticed that cadmium and lead responses are slightly higher when using HCl . The main difference can be seen in the oxidation peak of bismuth; in HCl , it is much higher and shifted to more negative potential compared to its shape and position in acetate buffer, which could be connected with the quality of bismuth film itself. Fig. 3 shows effect of acetate buffer and HCl concentration on the peak height of cadmium and lead.

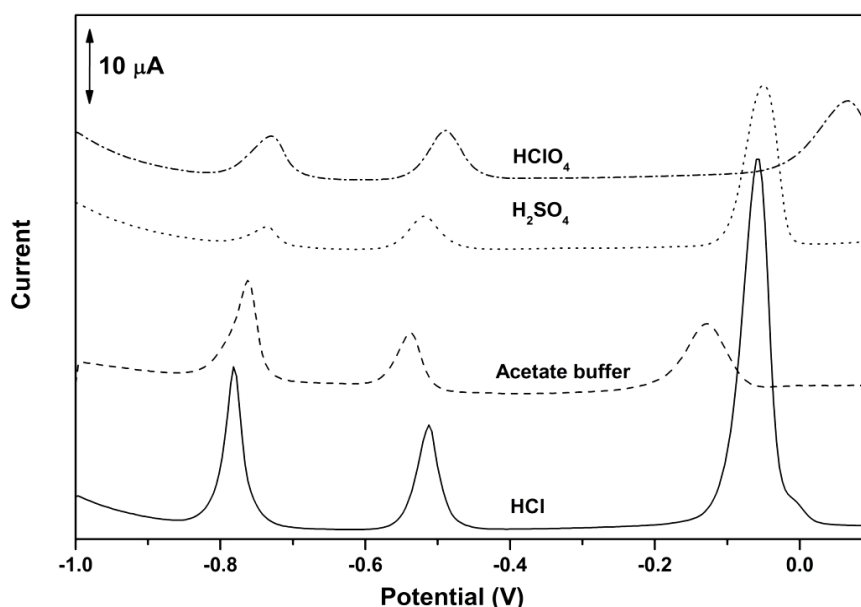


Fig. 2: Effect of electrolyte composition on responses of Cd(II) and Pb(II) using Bi-MWCNTPE.

Legend: Electrode: Bi-MWCNTPE. Solution: $c_{(\text{Cd})} = c_{(\text{Pb})} = 100 \mu\text{g}\cdot\text{L}^{-1}$, $c_{(\text{Bi})} = 1 \text{ mg}\cdot\text{L}^{-1}$. SWASV condition: deposition potential, $E_{\text{dep}} = -1 \text{ V}$; final potential, $E_{\text{fin}} = 0.1 \text{ V}$; deposition time, $t_{\text{dep}} = 90 \text{ s}$; equilibrium period, $t_{\text{eq}} = 15 \text{ s}$; frequency, $f_{\text{sw}} = 25 \text{ Hz}$; pulse height, $\Delta E = 20 \text{ mV}$; increment = 4 mV .

Acetate buffer (Fig. 3A) could be used in relative large concentration range but supporting medium based on HCl should be used as 0.1 M (pH \approx 1) solution in order to obtain the highest current signals.

