

Screen-printed electrodes made of a bismuth nanoparticle porous carbon nanocomposite applied to the determination of heavy metal ions

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Abstract This work reports on the simplified fabrication and on the characterization of bismuth-based screen-printed electrodes (SPEs) for use in heavy metal detection. A nanocomposite consisting of bismuth nanoparticles and amorphous carbon was synthesized by a combined one-step sol-gel and pyrolysis process and milled down to a specific particle size distribution as required for the preparation of an ink formulation to be used in screen printing. The resulting electrochemical devices were applied to the detection of Pb(II) and Cd(II) ions in water samples. The porous structure of carbon and the high surface area of the bismuth nanoparticles allow for the detection of Pb(II) and Cd(II) at concentration levels below 4 ppb. The application of the SPEs was demonstrated by quantifying these ions in tap drinking water and wastewater collected from an influent of an urban wastewater treatment plant.

Keywords Sol-gel process · Lead(II) · Cadmium(II) · Energy dispersive X-ray spectroscopy · Square wave anodic stripping voltammetry · Cyclic voltammetry · Water analysis

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Introduction

Bismuth (Bi) based electrodes have become valuable, attractive and environmentally friendly alternatives to mercury based electrodes for heavy metal analysis [1–7]. Nowadays, miniaturization and mass production of Bi based electrodes for commercial applications have attracted a lot of attention [7–9]. Screen printing technique is recognized as a low-cost method for the fabrication of disposable miniaturized electrodes [9–11]. Among the different materials that can be applied for the fabrication of screen printed electrodes, carbon inks are mainly preferred due to various advantages such as low-cost and wide electrochemical potential window.

Screen-printed electrodes showing the benefits of using both carbon and Bi components have been developed. However, the fabrication of such kind of devices is not straightforward. The incorporation of Bi is a challenging step of the production process that has been previously addressed by two different approaches. On one hand, two-step fabrication processes based on the addition of Bi after printing the carbon ink to define the electrode has been extensively described. They encompass in-situ [12, 13] or ex-situ [14] electroplating of Bi films, or drop-casting of pre-synthesized Bi nanoparticles on the carbon electrode surfaces [15]. Recently, Riman et al. [16] described another alternative where the surface of screen-printed carbon electrodes was modified with Bi oxide nanoparticles by a sparking process consisting of applying a high voltage between the carbon electrode and a Bi tip counter electrode. Among the different devices fabricated by these two-step processes, Chen et al. [13] reported the lowest detection limits of 0.03 and 0.34 ppb in the detection of Pb(II) and Cd(II), respectively, using in-situ Bi film modified screen-printed porous carbon electrodes. Overall, all these processes give rise to Bi modified screen-printed carbon electrodes displaying low detection

limits but the additional processing step to incorporate Bi hinders a cost-effective mass production process.

On the other hand, a one-step bulk modification process has also been developed, in which carbon and Bi precursor powders are thoroughly mixed to prepare the ink employed to print the working electrodes. Several Bi precursors can be used, such as Bi_2O_3 , Bi citrate or $\text{Bi}(\text{NO}_3)_3$, which have to be electrochemically reduced to metallic Bi at a selected potential for carrying out the electrochemical analysis [17, 18]. This methodology is simple in terms of electrode production. However, the process relies on a mechanical mixing step for the ink preparation and the analytical performance of the resulting devices strongly depend on the Bi precursor and some analytical parameters such as the Bi reduction potential. As examples, Kadara et al. [17] reported detection limits of 8 and 16 ppb for Pb(II) and Cd(II), respectively, with screen printed $\text{Bi}_2\text{O}_3/\text{C}$ electrodes, whereas Lezi et al. [18] obtained detection limits of 0.9 and 1.1 ppb for Pb(II) and Cd(II), respectively, using Bi citrate bulk-modified carbon electrodes.

Other screen-printing fabrication processes of Bi-based electrodes that do not use carbon as the main ink component or combine other techniques to produce thick-film Bi electrodes should also be mentioned. Hwang et al. [19] directly printed Bi_2O_3 powders on a substrate for the one-step preparation of screen printed Bi electrodes. Detection limits of 2.3 and 1.5 ppb for Pb(II) and Cd(II) were then achieved, respectively. Recently, Sosa et al. [20] reported on the manufacturing of Bi based screen printed electrodes, in which Bi films were generated by sputtering on ceramic substrates. A comparative study was carried out demonstrating that the sputtered Bi electrodes outperformed in-situ and ex-situ Bi film carbon screen-printed electrodes and $\text{Bi}_2\text{O}_3/\text{carbon}$ electrodes. However, these electrodes are not inexpensive and avoid the use of carbon in spite of its demonstrated advantages in electrochemical applications.

