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.

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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-

Heavily polluted water from the Meca river due to acid drainages from Tharsis mine (Huelva, Spain). These samples were analyzed as follows. Sample 1 was analyzed immediately after collection. Sample 2 contained a high amount of organic matter in suspension and was stored in the freezer. In order to carry out the measurements, the sample was thawed and left for the organic matter to deposit before use. Sample 3 was stored in the fridge and analyzed as received. Samples 4 and 5 were filtered immediately after collection through 0.2 μm Millipore filters, acidified in the field to pH < 2 with Suprapur® HNO_3 and stored at 4 °C in sterile polypropylene containers until analysis.

Water sample analyses were carried out in triplicate with the Bi-CPE sensor. Prior to the electrochemical measurements they were diluted using the appropriate buffer. The degree of dilution necessary to obtain a heavy metal concentration falling within the range of the calibration curves was determined from the stripping currents and peak shapes in preliminary measurements. The analyses were carried out according to the standard addition method, unless stated otherwise.

Samples 1 and 2 did not contain any detectable concentration of the three heavy metals under study. Then, they were spiked with known amounts of the heavy metals and the recovery was calculated. Results obtained in Sample 3 were compared with those provided by the certificate of analysis of this reference material. Sample 4 and 5 contain different concentrations of heavy metals and results were compared with those obtained with the ICP-MS standard method performed by an external laboratory. ICP-MS analyses were carried out using a Thermo Scientific XSERIES II instrument with detection limits of about 1 ppb for all the tested heavy metals. Multi-element standard solutions prepared from single certified standards supplied by SCP SCIENCE were used for calibration and run at the beginning and at the end of each analytical series. Certified Reference Material SRM-1640 NIST fresh-water-type and inter-laboratory standard IRMM-N3 wastewater test material (European Commission Institute for Reference Materials and Measurements) were also intercalated in between the samples for accuracy checking. Precision error was higher than accuracy and was always around 5%.

3. Results and Discussion

3.1. Microstructural Characterization

The SEM image of the Bi-C nanocomposites shown in Fig. 1 reveals the presence of spherical Bi NPs homogeneously distributed in the car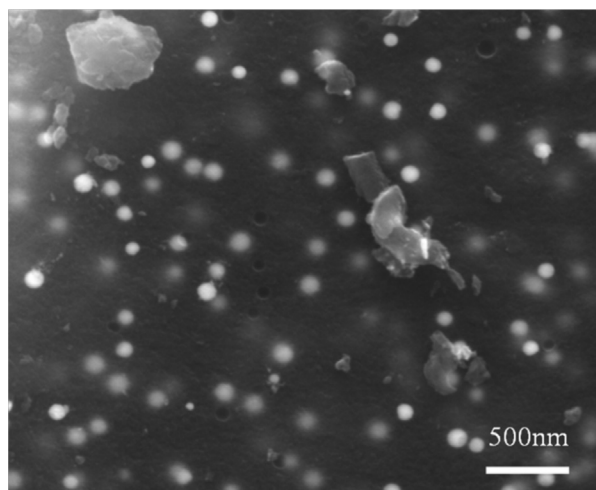bon matrix. The Bi NPs has a size distribution between 30 nm and 200 nm and an average size around 100 nm. Using EDX analysis, the obtained Bi concentration in the nanocomposites was around 6 wt. %.

The porosity of the Bi-C nanocomposite was studied by nitrogen adsorption/desorption isotherms (Fig. 2). The adsorption uptake observed at low nitrogen relative pressures indicates that the porosity is mainly due to micropores. The non-negligible slope of the curve at intermediate relative pressures and the increase in the adsorbed volume at relative pressures above 0.9 indicate the existence of some mesopores and macropores, respectively. A surface area calculation using BET model gave a value of 71.5 $m^2 \cdot g^{-1}$, and the total pore volume was calculated to be 0.049 $cm^3 \cdot g^{-1}$ according to the amount adsorbed at a relative pressure P/P_0 of ca. 0.995. The inset of Fig. 2 shows the BJH pore-size distribution curve obtained from the adsorption branch that confirms the dominant diameters in the micropore region with the coexistence of small amount of mesopores and macropores. The lack of overlap of the adsorption and desorption branches at low pressures could be related to the interaction of nitrogen with the material surface or to the elastic deformation of the material at increasing pressures.

