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Determination of Lead and Cadmium in Water Samples by Adsorptive Stripping Voltammetry Using a Bismuth film/1-Nitroso-2-Napthol/Nafion Modified Glassy Carbon Electrode

Rodrigo A. Segura[*], *Jaime A. Pizarro, María P. Oyarzun, Alejandra D. Castillo, Karina J. Díaz, Alan B. Placencio.*

Facultad de Química y Biología, Departamento de Química de los Materiales, Universidad de Santiago de Chile (USACH), Casilla 40, Correo 33, Santiago, Chile, 562–27181172.
[*]E-mail: rodrigo.segura@usach.cl

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The application and validation of a glassy carbon electrode modified with Nafion, 1-nitroso-2-naphthol and bismuth film (GC/NF-NN/BiFE) was studied using adsorptive stripping voltammetry (AdSV) for the determination of Pb^{2+} and Cd^{2+} in tap water. The parameters studied and optimized were pH, 1-nitroso-2-naphthol concentration (C_{NN}), Nafion concentration (C_{NF}), adsorption potential (E_{acc}) and adsorption time (t_{acc}). Optimal conditions were pH 4.5 (acetate buffer solution 0.10 mol L^{-1}); E_{acc}: -1.30 V; t_{acc}: 120 s; C_{NN} : 0.10% w/v, C_{NF}: 0.50 wt %. The detection and quantification limits were 0.08 and 0.29 μg L^{-1} for Pb^{2+} and 0.07 and 0.24 μg L^{-1} for Cd^{2+}, with a linear range of 10 to 70 μg L^{-1}. Certified reference material (ICP Multi Element Standard) and synthetic samples were determined to validate the methodology, with satisfactory results. The stripping voltammetry method was tested on tap water.

Keywords: Adsorptive stripping voltammetry, bismuth film electrode, Nafion, cadmium and lead

1. INTRODUCTION

There is growing concern about the contamination of natural water with heavy metals due to the detrimental impact of those elements on the environment. Considerable amounts of heavy metals are released into the water systems (lakes, rivers, oceans, etc.) from various anthropogenic sources like municipal sewage effluents, garbage incineration, combustion of fossil fuels, mining, metallurgical industry, agricultural runoff, etc. [1]. Even at low concentrations (10^{-7}-10^{-11} mol L^{-1}) heavy metals may present a serious hazard to the normal functioning of aquatic systems because some of them are very toxic, not biodegradable, and are involved in biogeochemical processes [2]. In natural waters heavy metals exist generally in particulate and dissolved form, such as inorganic species, organic complexes, and metal ions adsorbed on a variety of colloidal particles [3, 4]. Any variation in the speciation of heavy metals will influence their bioavailability, toxicity and geochemical behavior (e.g., mobility, adsorption and precipitation) in natural water [5, 6].

To evaluate and understand the contamination of aqueous system with heavy metals, are required analytical techniques with low detection limits. The different methods adopted for measuring the concentration of the metal ions are mainly focused on the use of atomic absorption spectroscopy (AAS) [7-9], inductively coupled plasma optical emission spectrometry (ICP-OES), inductively coupled plasma mass spectrometry (ICP-MS) [10-12], and ion chromatography [13]. However, spectroscopic methods are complex and not suitable for in situ measurements, but stripping analysis has been described as a very powerful electrochemical technique for trace metal measurement. The strength of stripping voltammetry lies in its extremely low detection limits (10^{-11}-10^{-13} mol L^{-1}), its multielement and speciation capabilities, and its suitability for in-situ applications [14, 15]. Using these methods, trace concentration of heavy metals can be determined directly without any sample pretreatment, such as external preconcentration or matrix separation, that are commonly required for other analytical techniques.

The most widely used electrochemical methods are anodic stripping voltammetry (ASV), cathodic stripping voltammetry (CSV), and adsorptive stripping voltammetry (AdSV), techniques that have attracted growing interest due to their high sensitivity, portability and low cost. Their remarkable sensitivity is attributed to the combination of an effective preconcentration step with pulse measurement that generates an extremely favorable signal to background ratio. Two electrode systems, the mercury film electrode (MFE) and the hanging mercury drop electrode (HMDE) have been traditionally employed to achieve high reproducibility and sensitivity in the stripping technique. The excellent performance of mercury based electrodes is due to their unique ability to preconcentrate the target metals during the accumulation step [16, 17], but because of the toxicity of mercury its use is being restricted [18], due to this, it is necessary to search alternative materials for the construction of electrodes in stripping analysis as boron doped diamond [19], bismuth film electrodes (BiFE) [20-23], antimony [24], lead and screen-printed electrodes, and chemically modified electrode (CMEs) [25, 26] have been developed.

