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Electrochemical Determination of Cu(II) Using a Glassy Carbon Electrode Modified with Multiwall Carbon Nanotubes Dispersed in Polyhistidine

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Abstract: We report the sensitive and selective quantification of Cu(II) at glassy carbon electrodes (GCE) modified with multiwall carbon nanotubes (MWCNT) dispersed in polyhistidine (Polyhis), (GCE/MWCNT–Polyhis) based on the complexation of Cu(II) by the histidine residues and further reduction by Differential Pulse Voltammetry in acetate buffer solution. The sensitivity was $(3.6\pm0.3)\times10^6$ μA M^{-1}, the reproducibility 6.6 %, and the detection limit 75 nM (4.8 μg L^{-1}). The quantification of Cu(II) was highly selective even in the presence of excess of Cd(II), Zn(II), Co(II), Fe(II), Fe(III), Al(III), Pb(II), Cr(III), Mn(II), and Ag(I). The proposed sensor was successfully used for quantifying Cu(II) in tap-water and groundwater samples without any pretreatment.

Keywords: Copper quantification · Carbon nanotubes dispersion · Polyhistidine · Glassy carbon electrode · Differential pulse voltammetry

1 Introduction

The determination of heavy metals has received increasing attention due to the importance of their toxicological effects on the environment and human health [1]. Copper is the third most abundant element among the transition metal ions found in human body having a complex role in several biological processes including enzymatic catalysis, hemoglobin synthesis, and oxidative phosphorylation [1,2]. Excessive intake of Cu(II) could cause liver and kidney damage, promote the formation of free radicals and lead to neurological disorders [1–3]. In addition, Cu(II) represents a hazardous pollutant in wastewater often discharged without treatment by metallurgical, plating, printing circuits and mining activities to open watercourses or underground aquifers, reducing the quality of large volumes of water and affecting, consequently, the drinking water standards [4,5]. Therefore, the monitoring of Cu(II) level in water or physiological samples is of toxicological and environmental concern. The World Health Organization published in 1993 a provisional guideline for copper in drinking water indicating that its concentration should not exceed 2 mg L^{-1} (31.5 μM) [6,7].

Different analytical techniques have been used for the determination of copper ions including atomic absorption spectroscopy, inductively coupled plasma-mass spectrometry, and spectrophotometry [8]. Even when these techniques provide accurate results, most of them are expensive and time consuming, and require laborious sample pre-treatment and specialized infrastructure. In contrast, stripping-based electrochemical sensors represent an interesting alternative for the quantification of a large number of metals, including traces of Cu(II) since they allows to obtain low-cost, sensitive and reliable analytical results [9]. Moreover, stripping methods that use chemically-modified electrodes exhibit higher selectivity due to the ability of the modifier to capture specific metal ions.

Due to their unique properties, carbon nanotubes (CNTs) have increasingly been used for the construction of electrochemical sensors aiming to improve their analytical response [10–13]. Still, one of the problems for the preparation of CNT-based sensors is their poor solubility in common solvents. In this sense, several strategies for dispersing CNTs and immobilizing them on the surface of electrochemical transducers have been proposed [10,13]. Recently, we have reported the efficient non-covalent functionalization of multiwall carbon nanotubes (MWCNTs) with the polycation polyhistidine (Polyhis) and the excellent performance of glassy carbon electrodes (GCEs) modified with the resulting dispersion for the sensitive and selective detection of uric acid [14], dopamine [14] and paracetamol [15] in the presence of ascorbic acid (AA), as well as for glucose quantification, previous assembling of glucose oxidase [16].

In this work we propose the use of MWCNT non-covalently modified with Polyhis immobilized at GCE as a sensing layer for the highly selective quantification of Cu(II) through its preconcentration by complex forma-

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tion with histidine residues and further reduction by Differential Pulse Voltammetry in acetate buffer solution. The analytical usefulness of the sensor was evaluated by detecting Cu(II) in the presence of several potentially interfering cations and in groundwater and tap water samples without pretreatment.