Compared to our previous report on this type of nanocomposite matrices [20], the lower pH of the *sol*, obtained by avoiding the use of NH_4OH, greatly accelerated the gelation process, resulting in materials with less surface area and porosity. However, as shown below, this decreased porosity is not detrimental to the performance of the nanocomposite in the electrochemical sensing of heavy metals.

3.2. Electrochemical Characterization

The large surface area of Bi NPs combined with the porosity of the carbon matrix results in an enlarged electroactive area available for the detection of heavy metals. The Bi-CPEs used in this work were single-use in order to make sure that the same working conditions were applied for all the analytical measurements. Generally, the surface of a CPE can be easily renewed by mechanical polishing after each measurement. However, since the electrode material under study is porous, it soaked up water solution and after the measurement most of the carbon paste packed inside the Teflon body was wet. Indeed, it was shown that a mechanical polishing renewal process did not result in a fresh CPE surface and as such could affect the reproducibility of the electrode signal. Figure S1 in the Supplementary Information (SI) shows that, even when the potential window at which the heavy metal
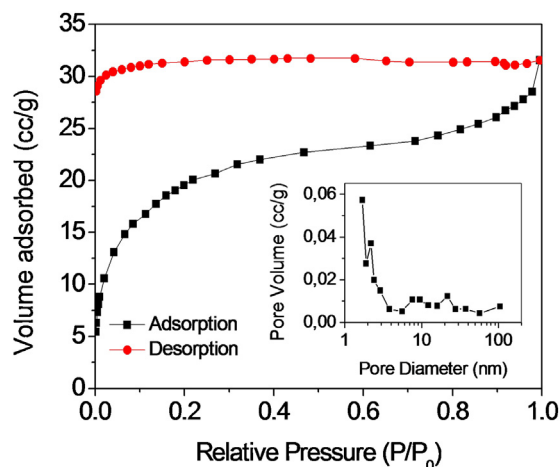

Fig. 1. SEM image of porous C-Bi nanocomposites.

Fig. 2. N_2 adsorption/desorption isotherm of the porous C-Bi nanocomposite. Inset shows the pore size distributions calculated using the BJH method.

stripping process took place was narrowed to avoid the Bi oxidation, the recorded signals were not reproducible if the electrode surface was just renewed by mechanical polishing. Therefore, a new CPE was prepared by packing a fresh Bi-C paste following each measurement.

Figure S1 (SI) also indicates that the Bi-CPEs could be applied to the simultaneous detection of Zn(II), Cd(II) and Pb(II) in water solutions. The electrochemical measurement of these three heavy metals is commonplace and previous approaches have been reported on this matter [8,21]. However, the work presented here was focused on the detection of Cd(II), Pb(II) and Ni(II), taking into account that these are the heavy metals, together with Hg(II), included in the list of priority substances in the field of water policy compiled in the 2013/39/EU Directive [5]. The environmental quality standards expressed as the maximum allowable concentrations (MAC-EQS) in surface waters set up in this directive are 0.45 ppb Cd(II), 14 ppb Pb(II) and 34 ppb Ni(II). Other directives released by the US Environmental Protection Agency and the World Health Organization (WHO) set up concentration values in drinking water in a range of 3–5 ppb Cd(II), 10–15 ppb Pb(II) and 70–100 ppb Ni(II). None of these directives identifies Zn(II) as a primary substance to be monitored in water and just EPA includes it in the water secondary drinking water regulation, setting up a maximum allowable concentration of 5 ppm. Nevertheless, the measurement of Zn(II) was also carried out by our group in an effort to show the potential of our material for the detection of a wider range of heavy metals. Some drawbacks were found and the whole study is included in the SI (Figure S2).