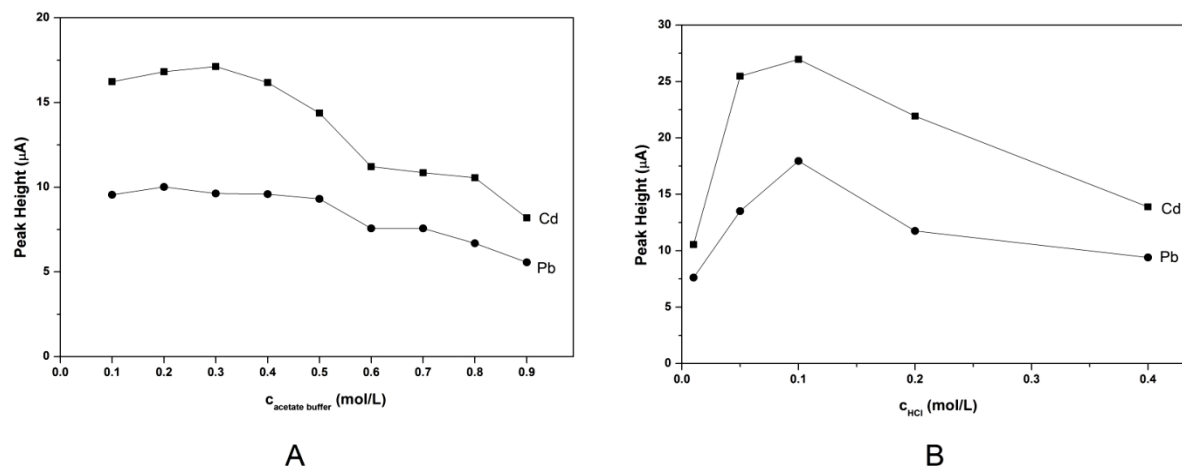


Fig. 3: Effect of electrolyte concentration on responses of Cd(II) and Pb(II).

Legend: Electrode: Bi-MWCNTPE. Solution: (A) acetate buffer, (B) HCl; $c_{(\text{Cd})} = c_{(\text{Pb})} = 100 \mu\text{g}\cdot\text{L}^{-1}$, $c_{(\text{Bi})} = 1 \text{ mg}\cdot\text{L}^{-1}$. SWASV condition: deposition potential, $E_{\text{dep}} = -1 \text{ V}$; final potential, $E_{\text{fin}} = 0.1 \text{ V}$; deposition time, $t_{\text{dep}} = 90 \text{ s}$; equilibrium period, $t_{\text{eq}} = 15 \text{ s}$; frequency, $f_{\text{sw}} = 25 \text{ Hz}$; pulse height, $\Delta E = 20 \text{ mV}$; increment = 4 mV .

Effect of Bi(III) Concentration for *in situ* Prepared Bi-MWCNTPE and its Impact on Current Responses of Cd(II) and Pb(II)

The concentration of Bi(III) in the solution to be analysed affects the formation of bismuth film layer on the electrode surface and has considerable influence on the current response of corresponding metals [30]. This key parameter was investigated at three different metal concentration level ($c_{(\text{Me})} = 10 \mu\text{g}\cdot\text{L}^{-1}$; $100 \mu\text{g}\cdot\text{L}^{-1}$ and $1 \text{ mg}\cdot\text{L}^{-1}$) with bismuth to metal concentration ratio from $c_{(\text{Bi})} : c_{(\text{Me})} = 0$ (for bare MWCNTPE) to $c_{\text{Bi}} : c_{\text{Me}} = 100$. At the low metal concentration level ($c_{(\text{Me})} = 10 \mu\text{g}\cdot\text{L}^{-1}$ and $100 \mu\text{g}\cdot\text{L}^{-1}$) the highest responses were obtained when using bismuth concentration $c_{(\text{Bi})} : c_{(\text{Me})} = 5$; respective $50 \mu\text{g}\cdot\text{L}^{-1}$ of Bi(III) for $c_{(\text{Me})} = 10 \mu\text{g}\cdot\text{L}^{-1}$ and analogically $500 \mu\text{g}\cdot\text{L}^{-1}$ of Bi(III) for $c_{(\text{Me})} = 100 \mu\text{g}\cdot\text{L}^{-1}$ (Fig. 4 A, B). At high metal concentration level ($c_{(\text{Me})} = 1 \text{ mg}\cdot\text{L}^{-1}$) current response of Cd(II) with the increased bismuth concentration is almost constant in contrast to the decreasing response of Pb(II) (Fig. 4 C). With respect to this and considering further experiments, the ratio of bismuth to metal ($c_{(\text{Bi})} : c_{(\text{Me})} = 5$) was used.

In order to keep this ratio constant during the whole calibration measurements, the bismuth concentration was adjusted after each metal addition, achieving thus the “ $c_{(Bi)} / c_{(Me)}$ ” ratio to remain unchanged.