A mass-production fabrication approach of screen-printed Bi-based electrodes that overcomes the limitations identified above is still to be achieved. To help meet this goal, here we report on the fabrication and analytical performance of screen-printed Bi-based electrodes prepared with a novel type of ink. This is based on a Bi nanoparticle porous carbon nanocomposite (Bi-C) recently synthesized by our group [21]. The nanocomposite material is obtained from the pyrolysis of Bi-containing resorcinol/formaldehyde gels prepared by sol-gel and its potential in the electrochemical analysis of heavy metals has been initially tested using carbon paste electrodes [21, 22]. The large surface area of Bi nanoparticles combined with the porous carbon matrix resulted in an enlarged available electroactive area and consequently a high sensitivity for heavy metal detection. Although carbon paste electrodes are suitable for laboratory testing they cannot be mass produced and their bulky configuration makes them of not practical use for in-field analytical purposes. In the present study a simple and cost-effective mass production of electrochemical sensors

for heavy metals by screen-printing the inks based on this Bi-C material was attained. The analytical performance of the resulting analytical devices was assessed by carrying out the analyses of Pb(II) and Cd(II) in standard solutions as well as in tap water and wastewater samples.

Experimental section

Reagents and material preparation

The following chemicals were purchased from Sigma-Aldrich (www.sigmaaldrich.com) and used as received: Glycerol formal (47 % 5-hydroxy-1,3-dioxane, 33 % 4-hydroxymethyl-1,3-dioxolane), acetic acid (CH_3COOH , 99.7 % pure), resorcinol ($m\text{-C}_6\text{H}_4(\text{OH})_2$, 99 % pure), formaldehyde water solution (CH_2O , 37 wt.%, methanol stabilized), bismuth nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, 98 % pure), $\text{K}_3\text{Fe}(\text{CN})_6$, $\text{K}_4\text{Fe}(\text{CN})_6$ and standard Cd(II), Pb(II) and Cu(II) solutions ($1000 \text{ mg} \cdot \text{L}^{-1}$).

The porous Bi-C nanocomposite material was prepared in bulk following the procedure previously reported by our group with slight differences [21]. The process was scaled up 20 times in order to get the required material amount for the screen printing process. In brief, 4 g $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, 20 g resorcinol, 27.2 mL formaldehyde, 100 mL glycerol formal, and 40 mL CH_3COOH were mixed thoroughly for 30 min and a transparent sol was formed. Afterwards, the sol was transferred into a closed glass bottle and kept at 60 °C for 8 h to form an organic gel. To obtain an electrically conducting porous carbon the organic gel was pyrolyzed at 900 °C for 2 h in N_2 or Ar atmosphere. This treatment also resulted in the formation of Bi nanoparticles with a Bi_2O_3 shell [21], evenly distributed within the porous carbon. Bismuth was partially lost during the pyrolysis treatment due to its low melting point (271 °C). The material had a Bi concentration of around 6 wt%, measured by energy dispersive X-ray spectroscopy (EDX) (Fig.S1 in the Electronic Supplementary Material, ESM), instead of the expected 9 wt% Bi, estimated from the initial amount incorporated in the sol solution. The total pore volume was $0.049 \text{ cm}^3 \text{ g}^{-1}$ measured by BET nitrogen adsorption and desorption isotherm procedure (Fig.S2 in ESM). For comparative studies, the same sol-gel procedure but without adding $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, was followed to synthesize a porous carbon material and fabricate screen-printed carbon electrodes.

Fabrication of the screen-printed Bi-C nanocomposite electrodes

Screen-printed electrochemical cells were fabricated onto ceramic substrates (L 34 mm × W 10 mm × H 0.5 mm) and included a porous Bi-C nanocomposite circular working electrode with a

diameter of 4 mm (12.6 mm² geometric area; Bi-C SPE), a graphite counter electrode and a silver pseudo-reference electrode. These cells were fabricated by DropSens S.L. (Oviedo, Spain; www.dropsens.com) and show the same geometry to the commercially available DRP-110 SPEs (www.dropsens.com/en/pdfs_productos/new_brochures/110-c110.pdf).