Fig. 3(A) shows an example of the SWASV signals recorded for the determination of Pb(II) and Cd(II) in a concentration range from 1 ppb to 100 ppb after a 180 s accumulation step at −1.4 V in acetate buffer solutions. Two peaks at around −0.8 V and −0.5 V are clearly visible and can be ascribed to Cd(II) and Pb(II) stripping processes, respectively. The calibration curves shown in Fig. 3(B) were linear in the whole concentration range tested. Limits of detection (LOD) of 0.81 ppb and 0.65 ppb for Cd(II) and Pb(II), respectively, were estimated using the formula: LOD = 3*(SD/S), where SD is the standard deviation of the intercept of three calibration curves, with S being the mean of the slopes of these calibration curves. These values are lower than those previously reported with Bi film based electrodes [22], a Bi powder modified carbon paste electrode [23], and a Bi NP modified screen printed carbon electrode [19], using similar or longer accumulation times. Among previously reported Bi NP based electrodes, Malakhora *et al.* [24] achieved similar detection limits (0.55 ppb for Pb(II) and 0.40 ppb for Cd(II)) after a 180 s accumulation time. Lee *et al.* [9] reported the lowest detection limit of 0.07 ppb and 0.15 ppb for Pb(II) and Cd(II) respectively, but using an accumulation time of 600 s. However, compared to our sol–gel approach, the Bi NP based electrodes used in those studies were prepared following a more complex and expensive gas condensation method. It is also worth noting that the LODs of the Bi-CPEs could be improved by increasing the Bi content in the nanocomposites and/or using longer accumulation times up to certain values without compromising the cost and the sensor response time.

The Bi-CPE sensor was then applied to the detection of Ni(II) by SWAdCSV in an ammonia buffer solution containing DMG as a chelating agent for this heavy metal. Here, an accumulation step was carried out at −0.8 V for 180 s, at which the corresponding Ni-DMG complex was adsorbed onto the electrode surface. Then, Ni(II) was reduced to metallic Ni by applying a negative potential scan from −0.8 V to −1.4 V. Reduction of Ni(II) induces fast desorption of the Ni-DMG complex from the electrode surface, as previously reported [18,25]. Fig. 4(A) shows the stripping voltammograms for different Ni(II) concentrations displaying a stripping cathodic peak at around −1.2 V. The absolute value of the
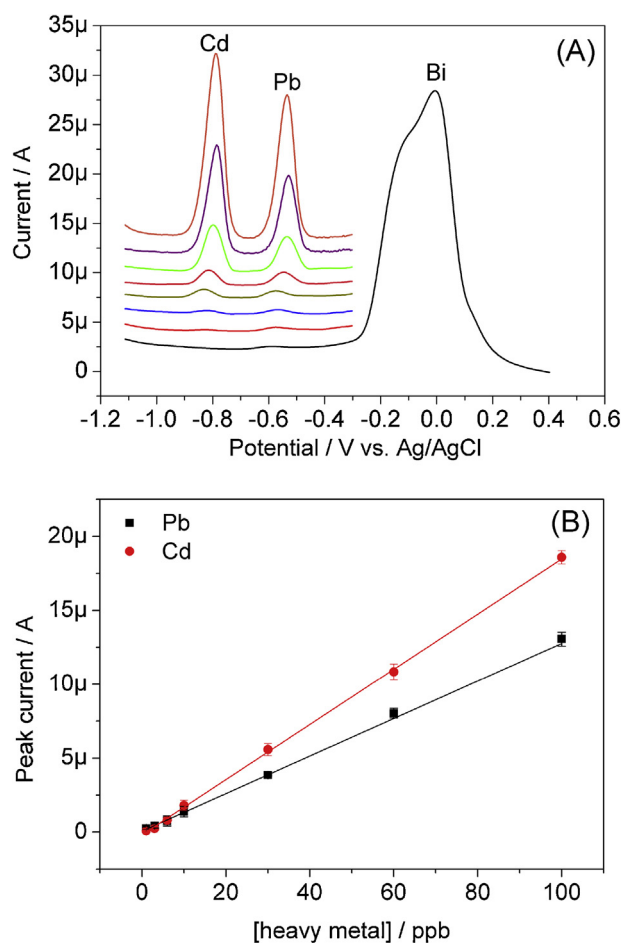

Fig. 3. (A) Square-wave anodic stripping voltammograms recorded in standard 0.1 M acetic buffer solutions pH 4.5 containing different concentrations of Cd(II) and Pb(II) (from bottom to top signals: 0, 1, 3, 6, 10, 30, 60 and 100 ppb). Electrodeposition was carried out at −1.4 V for 3 min. Potential was scanned from −1.4 V to +0.4 V. The potential windows of the different voltammograms shown in the figure were cut, and an offset was applied to them, for clarity of presentation. (B) Calibration curves for both heavy metals. Each point represents the mean value of three replicates. The error bars are the corresponding standard deviation.

stripping current increased linearly with the analyte concentration from 10 ppb to 150 ppb (see Fig. 5(B)) and a LOD of 5.47 ppb was estimated, using the criterion mentioned above.

