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Disposable screen-printed electrode modified with bismuth–PSS composites as high sensitive sensor for cadmium and lead determination

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ABSTRACT

Bismuth was incorporated in screen-printed carbon electrodes (SPCEs) modified with polystyrene sulfonate (PSS) and carbon nanopowder (CnP) composites. Different strategies, based on bulk approaches using bismuth oxide particles and bismuth (III) solutions, were assayed. The features of the modified electrodes were evaluated by differential pulse anodic stripping voltammetry (DPASV) of Pb(II) and Cd(II) solutions. The best results were obtained when bismuth was incorporated as bismuth oxide particles during the preparation of the PSS–CnP aqueous suspension used to modify the electrodes. Using this optimal modified sensor, the DPASV measurement conditions for Pb(II) and Cd(II) determination were optimized and their figures of merit were evaluated. Measurements were performed using two experimental approaches: the "drop method", by putting the test solution on the surface of the modified SPCE, and the "immersion method" performed by immersing the device in a stirred test solution. The limits of detection (S/N = 3) were 0.27 μg L^{-1} (1.3×10^{-9} M) for Pb(II) and 0.10 μg L^{-1} (9.0×10^{-10} M) for Cd(II), using the "drop method", and 0.029 μg L^{-1} (1.4×10^{-10} M) for Pb(II) and 0.012 μg L^{-1} (1.1×10^{-10} M) for Cd(II) employing the immersion procedure. The optimal bismuth modified SPCE was used for Pb(II) and Cd(II) determination in natural water samples with successful results.

1. Introduction

The presence of toxic elements, such as Cd(II) and Pb(II), in the environment is of particular concern due to their adverse effects on ecosystems and human health [1,2]. Pollution by these metals has been increasing in the environment and therefore international organisms have established guidelines and quality standards in drinking-water to protect public health [3,4].

Electrochemical techniques can be used for heavy metal determination and, contrary to the most used atomic methodologies, they are portable, low-cost and suitable for *in situ* and real-time analysis [5]. Anodic Stripping Voltammetry (ASV) presents adequate sensitivity for trace heavy metal analysis [6]. In spite of mercury toxicity, mercury electrodes have been traditionally employed for ASV measurements due to their high reproducibility [7]. Bismuth is one of the most used materials to replace mercury-based electrodes due to its environmental-friendly characteristics and its ability to form "fused alloys" with heavy metals [8]. The use of these electrochemical devices for Cd(II) or Pb(II) determination essentially involves formation of a bismuth film onto the electrode surface which is usually performed in three different ways, *ex situ*, *in situ* and *in bulk* [9–12]. In the *ex situ* approach, electroplating of the electrode surface with bismuth is carried out in a Bi(III) solution prior to the introduction of the electrode into the sample solution containing the analyte to perform the measurement. In the *in situ* methodology, an adequate volume of a Bi(III) solution is directly added into the sample solution, and the analyte is accumulated on the electrode surface at the same time that the bismuth film is formed. In the *in bulk* method, different chemical forms of bismuth are incorporated as a modifier of the electrode surface and the bismuth film is formed from these precursors during the measurement process. For instance, bismuth powder [13], bismuth nanostructures [14], bismuth nanoparticles [15], bismuth compounds as Bi_2O_3 or $(BiO)_2CO_3$ [16–18] and bismuth salts, as $Bi(NO_3)_3$ or NH_4BiF_4 [19–20], have been used as modifiers to develop sensitive sensors for heavy metals. Disposable screen-printed electrodes (SPEs) have been used as platforms to develop bismuth modified devices, employing *ex situ*, *in situ* or *in bulk* modification approaches [12,21–31], taking advantage of the interesting characteristics of SPEs such as their low cost and versatile and easy modification.