The BiFE was introduced as an extremely promising alternative because it does not has a toxic character compared to mercury-containing electrodes [23, 27-29]. BiFE has been used mainly in the determination of Cu [30], Cd [31, 32] , Pb[32] , Fe [33], Sn [34], Co [35-37], Ni [38, 39], Mo [40], Cr [41, 42] and V [43].This electrode has various characteristics such as high sensitivity, well defined and resolved signals similar to mercury electrode, but one of the most important interferences for this electrode is the presence of surfactants that are adsorbed on the electrode's surface. However, to reduce this interference, the electrode surface is covered with a semipermeable membrane of Nafion that provides mechanical stability, and because it is a cation exchanger it is used to pre-concentrate metal ions, excluding anion interference. In this paper we report the construction and the favorable adsorptive stripping performance of a mercury-free, Nafion/bismuth film-modified glassy carbon electrode incorporating a chelating agent (NN) for Cd^{2+} and Pb^{2+} determination in tap water.

2. EXPERIMENTAL PART

2.1 Instruments.

All electrochemical measurements were obtained with a CHI 660A electrochemical analyzer (CHInstruments) in a three−electrode configuration. A 10 mL capacity cell was equipped with a glassy carbon electrode (3 mm diameter, BAS, USA) which was used as working electrode. A reference electrode of Ag/AgCl/KCl (3 mol L^{-1}) and a platinum wire auxiliary electrode. An Orion 430 pH meter was used for pH measurements. All measurements were performed at room temperature. To compare results, an ICP-OES Perkin Elmer Optima 2000 DV was used.

2.2 Reagents

All solutions were prepared with ultra pure water from a Milli-Q system (18.2 MΩ cm^{-1} Millipore USA). Bismuth, cadmium and lead standard solutions were prepared by diluting the 1000 mg L^{-1} standard solutions from Merck (Darmstadt, Germany). Acetic acid buffers 0.10 mol L^{-1} (pH 3.0 to 6.0) were prepared by dissolving 5.7 mL of acid in water and diluting to 1 L. The pH was adjusted with sodium hydroxide solution. A 0.25% w/v solution of 1-nitroso-2-napthol (NN) (Sigma) was prepared by dissolving 0.2493 g in 100 mL of ethanol. Nafion (5 wt % in a mixture of lower aliphatic alcohols and water) was obtained from Sigma–Aldrich (USA).

2.3 Preparation of BiFE electrodes

The glassy carbon electrodes were polished with a polishing pad using 0.3 µm Al_2O_3 slurry. The electrodes were rinsed with doubly distilled water, methanol and sonicated in methanol to remove any residual materials. An aliquot (20 µL) of the coating solution with different NN and Nafion (%) ratios in ethanol was applied to the surface of the glassy carbon electrode. After solvent evaporation at room temperature, the electrode was inserted in a cell containing an aqueous solution of Bi^{3+} (100 mg L^{-1}) in 0.1 mol L^{-1} acetate buffer (pH 5.0). A film of bismuth was obtained by applying −1.0 V for 120 s. After, the BiFE was rinsed with water and immersed in the test solution.

2.4 General voltammetric procedure.

In the electrochemical cell were added 8 mL of deionized water (or tap water samples), 2.0 mL of acetate buffer solution (0.1 mol L^{-1}), and aliquots of Cd^{2+} and Pb^{2+} solutions (1.0 mg L^{-1}). The preconcentration step was studied using different t_{acc} and E_{acc} with a stirring rate of 700 rpm. After an equilibration time of 10 s, adsorptive voltammograms were recorded, while the potential was scanned from −0.10 to −1.10 V using square wave modulation with 5 mV step amplitude, 15 mV pulse amplitude, and a frequency of 25 Hz. Each voltammogram was repeated three times. Linear regression and limits of detection (LOD) were calculated. The LOD were calculated from $y\text{DL} = a + 3S_{x/y}$ and $y\text{DL} = a + bx\text{DL}$, where a is the intercept, $S_{x/y}$ is the random error in x and y, and b is the slope [43].

The proposed method was applied to the determination of Pb^{2+} and Cd^{2+} in tap water. To eliminate matrix effects the standard addition method was used. All data were obtained at room temperature (25 ºC).

