Electroanalytical Assessment of Heavy Metals in Waters with Bismuth Nanoparticle-Porous Carbon Paste Electrodes

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ABSTRACT

This work reports on a detailed analytical assessment of a bismuth nanoparticle-porous carbon paste electrode working as an electrochemical sensor for the sensitive detection of Cd(II), Pb(II) and Ni(II) in water samples of different origin. Detection limits of 0.81, 0.65 and 5.47 ppb for Cd(II), Pb(II) and Ni(II), were achieved, respectively, keeping the overall analysis time below 240 s. This sensor device was employed in the analysis of several contrasting samples such as tap water, ground water, polluted waters from an influent and effluent of an urban wastewater treatment plant and polluted river water due to acid mine drainages, thereby covering a wide spectrum of matrices and absolute and relative heavy metal concentrations. Results were shown to be in good agreement with the reference values. The one-pot mass production of this composite material and the use of Bi in the form of nanoparticles result in sensitive, reproducible and cost-effective electrochemical devices. Moreover, the sol–gel synthesis technology applied to the production of the electrode material can be easily adapted to the fabrication of thick or thin films on planar substrates for the development of electrochemical sensors that could be of practical use for the on-site heavy metal analysis in diverse water sources.

1. Introduction

The detection of heavy metal levels in natural or contaminated waters is of paramount importance because the persistence of these species in the environment can result in deleterious effects at different levels [1,2]. Anthropogenic activities have the potential to alter the natural concentrations of a variety of heavy metals in water, this posing a serious threat to the ecosystems and the human health. Indeed, an increasing number of regulations such as those set by the World Health Organization (WHO), the US Environmental Protection Agency (EPA) and the European Union, include heavy metals in the list of priority substances to be monitored [3–5], setting maximum concentration levels, guideline values or allowable concentrations in water following the environmental quality standards (EQS). Standard methods to analyze the presence and concentration of heavy metals in the environment include atomic absorption spectrometry (AAS) and

inductively coupled plasma mass spectrometry (ICP-MS) [6]. Both techniques make use of bulky and costly instrumentation operated by skilled personnel in dedicated centralized laboratories. Hence, the analyses are expensive and in practice these techniques cannot cope with the challenge of the semi-continuous monitoring of heavy metals in waters. The use of alternative reliable analytical tools such as chemical sensors is therefore highly desirable. These devices show the potential to be deployed and used on-site, providing real-time quantitative results. Electrochemical sensors require simple measurement protocols and employ a compact and low-power instrumentation that can be operated on-site. Among the different electrochemical devices, those based on a standard three electrode configuration, with the working electrodes showing a range of different materials and arrangements, and operated by the stripping voltammetry (SV) technique [7] have been long recognized to be an interesting alternative to be applied in this scenario.

Currently, many of the reported electrochemical sensor approaches make use of environmentally-friendly Bi-based electrodes [8–18]. These are increasingly replacing the highly hazardous Hg–based devices, which have long proved to be suitable for the sensitive detection of heavy metals. In this context, the generation of Bi films on the surface of carbon electrodes

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following a similar approach to that previously used with Hg, has been of widespread application in research. However, in order to become a real alternative to the standard analytical methods mentioned above, more progress is needed to improve the electrode analytical performance and avoid additional steps, such as those required for the *ex situ* plating to form a Bi film on the surface of the electrode [8], or the introduction of large amounts of Bi ions in the solution for the *in situ* plating of Bi film electrodes [16].

Several approaches that avoid additional processing steps have been reported to construct Bi electrodes showing different geometries. These include Bi rod-like electrodes [14], micro-fabricated thin-film Bi electrodes [11] and sputtered Bi screen-printed electrodes [17]. Also, electrochemical devices for heavy metal detection based on Bi nanoparticles (Bi NPs) have been developed aiming at reducing the amount of Bi and taking advantage of the superior analytical performance of nanomaterials [9,19]. The Bi NPs used in these systems were prepared by gas condensation [9] or chemical synthesis [19]. However, the corresponding sensors were fabricated by casting an aqueous solution containing Bi NPs on the surface of commercially-available standard electrodes, which still requires a second processing step to produce the final device.

In an effort to combine the benefits of both the one-step fabrication process and the application of Bi nanoparticles, our group is engaged in the one-step sol–gel synthesis of Bi nanoparticle porous carbon composite materials [20], which can be easily processed for the fabrication of different types of electrochemical devices from carbon paste to thick-film (screen printed) and thin-film planar electrodes. Conventional paste electrodes have been initially fabricated to analytically test these novel materials. Due to the high surface area of Bi NPs and the porosity of carbon, the resulting electrodes performed adequately in heavy metal detection, demonstrated by the simultaneous analysis of Pb(II) and Cd(II) at concentration levels below 1 ppb in aqueous standard solutions [20]. Such preliminary analytical results encouraged us to optimize the material synthesis process and then carry out an in depth analytical study of Bi NP porous carbon composite paste electrodes (Bi-CPEs) to fully demonstrate the potential of this material for heavy metal sensing. This work includes a thorough electroanalytical study for carrying out the detection of Cd(II), Pb(II) and Ni(II) in standard solutions using Bi-CPEs and its application to the rapid detection of these pollutants in water samples with significant differences in origin, composition and matrix complexity.