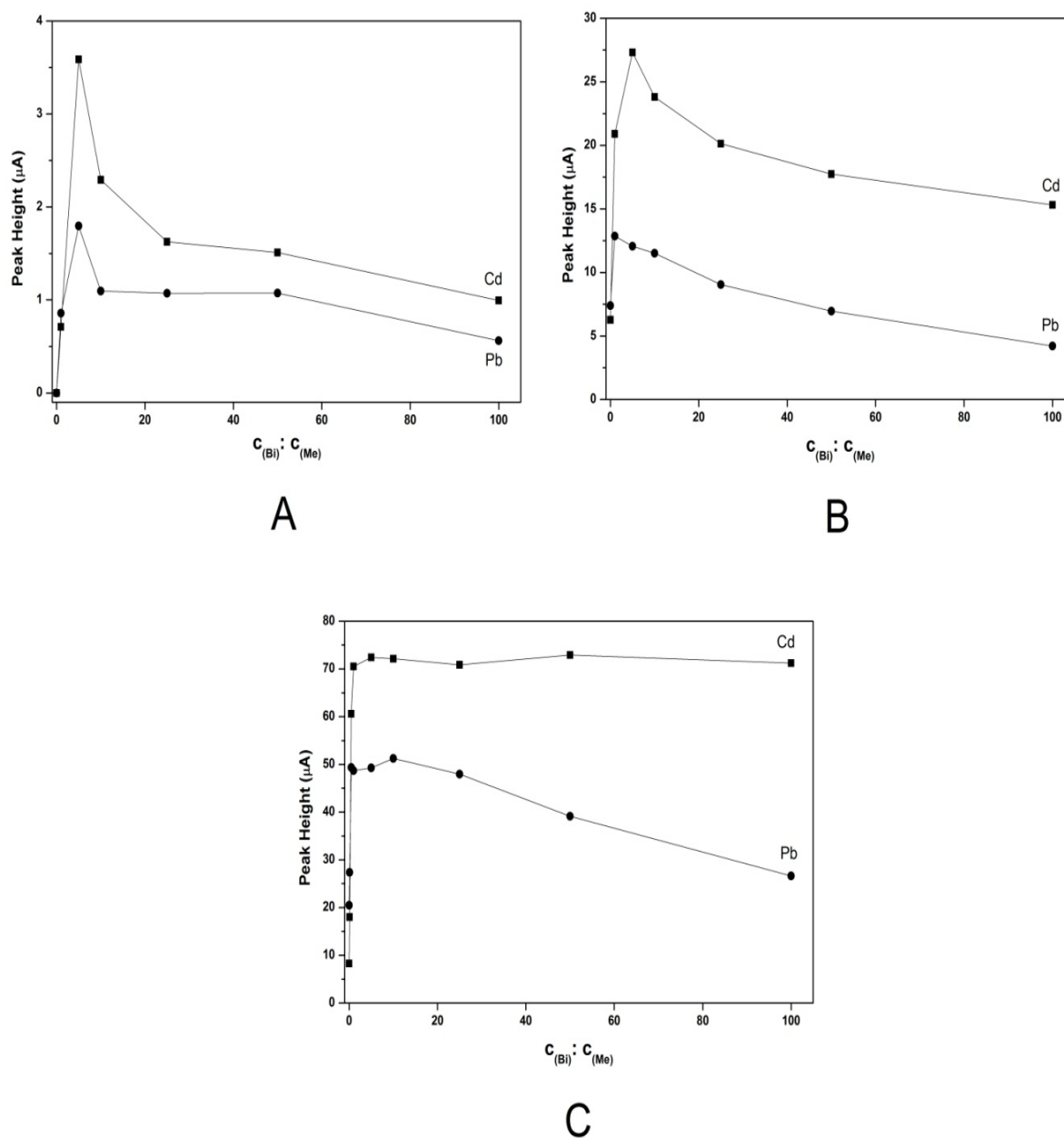


Fig. 4: Effect of bismuth concentration on responses of Cd(II) and Pb(II).

Legend: Electrode: Bi-MWCNTPE. Solution: 0.2 M acetate buffer; $c_{(Cd)} = c_{(Pb)} = 10 \mu g \cdot L^{-1}$ (A), $c_{(Cd)} = c_{(Pb)} = 100 \mu g \cdot L^{-1}$ (B), $c_{(Cd)} = c_{(Pb)} = 1 mg \cdot L^{-1}$ (C). SWASV condition: deposition potential, $E_{dep} = -1.0$ V; final potential, $E_{fin} = 0.1$ V; deposition time, $t_{dep} = 300$ s (A), $t_{dep} = 120$ s (B), $t_{dep} = 60$ s (C) equilibrium period, $t_{eq} = 15$ s; frequency of the SWV ramp, $f_{sw} = 25$ Hz; the pulse height, $\Delta E = 20$ mV; increment = 4 mV.