In our research group, we have developed composite materials based on polystyrene sulfonate (PSS) as transducers for electrochemical sensors [32]. PSS is a water-soluble polymer in which the negative charged sulfonate groups allow interaction with cationic species, as metal ions, by an ion-exchange mechanism [33]. This property has been exploited in electrochemical methods for heavy metals analysis, using PSS as a coating of the working electrode to favour the metal ions accumulation and as an anti-fouling agent to avoid interference from surfactants or organic matter [34–36]. Sensors based on PSS–carbon nanopowder (CnP) composites maintain the ion-exchange

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properties of this polymer and present excellent characteristics for the determination of metals such as Cu(II) [37]. The ion-exchange mechanisms can also be used to incorporate additional components in the PSS composite. In this way, we have introduced Ni^{2+} in a PSS–CnP composite to prepare electrochemical transducers for mercury sensing [38]. Moreover, PSS is a good dispersant of nanomaterials and therefore it is possible to prepare PSS composite materials for sensing purposes in which, in addition to the nanocarbon material, solids such as metal oxides are incorporated to get an adequate analytical performance. For instance, we have proposed a sensor based on a PSS–CnP–NiO composite for fragrance allergens detection [39].

Electrodes based on PSS composites could be modified with bismuth to get sensors with adequate characteristics for ASV metal ions determination. To our knowledge, there are only two bismuth modified sensors reported based on PSS–carbon nanomaterial composites, using carbon nanotubes [40] and graphene [41], respectively. In both cases, a bismuth film was deposited on the electrode surface by an *in situ* procedure.

In the present work, we have evaluated the analytical performance of screen-printed electrodes (SPEs) modified with PSS–CnP composites in which bismuth was introduced by means of three *in bulk* procedures. It was incorporated in the PSS–CnP membrane as Bi^{3+} by an ion-exchange mechanism or it was introduced in the PSS–CnP dispersion used to modify SPCE as bismuth nitrate solution or Bi_2O_3 particles. In a previous paper, we have assayed different procedures for the synthesis of Bi_2O_3 and carried out preliminary voltammetric studies using the Bi_2O_3 particles obtained as modifiers of electrodes. From these studies, it was deduced that the monoclinic α-Bi_2O_3 phase obtained by sonochemical synthesis route at 30 °C presented the best characteristics to be used as electrode modifier [42]. These Bi_2O_3 particles are the bismuth compound employed in one of the *in bulk* modification procedures assayed in the present paper. The features for Cd(II) and Pb(II) determination by differential pulse anodic stripping voltammetry (DPASV) on the bismuth modified electrodes, using the three assayed procedures, have been evaluated. The optimal bismuth modified electrode was used for DPASV determination of Cd(II) and Pb(II) in natural water samples.

2. Experimental

2.1. Reagents

All chemicals were of analytical grade, purchased from Sigma-Aldrich and used without further purification. Ultrapure water (resistivity ≥ 18.2 MΩ cm at 25 °C, Ultra Clear TWF UV EDI, Siemens) was used to prepare all aqueous solutions. Bismuth nitrate, $Bi(NO_3)_3 \cdot 5H_2O$, was used to synthesize bismuth oxide particles and prepare Bi(III) solutions. PSS aqueous solutions were prepared from poly (sodium-4-styrene-sulfonate) powder (average M_W 70 000) in ultrapure water. CnP (particle size < 50 nm) were used to prepare the PSS–carbon suspensions. Working stock solutions of Cd(II) and Pb(II) were prepared from 1000 mg L^{-1} atomic absorption standard solutions. Acetate buffer solution (0.2 mol L^{-1}, pH 4.5) was used as supporting electrolyte in the voltammetric measurements.

2.2. Instruments

Electrochemical measurements were performed using the μSTAT 400 bipotentiostat (DropSens) controlled by the Drop-View software. A specific connector (model DRP-DSC, Drop-Sens) was used to connect SPEs to bipotentiostat.

The morphology of modified working electrode surfaces was studied by Scanning Electron Microscopy (SEM)–Energy-dispersive X-ray spectroscopy (EDX) analysis, using the scanning electron microscope Hitachi S-3000N equipped with an Oxford Instruments X-ray analyser, model INCAx-sight.

An Elmasonic P30H model ultrasonic bath was used to synthesize Bi_2O_3 particles and prepare PSS–CnP suspensions.