2. Experimental

2.1. Chemicals and solutions

The following chemicals were purchased from Sigma-Aldrich and used as received: resorcinol (m-$C_6H_4(OH)_2$, 99% pure), formaldehyde water solution (CH_2O, 37 wt.%, methanol stabilized), glycerol formal (47% 5-hydroxy-1,3-dioxane, 33% 4-hydroxy-methyl-1,3-dioxolane), bismuth nitrate pentahydrate (Bi $(NO_3)_3 \cdot 5H_2O$, 98% pure), acetic acid (CH_3COOH, 99.7% pure); Cd (II), Pb(II), Ni(II), Cu(II), Zn(II), Co (II), Ga(III) standard solutions (1000 mg/L), dimethylglyoxime (DMG), potassium ferricyanide and potassium ferrocyanide ($K_3Fe(CN)_6$ and $K_4Fe(CN)_6$).

2.2. Preparation and Microstructural Characterization of the Nanocomposite

The porous Bi NPs-carbon composite (Bi-C) material was prepared in bulk as follows. Firstly 0.2 g Bi(NO_3)$_3 \cdot 5H_2O$ were dissolved in 5 mL glycerol formal containing 2 mL CH_3COOH. Then,

1 g of resorcinol and 1.36 mL of formaldehyde solution were added to it and stirred until a transparent *sol* was obtained. Gelation occurred by keeping the *sol* for 8 h at 60 °C. The wet gels were dried at ambient conditions under a fume hood for at least 48 h, and finally carbonized at 900 °C for 2 h in Ar or N_2 atmosphere. Microstructural characterization of the materials was performed using a FEI Quanta 200 F scanning electron microscope (SEM) with energy-dispersive X-ray microanalysis (EDX). Nitrogen adsorption-–desorption isotherms were recorded with Malvern Micromeritics equipment after degassing around 100 mg of sample for 48 h at 150 °C in vacuum (pressure <1 mPa). Nitrogen adsorption analysis was carried out for the estimation of specific surface areas using the BET (Brunauer–Emmet–Teller) method while pore size distributions, pore volume and mean pore diameters were measured by the BJH (Barret–Joyner–Halenda) method.

2.3. Preparation of the Carbon Paste Electrode

The pyrolyzed Bi-C nanocomposite was firstly ball-milled in a Retsch Mixer Mill to obtain a powder with an average diameter of *ca.* 10 μm. Hereafter, 1 g of this powder was thoroughly mixed in a mortar with 0.4 mL of spectroscopic grade liquid paraffin (Uvasol® from Merck) to produce a carbon paste. This paste was then packed into a 3 mm-diameter well, defined at one end of a 6 mm-diameter Teflon body, into which a 3-mm diameter stainless steel rod was inserted to make the electrical contact. The surface of the resulting carbon paste electrode (Bi-CPE) was eventually polished on a white paper sheet. After each measurement the Bi-CPE was renewed by packing a fresh paste.

2.4. Electrochemical Analysis

Electrochemical measurements were performed at room temperature in a 10 mL plastic cell and using a conventional three-electrode configuration that included a 3-mm diameter CPE together with a platinum counter electrode and a Ag/AgCl reference electrode (both from Metrohm AG, Switzerland). Electrochemical analysis of Pb(II) and Cd(II) was carried out simultaneously by square wave anodic stripping voltammetry (SWASV) whereas Ni(II) was detected by square wave adsorptive cathodic stripping voltammetry (SWAdCSV). An Autolab PGSTAT30 potentiostat (EcoChemie, The Netherlands) was used for all the measurements. Selected square wave parameters were 20 Hz frequency, 25 mV amplitude and 5 mV step potential for all the analyses. The following supporting electrolytes were used: a 0.1 M acetate buffer solution pH 4.5 (Ac buffer), for the detection of Pb(II) and Cd(II)), and a 0.1 M ammonia buffer solution pH 9.2 containing 1 mM (ca. 120 ppm) DMG chelating agent for the measurement of Ni(II) (NH_3 buffer). Calibration curves for the different heavy metals were constructed by plotting the stripping peak current versus the corresponding metal concentration. Each point in the calibration curves was the mean of three measurements with the error bars showing the corresponding standard deviation, unless stated otherwise.

2.5. Analysis of Real Water Samples

Water samples from different locations were collected and used to test the analytical sensor performance: Sample 1- Tap water from the Materials Science Institute of Barcelona (ICMAB, Bellaterra, Spain); Sample 2- Polluted water with a high organic load from an influent of an urban wastewater treatment plant (WWTP) located in Terrassa (Barcelona, Spain); Sample 3- Ground water certified reference material BCR® 610, purchased from Sigma- Aldrich; Sample 4- Treated water from an effluent of an urban WWTP located in el Prat (Barcelona, Spain); Sample 5-