Investigation of Key Parameters of Electrochemical Stripping Analysis and Model Calibrations of Cd(II) and Pb(II)

As can be seen in Fig. 5, the deposition potential has influence on the current response of cadmium and lead; the optimal value for the deposition and the determination of both Cd(II) and Pb(II) being -1.0 V vs. ref. Moreover, it is interesting to notice that the peak height for Pb was less affected by the deposition potential when compared to the signal for the reoxidation of Cd (see again Fig. 5)

It is well known that longer deposition times result in higher current responses due to the reduction of larger amount of the species deposited at the electrode surface [30]. Of course, the respective pathway is limited by the actual character of the electrode surface and its tendency to be saturated by the increased amount (layer) of the deposited metal. As found out for Bi-MWCNTPE, even a very long deposition time of 1800 s (≈ 30 min) used did not result in any more pronounced saturation (not shown).

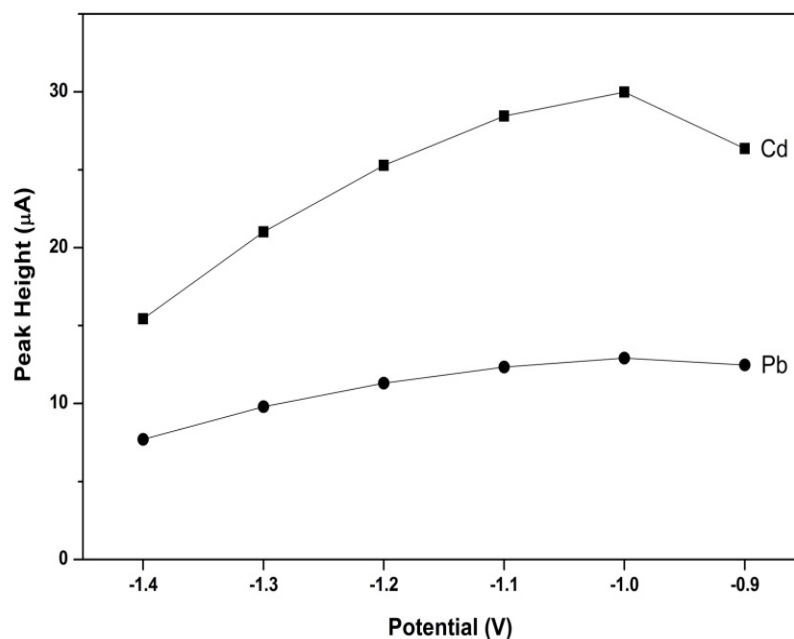


Fig. 5: Effect of deposition potential on responses of Cd(II) and Pb(II).

Legend: Electrode: Bi-MWCNTPE. Solution: 0.2M acetate buffer; $c_{\text{Cd}} = c_{\text{Pb}} = 100 \mu\text{g}\cdot\text{L}^{-1}$, $c_{\text{Bi}} = 500 \mu\text{g}\cdot\text{L}^{-1}$. SWASV condition: deposition potential, $E_{\text{dep}} = -1$ V; final potential, $E_{\text{fin}} = 0.1$ V; deposition time, $t_{\text{dep}} = 90$ s, equilibrium period, $t_{\text{eq}} = 15$ s; frequency, $f_{\text{sw}} = 25$ Hz; pulse height, $\Delta E = 20$ mV; increment = 4 mV.