3. RESULTS AND DISCUSSION

3.1 Adsorptive stripping voltammetry

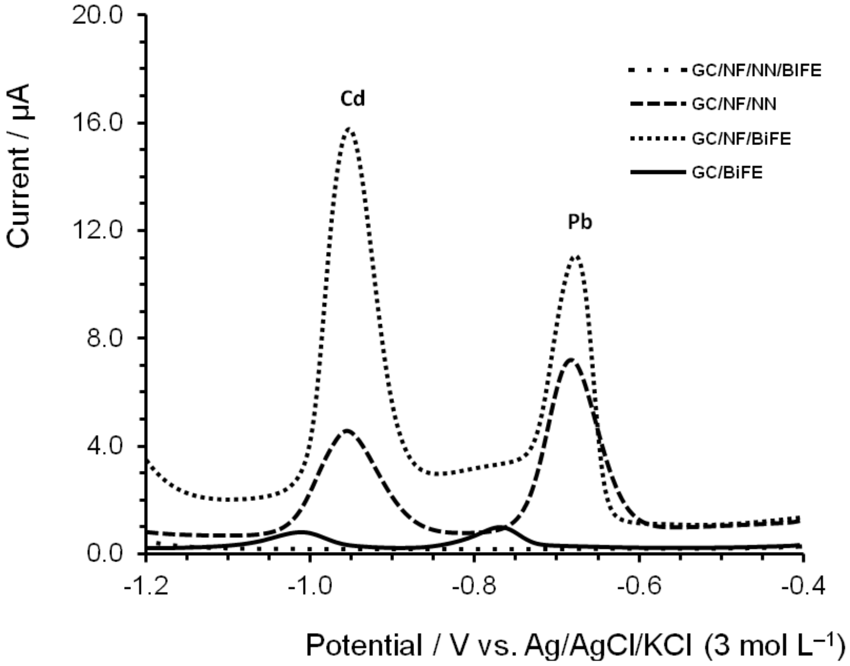

Figure 1. Adsorptive stripping signal (SWAdSV) of 30 µg L^{-1} Cd^{2+} and Pb^{2+} on modified glassy carbon electrodes: GC/BiFE, GC/NF/BiFE, GC/NF/BiFE and GC/NF/NN/BiFE. Measurement parameters: acetate buffer solution pH = 4.5, C_{NN} = 0.10% w/v, C_{NF} = 0.50 wt %, E_{acc} = -1.40 V, t_{acc} = 120 s, potential amplitude = 25 mV, frequency = 15 Hz, and stirring rate 700 rpm.

In preliminary studies, glassy carbon bismuth film electrode (GC/BiFE), glassy carbon nafion bismuth film electrode (GC/NF/BiFE), glassy carbon nafion 1-nitroso-2 naphtol electrode (GC/NF/NN) and glassy carbon nafion 1-nitroso-2 naphtol bismuth film electrode (GC/NF/NN/BiFE), were used to evaluate the effect on the current of 30 µg L^{-1} of Cd^{2+} and Pb^{2+}, and the results are shown in Figure 1. The GC/NF/BIFE, GC/NF/NN and GC/NF/NN/BIFE electrodes show well defined signals for Cd^{2+} and Pb^{2+}, and GC/BiFE just shows one signal associated with Pb^{2+} (-1.05 V). Potential shifts from –1.05 V to -0.87 V (Pb^{2+}) and –0.75 V to –0.62 V (Cd^{2+}) are seen. The highest current response was obtained using GC/NF/NN/BiFE, and this is attributable to three effects: (1) Nafion stabilizes the bismuth film and improves the preconcentration step, (2) the higher sensitivity and better selectivity due to the chelating effect of NN, and (3) the accumulation effect of the bismuth film [44-46]. This is due to the increase of the number of actives sites in the coating film caused by the incorporation of the chelating agent (NN), into the hydrophobic perfluorinated chains of the Nafion matrix [47].

3.2 Influence of pH

The effect of pH on the AdSV peak was studied between pH 3.5 to 6.0 in acetate/acetic acid buffer (0.10 mol L^{-1}), and the results are presented in Figure 2. The experimental conditions were: Pb^{2+} and Cd^{2+} 30.0 µg L^{-1}; C_{NN} = 0.10%, C_{NF} = 0.50%; E_{acc} = -1.40 V, and t_{acc} = 120 s.