2.3. Preparation of modified electrodes

2.3.1. PSS–CnP modified electrodes

Modified electrochemical sensors were prepared using commercial SPCEs (DRP110D, DropSens) as substrate. These commercial devices consisted of a ceramic substrate strip (3.4 × 1.0 × 0.05 cm) with the electrodes over it. The working (4 mm diameter) and the counter electrodes were made of carbon, whereas the pseudo-reference electrode and the electric contacts were made of silver.

Working electrodes of commercial SPCEs were coated with PSS–CnP composites by micropipette assisted deposition of 4 μL of PSS–CnP aqueous suspension. Homogeneous and stable PSS–CnP coating suspensions (3 wt% in PSS and 0.3 wt% of CnP) were prepared by mixing proper amounts of CnP and PSS with ultrapure water under ultrasonic agitation for 10 min at 80 MHz. These PSS–CnP composite modified SPCEs (hereafter named as PSS–CnP–SPE) were dried overnight at 30 °C.

2.3.2. In bulk bismuth-modified electrodes

Bismuth incorporation in PSS–CnP–SPE was performed by three *in bulk* modification methodologies.

In the first one, Bi(III) was incorporated by an ion-exchange process in the sulfonate groups of the PSS–CnP membrane. In the other two procedures, Bi_2O_3 particles or Bi(III) nitrate solution were incorporated during PSS–CnP aqueous suspension preparation. In the ion-exchange method (sensor hereafter named as BiCE–SPE), PSS–CnP–SPEs were immersed in 250 mL of a 100 mg L^{-1} Bi(III) solution for five hours under mechanical stirring at 500 rpm.

Incorporation of bismuth as solid Bi_2O_3 was performed by the addition of monoclinic α-Bi_2O_3 particles in the PSS–CnP aqueous suspension. These particles were synthesized according to our previously optimized sonochemical method [42]. In short, synthesis was carried out by heating, at 30 °C under ultrasonic stirring at 80 MHz and 100 W for 60 min, a mixture of Bi(III) nitrate and Tween 85® with a 4 M NaOH solution. The obtained particles were isolated by centrifugation, rinsed successively with ultrapure water and ethanol and dried out at 60 °C. These α-Bi_2O_3 particles were incorporated in the PSS–CnP aqueous suspension to form the PSS–CnP–Bi_2O_3 suspension (3 wt% PSS, 0.3 wt% Bi_2O_3 and 0.3 wt% CnP) used to modify commercial SPCEs by deposition of 4 μL on the working electrode. These electrodes (hereafter named as BiOxP–SPE) were dried overnight at 30 °C.

In the third *in bulk* method assayed, adequate amounts of CnP and PSS were weighted, suspended in 1.0 mL of ultrapure water and mixed with 2.0 mL of $Bi(NO_3)_3 \cdot 5H_2O$ solution, containing 500 mg L^{-1} of Bi(III) in 0.5 M HNO_3. Then, 1 M NaOH solution was added dropwise into this suspension until a neutral pH value was achieved. Finally, it was made up to 10.0 mL with ultrapure water to obtain a 3 wt% PSS, 0.3 wt% CnP and 100 mg L^{-1} Bi(III) suspension. The working electrode of SPCEs was modified by deposition of 4 μL of this suspension onto its surface. These electrodes (hereafter named as Bi^{3+}–SPE) were dried overnight at 30 °C.

2.4. Electrochemical measurements

Analytical performance of bismuth modified screen-printed devices was evaluated by DPASV of Cd(II) and Pb(II) stock solutions. For comparison, Bi(III) oxide modified screen-printed carbon electrodes from DropSens, Ref. DPR-110BI (hereafter named as C–BiOx–SPE) were also used.

For the DPASV measurement, the bismuth film formation in all assayed electrodes was performed simultaneously to Cd and Pb electrodeposition. For this purpose, 180 μL of Cd(II) and Pb(II) solution in acetate buffer were placed onto the electrodes and a potential of −1.2 V was applied for 420 s. After that, the reoxidation sweep from −1.2 V