2 Experimental

2.1 Reagents

MWCNTs of 15–45 nm diameter and 1–5 microns length were obtained from NanoLab, USA. Polyhistidine (Polyhis, catalog number P9386, mol wt 5000–25 000) was purchased from Sigma. Hydrochloric acid, acetic acid, sodium acetate, mono and dibasic sodium phosphate were purchased from J. T. Baker. Copper(II) sulfate pentahydrate and silver nitrate were received from Biopack; nickel(II) nitrate hexahydrate, lead(II) nitrate, cobalt(II) chloride hexahydrate, iron(II) sulfate heptahydrate, zinc nitrate hexahydrate, aluminum nitrate nonahydrate and cadmium sulfate octahydrate were obtained from Anhedra; chromium(III) chloride hexahydrate was from Fluka, iron(III) chloride hexahydrate was purchased from Mallinckrodt, and manganese(II) sulfate hydrate was acquired from Cicarelli. The cations stock solutions were prepared in a 0.200 M acetate buffer solution pH 5.00 of ionic strength (IS) 0.150 M and then diluted to the desired concentration. Cu(II) solutions were also prepared in 1.00×10^{-5} M HCl and 0.150 M phosphate buffer solutions, IS 0.150 M, pH 5.00. The IS in the different supporting electrolytes was modified by adding 3.00 M NaCl. Ultrapure water ($\rho = 18$ MΩ cm) from a Millipore-MilliQ system was used to prepare all the solutions.

2.2 Apparatus

The electrochemical measurements were performed with a μAutolab (EcoChemie/Metrohm) potentiostat controlled by software NOVA 1.7 for data acquisition and experimental control. A conventional three-electrode system was inserted into the cell (BAS, Model MF-1084) through holes in its Teflon cover. GCE (3 mm diameter, from CH Instruments) modified with MWCNT dispersed in Polyhis was used as working electrode. A platinum wire and Ag/AgCl, 3 M NaCl (BAS, Model RE-5B) were used as counter and reference electrodes, respectively. All potentials are referred to the latter. During the accumulation step, a magnetic stirrer provided the convective transport rotating at approximately 800 rpm.

2.3 Preparation of MWCNT Dispersions

The MWCNT-Polyhis dispersion was prepared according to the conditions previously reported [14]. Briefly, it was obtained by mixing 1.00 mg of MWCNTs with 1.00 mL of 0.25 mg mL^{-1} Polyhis solution (prepared in 75:25 (v/v) ethanol/0.200 M acetate buffer solution pH 5.00) followed by sonication for 30 min. The MWCNT-ethanol dispersion was prepared by mixing 1.00 mg mL^{-1} MWCNT in 1.00 mL of 75:25 (v/v) ethanol/0.200 M acetate buffer solution pH 5.00 and sonicated for 30 min. As it was previously reported [14], MWCNT-Polyhis dispersions are stable for 45 days.

2.4 Preparation of GCE Modified with MWCNT–Polyhis (GCE/MWCNT–Polyhis) or MWCNT–Ethanol (GCE/MWCNT) Dispersions

2.4.1 Conditioning of GCE

The electrodes were polished with alumina slurries of 0.30 and 0.05 μm for 1 min each. After polishing, the electrodes were rinsed with water and cycled 10 times in supporting electrolyte between −0.200 V and 0.800 V at 0.100 V s^{-1}.

2.4.2 Preparation of GCE/MWCNT-Polyhis and GCE/MWCNT

An aliquot of 10 μL of MWCNT-Polyhis or MWCNT-ethanol was dropped on top of the polished GCE, allowing the solvent to evaporate at room temperature for 60 minutes. Before use, the modified GCE was copiously rinsed with water to remove any free Polyhis not attached to MWCNT.

2.5 Procedure

The methodology for the quantification of Cu(II) at the modified electrodes consisted of two steps:

I) Preconcentration of Cu(II): performed by the immersion of GCE/MWCNT-Polyhis in the solution of acetate buffer containing Cu(II) for a given time at open circuit potential under stirring conditions.