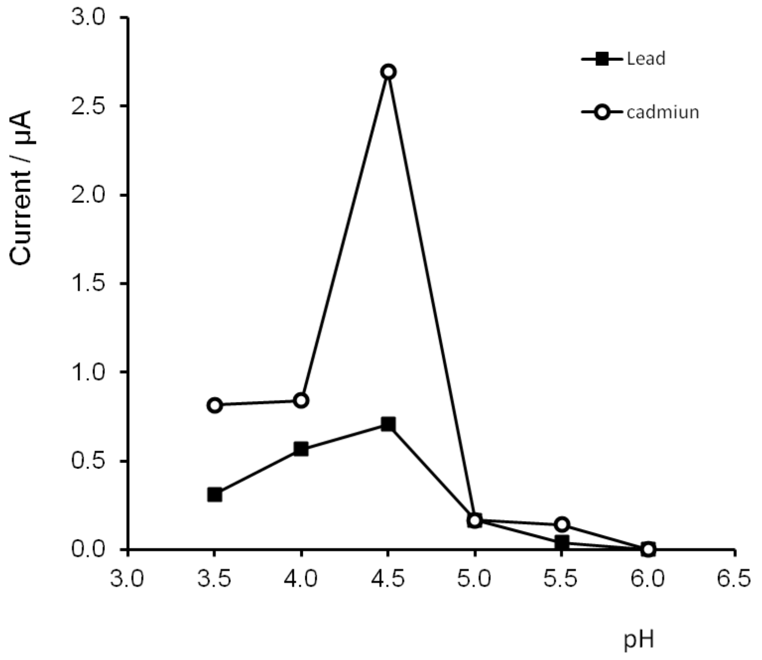

Figure 2. Effect of pH. Acetate buffer solution 0.1 mol L^{-1}; $C_{Pb}{}^{2+}$ and $C_{Cd}{}^{2+}$ = 30 µg L^{-1}; C_{NN} = 0.10% w/v C_{NF} = 0.50 wt %; E_{acc} = -1.40 V; t_{acc} = 30 s, pulse amplitude = 25 mV; step potential = 4 mV; frequency = 15 Hz; and stirring rate 700 rpm.

It was found that at pH 4.5 the peak current of Cd^{2+} and Pb^{2+} presents a maximum, at lower pH the current decreases, this can be attributed to the competition between the analyte and the proton for the ionic exchange sites of the nafion and the binding sites of 1-nitroso-2-naphthol (complexing agent) [47]. At higher pH the current signal of the complex decreases and this can be attributed to precipitation of the metal ions.

3.3 Influence of Adsorption Potential (E_{acc})

The adsorption of analyte on the modified electrode surface depends on the charge of the analyte at a specific potential and supporting electrolyte. Positively charged compounds are adsorbed on negatively charged surfaces, or conversely, as well as neutral compounds will be absorbed on neutral surfaces (zero charge potential) [48]. Figure 3 shows the influence of potential on the peak current signal of Cd^{2+} and Pb^{2+}. With lead the current increases sharply from -0.65 V, and this is attributed to the contribution of the diffusion and adsorption processes. With cadmium there is a two-step signal increase from -0.30 to -0.75 V, reaching a plateau at -0.80 V attributable to an adsorptive process, and there is an increased current attributable to diffusion and adsorption processes. The optimum accumulation potential was -1.40 V.

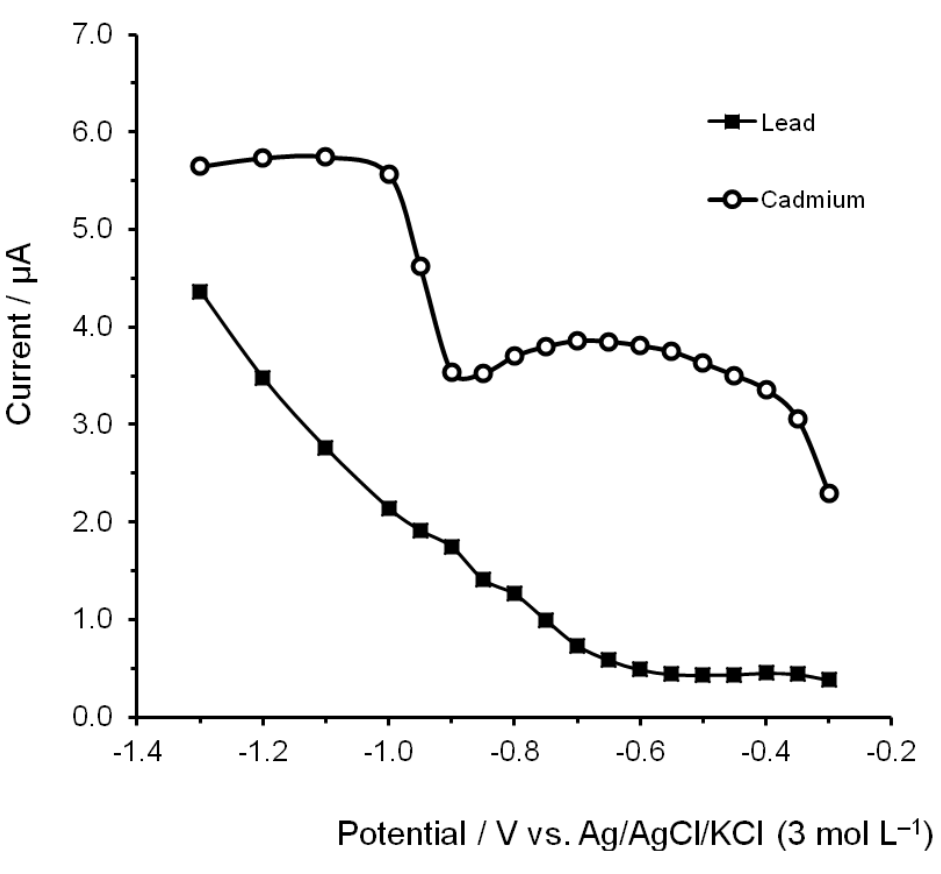

Figure 3. Effect of accumulation (E_{acc}). Conditions: acetate buffer solution 0.1 mol L^{-1}, pH = 4.5; C_{Pb}^{2+} and C_{Cd}^{2+} = 30 µg L^{-1}; C_{NN} = 0.10 w/v%; C_{NF} = 0.50 wt %; t_{acc} = 30 s; pulse amplitude = 25 mV; step potential = 4 mV; frequency = 15 Hz; and stirring rate 700 rpm.