The screen-printing of one batch of electrodes was carried out as follows. To obtain a powder of the Bi-C nanocomposite with the required particle size and distribution, 15 g of material were ball-milled in quantities of 1 g for 7 min without addition of any solvent. This process was carried out in a Retsch Mixer Mill (www.retsch.com), including 100 mL agate containers together with 2 agate balls of 12 mm in diameter. Particle counting was carried out by analyzing more than 10 scanning electron microscopy (SEM) images taken with a FEI Quanta 200F SEM (www.fei.com) equipped with an energy-dispersive X-ray spectroscopy (EDX) analysis system and processed using imageJ software (imagej.nih.gov/ij/). Then, these powders were mixed with other components in order to get the required ink, following a formulation set by the company (proprietary information). The ink curing process was carried out in an oven at 120 °C for 10 min and then at 80 °C for 2 min. Micro-structural characterization of the fabricated electrodes was performed also by SEM.

Electrochemical characterization and application to water analysis

Electrochemical detection of the Pb(II) and Cd(II) was carried out at room temperature in a 20 mL plastic cell using square wave anodic stripping voltammetric technique (SWASV) operated by an Autolab PGSTAT30 potentiostat (Metrohm Autolab B.V, the Netherlands; www.ecochemie.nl). The supporting electrolyte was 0.1 M acetate buffer solution pH 4.5 (Ac buffer). No pretreatment of the Bi-C SPE surface was applied. Pb(II) and Cd(II) were simultaneously reduced to their metallic counterparts onto the electrode surface by applying a deposition potential of -1.7 V under stirring at 700 rpm for a set time. Then, the stirring was stopped and the system was equilibrated for 20 s. Stripping voltammograms were recorded in the potential window from -1.4 to -0.3 V. The squared-wave potential scan was applied with amplitude of 25 mV, frequency of 20 Hz and step potential of 5 mV. All the screen-printed electrodes were single-use. Calibration curves were constructed by plotting the stripping peak current against the corresponding metal ion 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.

Considering the advantages of screen printed electrodes for the analysis of small volume samples, 80 μ L acetate buffer solutions containing different concentrations of Pb(II) and

Cd(II) were drop - cast on the device fully covering the area of the screen-printed electrochemical cell and the previous analyses repeated under quiescent conditions.

Finally, in order to study the practical application of the developed Bi-C SPE, tap drinking water and waste water from an influent of an urban waste water treatment plant located in Terrassa (Barcelona, Spain), were collected and spiked with known concentrations of Pb(II) and Cd(II). A 1:1 dilution using a 0.2 M acetate buffer solution pH 4.5 was carried out in all cases. The waste water sample contained a high load of organic matter but did not contain any detectable amount of the heavy metal ions to be analyzed.

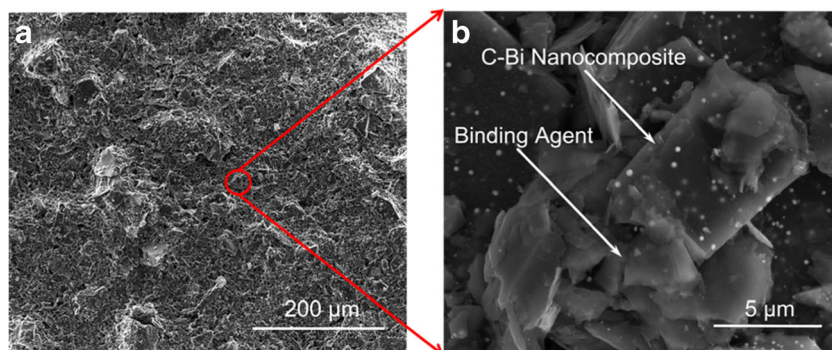
Results and discussion

Screen-printing fabrication and micro-structural analysis of the Bi-C electrodes

The fabrication of the screen-printed electrodes included the preparation of a paste ink using the Bi-C nanocomposite material. The material particle size was critical in order to get an adequate ink formulation that could be printed and gave rise to stable electrode devices. The optimum particle size distribution was found to be between 2 and 50 μ m, with an average size below 10 μ m (Fig.S3 in ESM). Particle sizes above these values produced inks that could not be printed as they did not go through the mesh of the mask whereas narrower particle size distributions not containing a small fraction of bigger particles produced electrodes that easily detached from the ceramic substrate. The resulting paste ink contained 60 % of the Bi-C material while the other 40 % corresponded to the required binding agent and other additives used in its preparation.