Table 1 gathers all the analytical parameters extracted from the corresponding calibration curves for the three heavy metals tested. The small relative standard deviations of the electrode responses, indicated by the error bars of the calibration curves in Fig. 3(B) and 4(B), illustrate the good reproducibility and overall performance of the sol–gel derived nanocomposite electrodes.

Before undertaking the analysis of water samples, the effect on the electrochemical signal of possible interfering substances that may be present in water, should be considered. Apart from the organic matter, which has long been identified to mask to a certain degree the presence of heavy metals [26] and after carrying out a literature search, the effect of two metal ions was studied. From the chemical point of view, previous works on Bi film electrodes showed that one of the main interferents in the detection of Pb(II) and Cd(II) is Cu(II). For instance, Yang *et al.* [27] found that the presence of Cu(II) at concentration levels 10 times higher than those of Pb(II) and Cd(II) would result in an approximately 70% and 90% decrease in the peak signals of Pb(II) and Cd(II), respectively. They report that this effect was likely to be related to the formation of Cu(II)/Pb(II) and Cu(II)/Cd(II) inter-metallic compounds and the
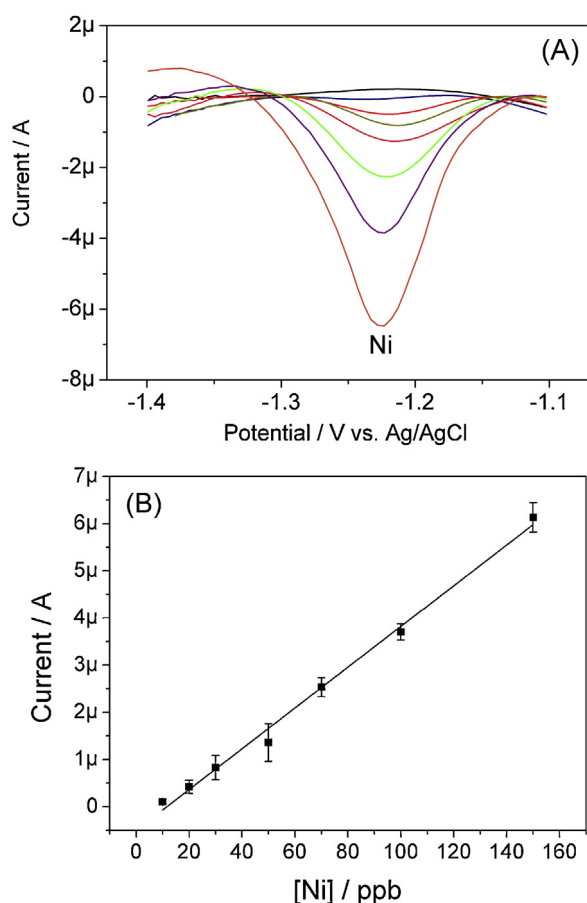
Fig. 4. (A) Stripping voltammograms recorded in standard 0.1 M ammonia buffer solutions pH 9.2 containing different concentrations of Ni(II) at (from top to bottom signals: 0, 10, 20, 30, 50, 70, 100, and 150 ppb) and 1 mM DMG. Activation step was carried out at −1.4 V for 3 min followed by electrodeposition at −0.8 V for 3 min. The potential windows of the different voltammograms shown in the figure were cut for clarity of presentation. (B) Calibration curve. Each point represents the mean value of three replicates. The error bars are the corresponding standard deviation.