3.4 Influence of time on the accumulation step (t_{acc})

Accumulation time depends on the analyte concentration in the sample; at lower concentrations more time is needed to reach saturation of the electrode. At higher analyte concentrations the binding sites of the modified electrode can be saturated in a shorter time. Therefore, the measurement range can be controlled by choosing a suitable preconcentration time, which must be within the linearity zone [49-52]. Figure 4 shows an increase of the peak currents of Cd^{2+} and Pb^{2+} between 15-120 s, with a maximum at 120 s for both ions, at which time the current reaches a plateau attributed to the saturation of the active sites.

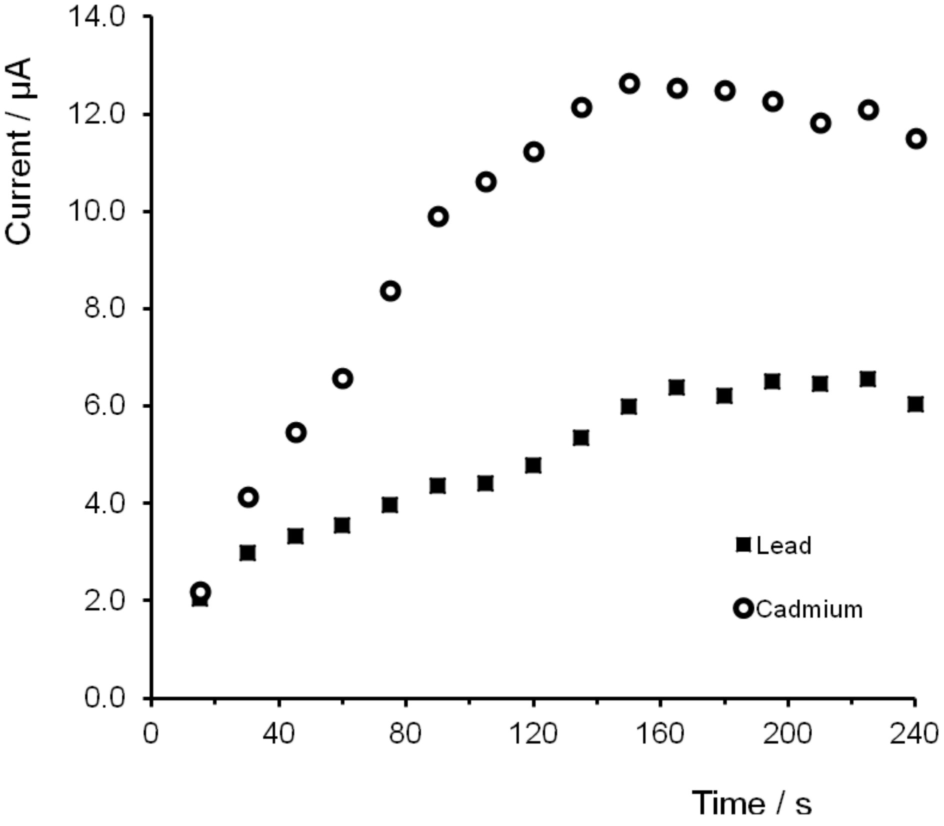

Figure 4. Effect of accumulation time (t_{acc}). Conditions: acetate buffer solution 0.10 mol L^{-1}, pH = 4.5; C_{Pb}^{2+} and C_{Cd}^{2+} = 30 µg L^{-1}; C_{NN} = 0.10 w/v %; C_{NF} = 0.50 wt %; E_{acc} = -1.40 V; pulse amplitude = 25 mV; step potential = 4 mV; frequency = 15 Hz; and stirring rate 700 rpm.

3.5 Influence of Nafion (NF) and NN concentrations

The effect of the concentration of Nafion in current peak for Cd^{2+} and Pb^{2+} was evaluated by preparing modified electrodes by the drop coating technique using 20 µL aliquots with different concentrations of NF (0.20 - 1.50 wt %) and a constant concentration of NN (0.10 w/v %). Figure 5 shows the effect of NF film thickness on the current response of the electrode towards Cd^{2+} and Pb^{2+}. The response of both metal ions increases from 0.20 wt %, reaching a maximum at 0.50 wt %, and at higher concentrations it decreases; similar results have been reported [24, 44-46]. This phenomenon can be explained by the fact that thick Nafion films displayed large cracks due to contractive forces within the film. Through these openings in the polymer structure the oxidized species can diffuse away from the electrode's surface to the bulk of the solution, decreasing its concentration at the electrode solution interface [47, 53, 54].