Figure 1a presents the backscattered electron SEM image of the rough surface of a screen-printed Bi-C working electrode, this being similar to the surface of any carbon (graphite) screen-printed electrode. A close-up SEM image recorded using the secondary electron detector is shown in Fig. 1b. Both the carbon and the Bi nanoparticle components were observed to be dispersed in the ink. EDX analysis of the electrode surface revealed the presence of 93 wt% carbon, 2.8 wt% bismuth, 2.0 wt% chlorine and 2.2 wt% oxygen, with chlorine being part of the binding agent. The percentage of Bi in the SPE is in agreement with the percentage of the Bi in the initial Bi-C material (≈ 6 %) and the proportion of this material in the ink used in the printing process (≈ 60 %). About 20 g of the Bi-C material were produced using the quantities of the different components mentioned in the [Experimental Section](#). With this amount, 450 electrochemical cells containing the Bi-C electrodes were batch fabricated.

Fig. 1 SEM images of the surface of a screen-printed Bi nanoparticle porous C composite electrode



Electrochemical characterization

Figure 2 shows the cyclic voltammograms recorded in a solution containing 1 mM ferrocyanide/ferricyanide electroactive redox pair using the Bi-C SPE at a potential scan rate of $0.04 \text{ V} \cdot \text{s}^{-1}$. A quasi-reversible signal is observed with a formal potential (E°) and peak-to-peak potential separation (ΔE_p) of ca. 200 mV and of 400 mV, respectively. The scan rate was varied from $0.04 \text{ V} \cdot \text{s}^{-1}$ up to $0.15 \text{ V} \cdot \text{s}^{-1}$. The anodic to cathodic peak current ratio was 1 for all the scan rates tested. The peak current also increased linearly with the square-root of the scan rate, which demonstrates a diffusion-controlled electrochemical process (data not shown). A commercial graphite-based screen printed carbon electrode (DRP 110 from DropSens) showed a ΔE_p of ca. 190 mV at the $0.04 \text{ V} \cdot \text{s}^{-1}$ scan rate. The higher ΔE_p value of the Bi-C SPE indicates a slower electron transfer at the electrode solution interface. This was the expected behavior taking into account the resistance of the Bi-C and commercial graphite screen-printed electrode materials being around 5000Ω and 300Ω , respectively. Nevertheless, the Bi-C SPEs were suitable for the development of electrochemical sensors, as demonstrated with the studies shown below.

Figure 3 shows the SWASV signal for the determination of Pb(II) and Cd(II) in a concentration range from 5 to 100 ppb after an accumulation time of 90 s at -1.7 V in Ac buffer solution. Two clearly visible peaks at around -0.85 and

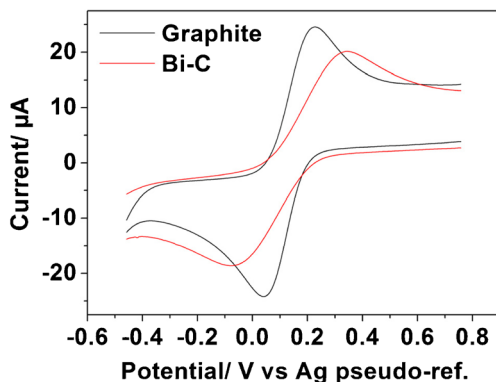


Fig. 2 Cyclic voltammograms recorded in 0.1 M KNO_3 solution containing 1 mM ferrocyanide and 1 mM ferricyanide redox couple recorded at $0.04 \text{ V} \cdot \text{s}^{-1}$ with the Bi-C SPE and a commercial graphite SPE

-0.60 V were ascribed to the stripping process of Cd^0 and Pb^0 , which were originated from the reduction of metal ions and accumulation on the surface of Bi in the deposition step, to produce Cd(II) and Pb(II), respectively. The peak current is directly proportional to the added Pb(II) and Cd(II) in the whole concentration range studied. The corresponding linear calibration curves for Cd(II) and Pb(II) were plotted (Fig. S4 in ESM) and fitted to a linear equation, from which the corresponding sensitivity and limit of detection values were calculated. These are shown in Table 1. The limit of detection (LOD) was calculated according to the formula: $\text{LOD} = 3 \cdot \text{SD}/S$, where SD is the standard deviation of the blank signal obtained from 3 different calibration curves recorded successively and S is the mean of the corresponding slopes [23]. The estimated values were 2.2 and 3.8 ppb for Cd(II) and Pb(II), respectively.