Fig. 5. (A) Stripping voltammograms showing the Cu(II) interference on Pb(II) and Cd(II) and the effect of the addition of ferricyanide or ferrocyanide to reduce this interference. Accumulation at −1.4 V for 3 minutes in 0.1 M pH 4.5 acetate buffer solution containing 50 ppb Cd(II) and 50 ppb Pb(II). An offset was applied to some voltammograms for clarity of presentation (B) Stripping voltammograms showing the interference of Co(II) on the measurement of Ni(II). Activation at −1.4 for 2 min and accumulation at −0.8 V for 3 min in 0.1 M ammonia buffer pH 9.2.

deposition competition between Cu(II) and Cd(II), Pb(II) on the electrode surface. Jia *et al.* [28] reported that even a Cu(II) concentration only doubling that of Cd(II) and Pb(II) would affect the determination of these pollutants on CNTs-PSS/Bi composite film electrodes. Fig. 5(A) displays the SWASV signals recorded in solutions containing 50 ppb Pb(II) and Cd(II) and different concentrations of Cu(II). With increasing the Cu(II) concentration, the signals of Pb(II) and Cd(II) were rapidly attenuated and even no signals were recorded when 500 ppb Cu(II) were present in solution (i.e. 10 times higher than that of Pb(II) or Cd(II)). To alleviate this interference, potassium ferricyanide and potassium ferrocyanide were selected as masking agents for Cu(II). Both of them form relatively stable complexes with this metal ion and therefore may help neutralize its effect on the analyses of Pb(II) and Cd(II). The results show that potassium ferrocyanide is a more efficient masking agent than potassium ferricyanide. 100% and 70% signal recoveries for Pb(II) and Cd(II) were achieved, respectively. From the electrochemical point of view, other heavy metals that may simultaneously accumulate on the Bi-CPE surface and whose corresponding stripping signals are recorded at potentials lower than those of Cd(II) and Pb(II) could also interfere. Depending on the relative concentrations of the different heavy metals in solution, Mn(II) and Zn(II) have been identified as possible interferents and their effect should be studied for every particular sample to be analyzed.
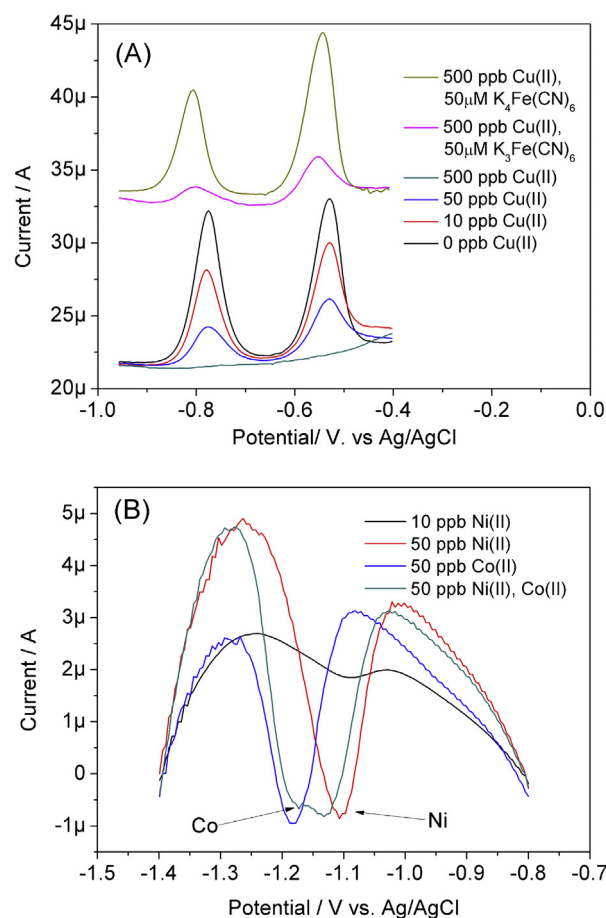
Regarding the detection of Ni(II), and from the chemical point of view, other heavy metals that may be complexed by DMG could have a negative effect on Bi-CPE response to this target analyte. Divalent cations such as Co(II), Cu(II) and Zn(II) should be taken into account when present in the measuring sample. From the electrochemical point of view, the Ni(II) stripping voltammetric signal can be hampered by the presence of Co(II), which also forms a complex with DMG and whose stripping peak appears at a potential close to that of Ni. A study was conducted with the Bi-CPEs in ammonia buffer solutions containing different relative concentrations of Ni(II) and Co(II). Fig. 5(B) shows SWAdCV signals for Ni(II) or Co(II) recorded individually with the Bi-CPE and those recorded when both metals were present in the buffer solution. It is clearly observed that both signals are overlapped but the peak currents are similar to those of the individual signals. This behavior was observed in all the concentration range studied and should be taken into account when analyzing real water samples. Well-resolved peaks for both metals were previously reported using bismuth film modified glassy carbon electrodes [29], and macro-porous bismuth modified screen printed carbon electrodes [18].