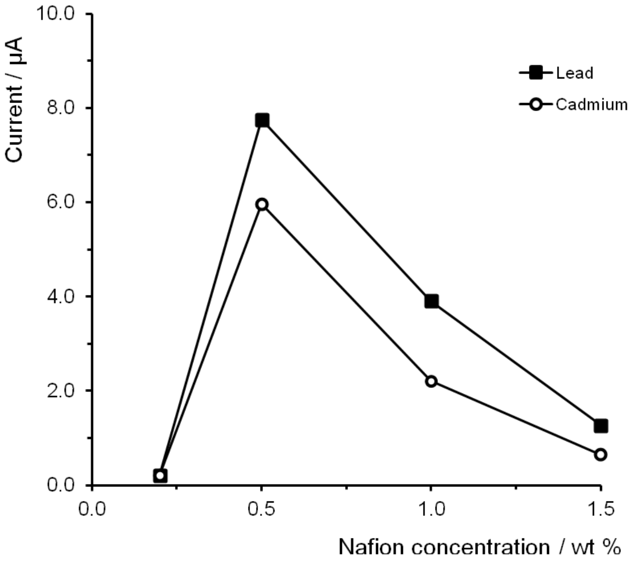

Figure 5. Effect of the concentration of NF used in the mix with NN. Conditions: Acetate buffer solution 0.10 mol L^{-1}, pH = 4.5; C_{Pb}^{2+} and C_{Cd}^{2+} = 30 µg L^{-1}; C_{NN} = 0.10 %; E_{acc} = -1.40 V; t_{acc} = 120 s; step potential = 4 mV; pulse amplitude = 25 mV; frequency = 15 Hz; and stirring rate 700 rpm.

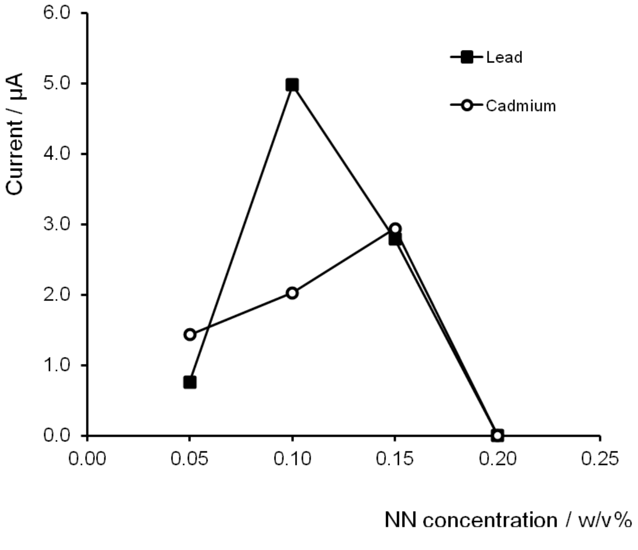

Figure 6. Effect of NN concentration on the peak current of Cd^{2+} and Pb^{2+} at 30 µg L^{-1}. SWAdSV measurement parameters are: acetate buffer solution 0.10 mol L^{-1}, pH = 4.5; C_{NF} = 0.50 wt %; E_{acc} = -1.40 V; t_{acc} = 120 s; step potential = 4 mV; pulse amplitude = 25 mV; frequency = 15 Hz; and stirring rate 700 rpm.

The influence of the NN concentration on the film was investigated between 0.05 - 0.25% w/v in the coating solution, while the Nafion 0.5 wt % concentration remained constant. Figure 6 indicates that the peak current reaches a maximum value at 0.10 and 0.15% w/v for Cd^{2+} and Pb^{2+} respectively.

The higher voltammetric response can be explained by the increase of binding sites in the nonpolar part of the Nafion film, while the decrease in response is associated with the lower adhesion between the film and the glassy carbon as a consequence of the increased amount of NN–metal ion complex in the film [24, 48]. Electrodes prepared with the optimum composition of the coating solution, i.e., containing 0.50 wt % Nafion and 0.10 % w/v NN content, were used in all subsequent work.

3.6 Effect of frequency

The effect of the frequency of SWAdSV was studied in relation to the peak current of both metal ions, and the results are presented in Figure 7. It shows that current increases with frequency, reaching a maximum in 40 and 20 Hz for Cd^{2+} and Pb^{2+}, respectively. After reaching the maximum, the current signal is distorted for both metals, presenting oscillations. A frequency must be chosen that does not affect the reproducibility of the signals, so it is not recommended to use values above 30 Hz. A frequency of 15 Hz was chosen as the optimum because clear and well defined currents peaks are obtained, with good sensitivity for both metals.