In order to demonstrate that the Pb(II) and Cd(II) stripping responses originated from the presence of Bi nanoparticles in the electrode material, Fig. 4 compares the SWASV signals recorded with the Bi-C SPE in Ac buffer solutions containing 10 and 50 ppb of both Pb(II) and Cd(II), using 90 s accumulation time, as well as those responses recorded with screen-printed porous carbon electrodes without Bi after accumulation times even longer than 300 s. As expected, the results clearly evidence that the Bi-C SPE showed superior performance, which is likely related to different accumulation

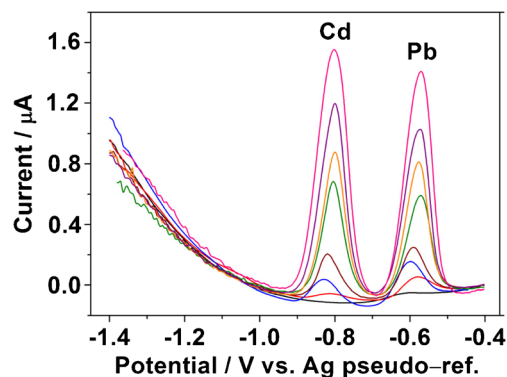


Fig. 3 SWASV signals recorded in standard Ac buffer solutions containing different concentrations of Pb(II) and Cd(II), (from bottom to top 0, 5, 10, 20, 40, 60, 80, 100 ppb). Electrodeposition was carried out at -1.7 V for 90 s

Table 1 Calibration data of the Bi-C SPEs

Accumulation time (s)	Heavy metal	Slope (nA · ppb ⁻¹)	Intercept (nA)	Linear range (ppb)	LOD (ppb)	n	r
90 s	Cd(II)	16±1	-12±11	5–100	2.1	7	0.994
	Pb(II)	13±1	96±17	5–100	3.9	7	0.994
300 s	Cd(II)	24±1	-50±12	1–50	1.5	6	0.999
	Pb(II)	25±1	6±19	1–50	2.3	6	0.998

mechanisms on the surface of both types of electrodes. While these heavy metals form fused alloys with Bi, they simply adsorb on the surface of C. The latter is a competitive process where both Pb(II) and Cd(II) can deposit either on the C electrode material or on top of each other, thus producing stripping peaks that are not well-resolved, are much smaller and are shifted towards more positive potentials compared with those recorded with Bi-C SPE electrodes.

The LOD of our fabricated Bi-C SPE can be enhanced by, 1) increasing the Bi content during the material synthesis process, as it was reported in our previous publication [21], or 2) simply using longer accumulation times. In the present work, the accumulation time was increased up to 300 s. Figure 5 shows the SWASV signals recorded in Ac buffer solutions containing Pb(II) and Cd(II) in the concentration range of 1–100 ppb after a 300 s accumulation at -1.7 V. The calibration curves were plotted (Fig. S5 in ESM) and the corresponding analytical parameters are included in Table 1. A comparison of the calibration curves for both tested accumulation times reveals that a longer accumulation time results in an increased slope and thus in a better sensitivity. The LOD calculated from 3 different calibration curves recorded successively and using the formula mentioned above were 1.5 ppb for Cd(II) and 2.3 ppb for Pb(II). These are about 30 and 40 % lower than those estimated using a 90s accumulation time, respectively, thus demonstrating the validity of this strategy for improving the analytical performance of these electrochemical sensors