3.3. Analysis of Real Water Samples

To test the applicability of the Bi-CPEs, tap water and wastewater from an influent of a WWTP (named as Samples 1

Table 1
Parameters of calibration curves plotted for the different heavy metals.

Heavy metals	Linear range (ppb)	Sensitivity (μA/ppb)	Detection limit (ppb)	Number of points (n)	Correlation Coefficient (R)
Cd	1-100	0.19 ± 0.04	0.81	7	0.997
Pb	1-100	0.13 ± 0.02	0.65	7	0.999
Ni	10-150	0.04 ± 0.01	5.47	7	0.993

and 2 in the experimental section) were firstly analyzed. Different aliquots of both samples were diluted with either 0.2 M Ac buffer or 0.2 M NH_3 buffer, in a 1:1 volume ratio, depending on the heavy metal to be analyzed. No detectable amounts of the three heavy metals under study were found. Then, two aliquots of both samples diluted with 0.2 M Ac buffer were spiked with 10 ppb (Sample 1) and 5 ppb (Sample 2) of Cd(II) and Pb(II). The analysis was carried out by the standard addition method. Figures S3 and S4 (SI) show representative stripping voltammograms before and after the addition of different concentrations of Cd(II) and Pb(II) for the two samples, together with the corresponding calibration curves. In addition, two aliquots already diluted with 0.2 M NH_3 buffer, were spiked with 10 ppb Ni(II). Figure S5 (SI) shows the voltammograms of the standard addition method and the corresponding calibration curve carried out for the detection of Ni(II) in Sample 1. Table 2 shows the concentration values recovered for the three heavy metals in both samples. A good agreement between the added values and the estimated ones was found in all cases except for the Ni(II) in Sample 2. The detection of this heavy metal in the spiked sample did not produce any signal. As discussed in section 3.2., the presence in the sample of other divalent metal cations or a high content of organic matter, to which Ni(II) could be strongly adsorbed, may be the reason for this negative result. By contrast, the Cd(II) and Pb(II) detection was not affected by this.

Afterwards, the Bi-CPE was used to analyze two water samples containing the three heavy metals under study. Namely, Sample 3 is a certified reference groundwater with relatively high concentrations of the heavy metals under study and Sample 4 is another waste water collected in an effluent of a WWTP with relatively wide spectrum of heavy metals (Mn, Ba, Cu, Zn) but low amount of Cd(II), Pb (II) and Ni(II). Both samples were diluted and analyzed following the same protocol as with the previous samples. The concentration values measured with the Bi-CPE are shown in Table 2. The values of Pb(II) and Ni(II) in Sample 3 showed a good agreement with the reference values. Cd(II) detection proved to be more difficult. Figure S6 (SI) shows representative stripping voltammograms of Pb(II) and Cd(II) for Sample 3, recorded following the standard addition method. Although the Cd(II) concentration of 1.4 ppb after the 1:1 dilution was still slightly higher than the estimated LOD of Bi-CPE, the presence of 22 ppb Cu(II) negatively affected the Cd(II) determination, as shown below. Following the results of the interference study previously carried out, 0.1 mM $K_4Fe(CN)_6$ was added to the solution in order to alleviate the Cu(II) interference. The recorded peak currents were significantly enhanced (see Figure S7, SI) but the recovery appeared to be well below the 100%, which still

resulted in the non-detectability of this analyte. The analyses of Sample 4 showed that the Bi-CPE detected Cd(II) and Pb(II) at very low concentrations, at which the ICP-MS standard technique just provided with estimated values below 2 ppb for both heavy metals. However, Ni(II) could not be measured with our device because its concentration appeared to be below the estimated LOD after carrying out the 1:1 dilution, required to pre-condition the sample.