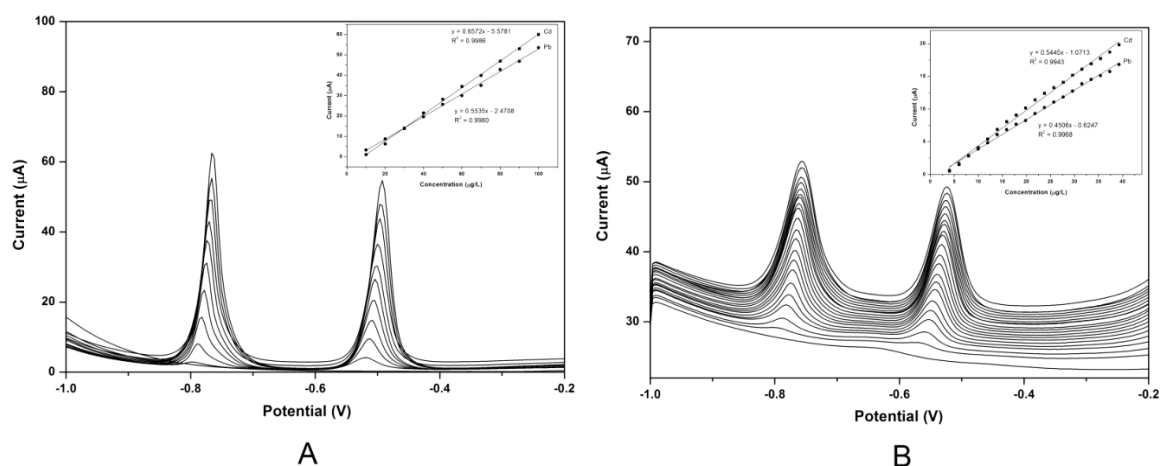


Fig. 6: Effect of deposition potential on responses of Cd(II) and Pb(II).

Legend: Electrode: Bi-MWCNTPE. Solution: (A) 0.1M HCl; $c_{(Cd)} = c_{(Pb)} = 10\text{--}100 \mu\text{g}\cdot\text{L}^{-1}$; (B) 0.2M acetate buffer, $c_{(Cd)} = c_{(Pb)} = 4\text{--}40 \mu\text{g}\cdot\text{L}^{-1}$; $c_{(Bi)} = 5 \times c_{(Me)}$. SWASV condition: deposition potential, $E_{dep} = -1 \text{ V}$; final potential, $E_{fin} = 0.1 \text{ V}$; deposition time: (A) $t_{dep} = 300 \text{ s}$, (B) $t_{dep} = 600 \text{ s}$; equilibrium period, $t_{eq} = 15 \text{ s}$; frequency, $f_{sw} = 25 \text{ Hz}$; pulse height, $\Delta E = 20 \text{ mV}$; increment = 4 mV .

Fig. 6A illustrates a very fine linearity of the signals Cd(II) or Pb(II) calibrated over the concentration range of $10\text{--}100 \mu\text{g}\cdot\text{L}^{-1}$ (in the inset, the respective correlation coefficients are: $r^2(\text{Cd}) = 0.9986$ and $r^2(\text{Pb}) = 0.9980$). The calibration in the concentration range of $4\text{--}40 \mu\text{g}\cdot\text{L}^{-1}$ Cd(II) or Pb(II) for more precise analysis at low $\mu\text{g}\cdot\text{L}^{-1}$ level shows fig 6B (in the inset, the respective correlation coefficients are: $r^2(\text{Cd}) = 0.9943$ and $r^2(\text{Pb}) = 0.9968$).

Conclusions

In this article, a novel type of carbon nanotube paste electrode with *in situ* coated bismuth film has been introduced and tested for determination of Cd(II) and Pb(II) by square-wave anodic stripping voltammetry (SWASV). All the key parameters were studied and systematically optimized, having found that:

- (i) Carbon nanotube paste electrode prepared from multi-walled carbon nanotube (MWCNTPE) seems appropriate for SWASV of heavy metals. Electrode prepared from single-walled CNTs did not exhibit satisfactory results.
- (ii) MWCNTPE coated with bismuth film provide enhanced current responses of Cd(II) and Pb(II) when compare with classical bismuth coated carbon paste electrode.

(iii) Optimal supporting medium is hydrochloric acid-based solution (with $\text{pH} \approx 1$) and acetate buffer ($\text{pH} \approx 4.5$) in the concentration range 0.1 – 0.5 M.

(iv) The proper concentration of Bi(III) for depositing the bismuth film *in situ* was found to be a 5-fold excess with respect to the metal concentration analysed; $c_{\text{Bi}} = 5 \times c_{\text{Me}}$.

(v) Optimal deposition potential: $E_{\text{dep}} = -1.0 \text{ V vs. ref.}$

It can be concluded that the Bi-MWCNTPE could be used for determination of Cd(II) and Pb(II) ions at the $\mu\text{g-per-litre}$ level (4–100 $\mu\text{g}\cdot\text{L}^{-1}$). Otherwise, the initial study presented in the above sections requires yet further continuation. For instance, some second-phase investigation should be focused on more detailed optimization, inevitable interference studies with other heavy metals (*e.g.* Zn, Tl, In, and Sn) or even other potentially competing species, such as other co-alloying metals, complex forming agents, or some industrial surfactants.

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