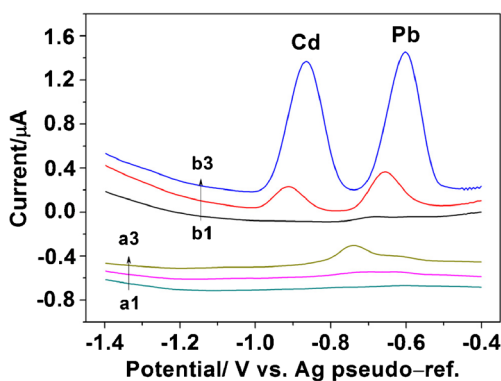


Fig. 4 SWASV signals recorded in standard Ac solutions containing 0, 10, 50 ppb of both Pb(II) and Cd(II) with, (a1 to a3) C-SPEs without Bi nanoparticles (C-SPE), and (b1 to b3) Bi-C SPEs. Electrodeposition was carried out at -1.7 V for 90 s and at -1.7 V for 300 s with Bi-C SPEs and C-SPEs, respectively. An offset was applied to some of the signals, for clarity of presentation

without compromising the rapidity of the analyses. These values are higher than those obtained with a carbon paste electrode (CPE) using the same Bi-C material [22]. Such performance can be related to the ink preparation process that reduces the Bi percentage from around 6 % in the initial Bi-C material to 2.8 % in the ink. Also, ink formulations have an unavoidable negative effect on the performance of the resulting devices that can be related to the incorporation of binding agents and other components. Nevertheless, it should be stressed the practical application of both approaches. The CPE proved to be useful for the characterization and application of the material in the laboratory carried out using a conventional three-electrode electrochemical cell [22]. But since CPE have to be manually prepared, the electrode production cannot be scaled-up. By contrast, Bi-C SPEs can be prepared in large quantities by a parallel process resulting in more cost-effective, reproducible and robust devices.

Table 2 shows that the LOD values of the Bi-C SPEs compare well with those achieved with previously reported Bi based screen-printed electrodes. Bi modified screen-printed carbon electrodes produced by a two-step fabrication approach [13, 16], mostly show lower LODs. However, the Bi-C SPE approach presented here clearly outperforms them if the fabrication process is taken into consideration. The estimated LOD values of our device are within the same order of magnitude than the threshold values recommended by the European Commission [24], the US Environmental Protection Agency [25] and the World Health Organization

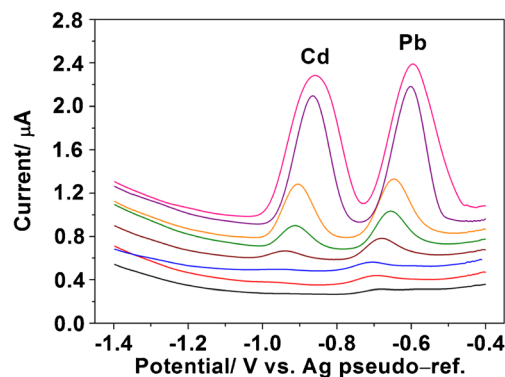


Fig. 5 SWASV signals recorded in standard Ac buffer solutions containing different concentrations of Pb(II) and Cd(II), (from bottom to top 0, 1, 3, 6, 10, 20, 50, 100 ppb). Electrodeposition was carried out at -1.7 V for 300 s

Table 2 Fabrication and performance of bismuth based screen printed electrodes

Bi electrodes	Fabrication process	Linear range (ppb)		LOD (ppb)		Accumulation time (s)	Ref.
		Pb(II)	Cd(II)	Pb(II)	Cd(II)		
In-situ Bi film modified SPC _p E	Two-step	0.05–30	1–30	0.03	0.34	300	[13]
Bi NPs modified SPCE		Not Shown	Not shown	1.3	1.7	120	[15]
Bi ₂ O ₃ modified SPCE		0–12	0–12	0.2	0.2	120	[16]
Bi ₂ O ₃ powder bulk modified SPCE	One-step	20–300	20–300	8	16	120	[17]
Bi citrate bulk modified SPCE		10–80	5–40	0.9	1.1	120	[18]
Bi ₂ O ₃ SPE		20–100	20–100	2.3	1.5	300	[19]
Bi NPs bulk modified SPC _p E		5–100	5–100	3.9	2.1	90	This work
Bi NPs bulk modified SPC _p E		1–50	1–50	2.3	1.5	300	This work

SPC_pE screen printed porous carbon electrode, SPCE screen printed carbon electrode, SPE screen printed electrode, NPs nanoparticles

[26] in surface waters (0.45–5 ppb Cd(II); 10–15 ppb Pb(II)). Nevertheless, it should also be mentioned that the corresponding directives of these three bodies also state that the analytical techniques applied in this context should accurately measure these pollutants at minimum reporting levels that are 5 to 10 times lower than the values mentioned above. Therefore, from the reported values shown in Table 2, it can be said that up to now the potential application of this kind of devices developed by screen-printing is restricted to the rapid detection of, for instance, sudden contamination spills or the monitoring of industrial wastewater treatment processes.