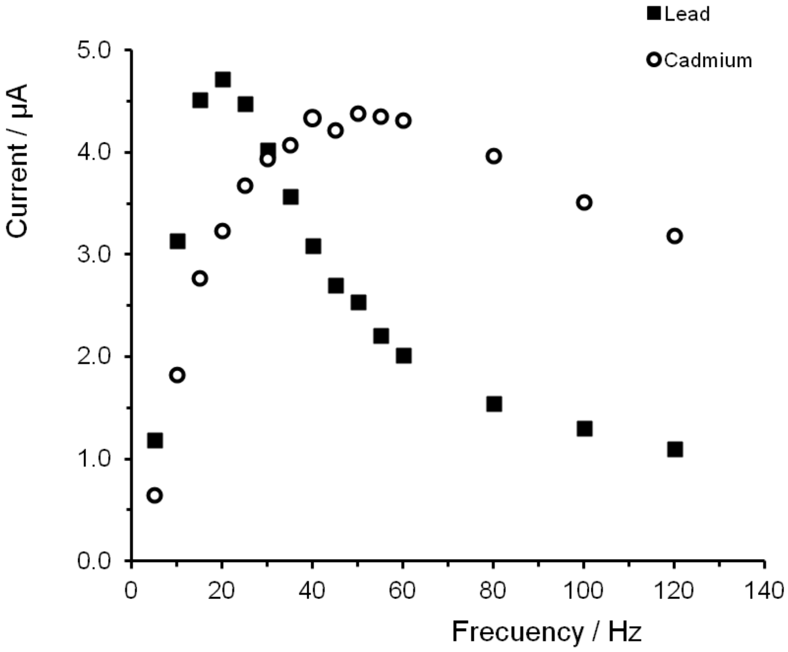

Figure 7. Effect of frequency in acetate buffer 0.10 mol L^{-1}, pH = 4.5; C_{Pb}^{2+} and C_{Cd}^{2+} = 30 µg L^{-1}; C_{NN} = 0.10 w/v %; C_{NF} = 0.50 wt %; E_{acc} = -1.40 V; t_{acc} = 120 s; step potential = 4 mV; pulse amplitude = 25 Hz; frequency = 15 Hz; and stirring rate 700 rpm.

3.7 Linear range, detection limit, and reproducibility of the method

Stripping voltammograms and calibration curves are shown in Figures 8a and 8b, respectively. Each measurement was performed with the same electrode.