Finally, the analysis of Sample 5, a heavily polluted river water sample due to acid mine drainages was attempted with the aim of assessing the potential of the Bi-CPEs in the analysis of very complex water samples. This sample contained ppm-levels of Zn (II), Cu(II) and Mn(II) but ppb-levels of Pb(II), Cd(II) and Ni(II). Sample dilution was adjusted to a 1:10 volume ratio with the corresponding buffer solution, this being the highest feasible dilution in an attempt to minimize the matrix effects while the target analytes could still be detected. Figure S8 shows the stripping voltammograms of Pb(II) and Cd(II) in this sample. They displayed a steep background signal at potentials below -0.6 V that significantly reduced the potential window and hindered the detection of the stripping peak of Cd(II). This effect may be related to the presence of Mn(II) and Zn(II) at concentrations above 10 ppm in the original sample and whose stripping peaks are usually recorded at potentials lower than that of Cd(II). A Bi stripping peak at around 0 V was recorded, which is wider, rounder and much bigger than the Bi peak recorded in the solutions with a lower content of Cu(II). This peak shape is likely to be related to the overlapping of Bi (III) and Cu(II) stripping peaks. Cu(II) was present in the original sample at concentrations around 10 ppm and its interference on the detection of Cd(II) was described above. Surprisingly, the Pb(II) signals did not seem to be affected by the presence of Cu(II) and increased linearly with the standard additions of Pb(II) into the solution. Regarding the Ni(II) detection, DMG was added in the NH_3 buffered solution for the formation of the Ni(II)-DMG complex. However, DMG forms complexes with many metallic cations, such as Mn(II), Zn(II), Pb(II), Co (II), and Cu (II), some of which are also present at high concentrations in Sample 5. The Ni(II) current signals did not increase linearly with the standard additions of Ni(II) into the solution. We believe that all the DMG added to the solution was complexing the different heavy metals and then could not chelate the added Ni(II). However, increasing the concentration of DMG in the solution resulted in the production of a clearly visible white precipitate making the measurements unreliable. For all this, the Ni(II) concentration was measured by interpolating the signal recorded in the sample into the corresponding sensor calibration curve. From Table 1, the ICP-MS results and the values of the electrochemical analysis are in

Table 2
Results of the analyses of five water samples using the Bi-CPE.

Sample	Added/Reference/ICP-MS values (ppb)			Sensor values (ppb)		
	Cd(II)	Pb(II)	Ni(II)	Cd(II)	Pb(II)	Ni(II)
Tap water (1)	10	10	10	9.2 ± 1.0	9.1 ± 0.7	9.4 ± 0.9
Polluted water - influent (2)	5	5	10	4.7 ± 0.6	5.1 ± 0.8	$\leq$LOD
Certified water (3)	2.78	7.98	27	$\leq$LOD	7 ± 2	25 ± 4
Polluted water - effluent (4)	<2	<2	7.8	3.7 ± 0.8	1.3 ± 0.4	$\leq$LOD
Heavily polluted–mine drainages (5)	55 ± 3	38 ± 2	273 ± 14	$\leq$LOD	40.9 ± 0.6	$262 \pm 73^*$

*- analyzed by the interpolation method.

reasonable good agreement. However, this last analysis proves that the performance of electrochemical devices, such as the one presented here, for analysis of complex samples containing a variety of heavy metals in a wide range of concentrations, should be studied in detail for any particular case. Nevertheless, alarm systems based on this kind of sensors with the ability to detect increased concentrations of these pollutants due to sudden spills, could be implemented.

4. Conclusion

Bi-C nanocomposites prepared following a versatile soft chemistry approach successfully performed as working electrode materials for the electrochemical analysis of heavy metal pollutants in water. The materials consist of a highly porous carbon matrix with well-distributed Bi nanoparticles that provide a large active area for the electrochemical reduction of heavy metals in solution and are responsible for the superior electrode sensitivity.

Low detection limits and wide linear calibration ranges were obtained for Cd(II), Pb(II) and Ni(II). The electrodes were tested in the analysis of real water samples of different origin presenting complex and distinct heavy metals matrices. The results of the Cd (II), Pb(II) and Ni(II) analysis showed good recoveries in the spiked samples and were in good agreement with the reference values and those obtained by the standard ICP-MS method in samples of different nature containing these pollutants at different concentrations.

The C-Bi nanocomposite materials can be processed as inks for the fabrication of thick-film screen-printed electrodes and also as thin-films for the production of miniaturized electrodes. This opens the door to future developments of portable, low cost electrochemical sensors, which enabled a reliable on-site semi-continuous monitoring of heavy metals. Work is in progress in such direction.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.electacta.2015.03.001.

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