One advantage of the screen printed electrodes is the small sample volume required for carrying out the measurements. Herein, electrochemical analysis in a single solution drop containing Pb(II) and Cd(II), coating the entire area of the screen-printed electrochemical cell, was also investigated. Fig. S6 (ESM) presents the SWASV signals and the corresponding calibration curves extracted from the voltammograms recorded in 80 μ L drops of the Ac buffer solution containing Pb(II) and Cd(II) in a concentration range from 0 to 100 ppb, after 300 s deposition at -1.7 V. Signals for 10 ppb of Pb(II) and Cd(II) were clearly visible and the peak current increased linearly with the concentration of heavy metal ions in the concentration range from 10 to 100 ppb.

Real sample analysis

Aiming at investigating the potential application of the Bi-C SPE for water analysis, two different types of water samples, namely tap drinking water and urban waste water, were collected and analyzed. Two tap water samples were spiked with 20 and 50 ppb of both Cd(II) and Pb(II) and then analyzed by interpolating the recorded peak currents of Cd(II) and Pb(II) into the corresponding calibration curves. The estimated values of both heavy metals were compared with the added ones. Results are summarized in Table 3. Recovery values between 89 and 117 % were obtained, which reveal the good

analytical performance of the Bi-C SPEs. Chloride is known to interfere in the detection of heavy metals. Although this has not been studied in detail, it can be said from the results shown in Table 3 that this interference show little influence, if any, in the analyses of these samples.

Urban waste water with a high load of organic compounds was also analyzed. Although the 90 s accumulation time, set for all the previous experiments, was applied in the first place, this was further increased to 300 s in order to make sure that no measurable concentrations of Cd(II) and Pb(II) were present in the sample. Afterwards, 5 ppb of Cd(II) and Pb(II) were simultaneously added to one water sample. This was analyzed by the standard addition method so that the possible matrix effects were taken into account. Fig. S7 (ESM) shows the typical SWASV responses recorded in the waste water before and after the addition of Cd(II), Pb(II), together with the corresponding standard addition plots. A good agreement between the measured heavy metal concentrations and the added ones was found (Table 3). The presence of a high load of organic matter can mask the presence of heavy metals as they tend to adsorb on it. Here, the results point out that such negative effect did not take place in the tested sample. Overall, these results show the adequate analytical performance and potential applicability of the fabricated Bi-C SPE

Table 3 Results of the analysis of real water samples

Water samples	Heavy metals elements	Added concentration (ppb)	Analyzed concentration (ppb) ^a	Recovery (%)
Tap water	Pb(II)	20.0	23 \pm 2	115
		50.0	58 \pm 5	117
	Cd(II)	20.0	18 \pm 4	89
		50.0	44 \pm 5	90
Waste water	Pb(II)	5.0	5.3 \pm 0.3	106
	Cd(II)	5.0	6.0 \pm 0.9	120

^a Mean value \pm standard deviation of three replicates

for the detection of the studied heavy metal pollutants in water samples, even when containing complex matrices.

Conclusion

The application of Bi-based electrodes in the deployed in-situ analysis of heavy metals requires the cost-effective mass-production of easy-to-use electrode architectures. Conventional electrochemical approaches based on in-situ or ex-situ incorporation of Bi on the surface of conventional electrodes are far from fulfilling these requirements. What we have presented in this work is the fabrication of screen-printed bismuth nanoparticle porous carbon electrodes by a one-step approach that are feasible candidates to be applied in the above-mentioned scenario. The fabrication process included the synthesis of the Bi-C material in bulk, the optimization of the milling process and the preparation of the corresponding ink in order to obtain stable and reproducible electrochemical devices. These were successfully applied to the detection of Pb(II) and Cd(II). Thanks to the large active surface area of bismuth nanoparticles, low detection limits were obtained for both Pb(II) and Cd(II). The analytical performance of these electrodes demonstrated its adequacy for the analysis of heavy metals in waters, although some improvements and further validation studies should be carried out in order to comply with the strict regulations set by the different water bodies. In this context, further investigation will also be directed toward the optimization of the Bi-C nanocomposite ink preparation and the study of other trace heavy metals in water samples.

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