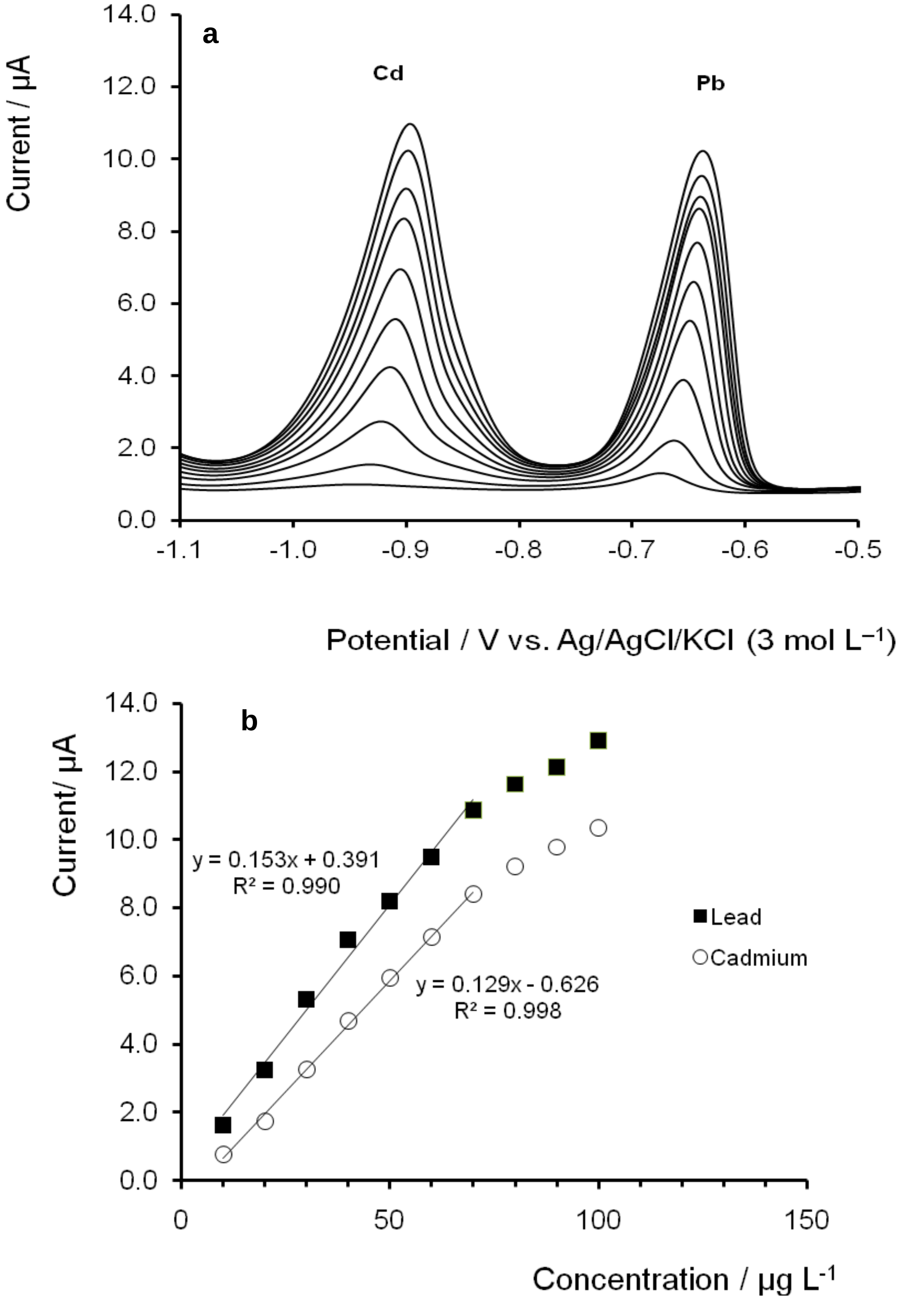

Figure 8. a Linear range and calibration curve of **b** AdSV voltammogram for additions of 10, 20, 30, 40, 50, 60,70, 80, 90, 100 μg L^{-1} Cd^{2+} and Pb^{2+} in acetate buffer solution 0.1 mol L^{-1}, pH = 4.5**;** C_{NN} = 0.10 w/v %**;** C_{NF} = 0.50 wt %**;** E_{acc} = -1.40 V**;** t_{acc} = 120 s**;** step potential = 4 mV**;** pulse amplitude = 25 Hz**;** frequency = 15 Hz**;** and stirring rate 700 rpm.

Under these optimal conditions the peak current was proportional to the concentration of Pb^{2+} between 10.0 – 70.0 μg L^{-1}, with a 3σ detection limit of 0.03 μg L^{-1}, and for Cd^{2+} between 10.0 –100.0

µg L^{-1} , with a 3σ detection limit of 0.02 µg L^{-1}. The reproducibility of the electrode preparation procedure was evaluated considering the current signal of 10 µg L^{-1} of Cd^{2+} and Pb^{2+} using five modified electrodes founding a RSD of 7.32 % for Cd^{2+} and 5.24 % for Pb^{2+}. The repeteatibility was evaluated using the same electrode and a solution containing 10 µg L^{-1} of each metal ion with a RSD (n=6) of 3.78 % (Cd^{2+}) and 6.34 % (Pb^{2+}). These results confirmed a good reproducibility and repeatability of the prepared electrode in voltammetric determinations. The accuracy was evaluated with ICP certified standard XXIV with a relative error of 4.38 % (Cd^{2+}) and 6.89 % (Pb^{2+}). A solution of 30 µg L^{-1} of Pb^{2+} and Cd^{2+} was prepared using ICP certified standard XXIV and analyzed by AdSV and ICP-MS, not founding statistical differences between both results (Table 1).

Table 1. Accuracy of the methods

Metal	***AdSV [µg L^{-1}]***	***ICP-MS [µg L^{-1}]***
Pb^{2+}	28.8	28.6
Cd^{2+}	30.5	28.9

3.8 Interference study

The interference study was performed by adding (up to 100 µg L^{-1}) Fe^{3+}, Mo^{3+}, Cu^{2+}, As^{3+}, Al^{3+}, Zn^{2+}, Co^{2+}, and Ni^{2+} to a buffer solution containing 20 µg L^{-1} of Pb^{2+} and Cd^{2+} under the optimum conditions. It was found that all these elements do not interfere in the measurements. The criterion for interference was ± 10% of change in the signal current.

3.9 Real water samples

The method was also applied to two real tap water samples fortified with 20 µg L^{-1} of Cd^{2+} and Pb^{2+}. The samples were analyzed (n = 6) without prior treatment using the standard addition method, and the results are presented in Table 2, showing that for all measurements the RSD is less than 5%.

Table 2. Analysis of Pb^{2+} and Cd^{2+} in real tap water samples.

	Metal	**$\bar{x}$ (µg L^{-1})**	**RSD**
M1 (n=6)	Pb^{2+}	19.21	4.74
	Cd^{2+}	21.07	2.03
M2 (n=6)	Pb^{2+}	20.88	2.90
	Cd^{2+}	19.27	3.06

4. CONCLUSION

In this work, a GC/NN-NF/BiFE electrode was developed and used for the simultaneous determination of lead and cadmium by adsorptive stripping voltammetry. Nafion provides mechanical stability to the bismuth film, and the incorporation of 1-nitroso-2-naphthol improved sensitivity and selectivity. Chemical and electrochemical parameters were optimized and applied to the simultaneous determination of tap water fortified with cadmium and lead.

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