II) Differential pulse voltammetry-stripping analysis was performed in 0.200 M acetate buffer solution IS 0.150 M pH 5.00 previous washing with the acetate buffer and medium exchange, under aerated or deaerated conditions. DPV parameters are the following: pulse height of 0.004 V, pulse amplitude of 0.050 V, period of 200 ms, and potential range between −0.300 V and 0.800 V. The analytical signals were obtained after subtracting the background currents.

2.6 Preparation of Real Samples

The tap water was obtained from the laboratory while the groundwater samples were extracted using a windmill. The samples without pretreatment were diluted with 0.200 M acetate buffer solution IS 0.150 M pH 5.00. Since Cu(II) was not detected in these samples, different volumes of the Cu(II) stock solution were spiked into the water samples to analyze the recovery. The content of copper ions in these samples was also determined by inductively coupled plasma-mass spectrometry (ICP-MS).

3 Results and Discussion

3.1 Electrochemical Behavior of Cu(II) at MWCNT–Polyhis Modified GCE

Figure 1 shows cyclic voltammograms obtained in a 5.00×10^{-5} M Cu(II) solution (prepared in acetate buffer solution IS 0.150 M pH 5.00) at GCE/MWCNT (dotted line) and GCE/MWCNT-Polyhis (solid line). At GCE/MWCNT there is a broad reduction current peak at −0.108 V. On the contrary, at GCE/MWCNT-Polyhis this peak is better defined, the associated current drastically increases (8 times) and the overvoltage for the reduction of Cu (II) decreases 0.187 V compared to GCE/MWCNT. These changes are due to: i) the complexation of Cu(II) with the histidine residues of MWCNT-Polyhis that produces an enhancement in the amount of Cu(II) at the electrode surface and ii) to the catalytic activity of MWCNTs that makes possible the reduction of his-Cu(II) at lower potentials. The broadening of the redox peaks at GCE/MWCNT-Polyhis would obey to the different distribution of his-Cu(II) residues close to the electroactive CNTs that originate different electron transfer energy for his-Cu(II) reduction originating a broad range of nearby potentials at which the reduction process of the his-Cu(II) may occur. This effect is not observed at GCE-MWCNT (Figure 1 dotted line) and bare GCE (Figure 1 Inset) because the reduction of Cu(II) occurs in the absence of the polymer. For comparison, the electrochemical behavior of 5.00×10^{-5} M Cu(II) solution at bare GCE is shown in the Inset.

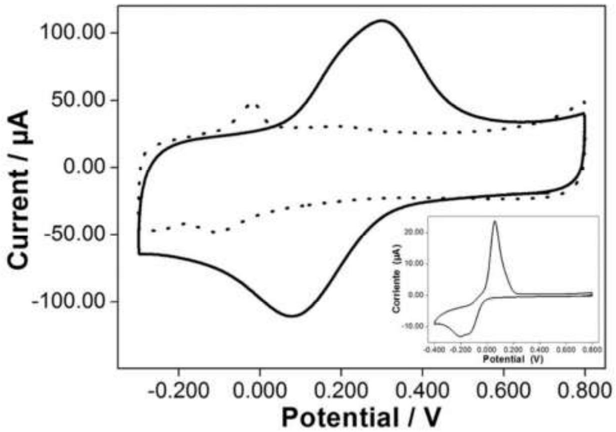

Fig. 1. Cyclic voltammograms for 5.00×10^{-5} M Cu(II) solution obtained at GCE/MWCNT (dotted line) and GCE/MWCNT–Polyhis (solid line) after 10 min of accumulation at open circuit potential without medium exchange. The inset shows the cyclic voltammogram at bare GCE. Supporting electrolyte: 0.200 M acetate buffer solution IS 0.150 M pH 5.00. Scan rate: 0.100 V s^{-1}.

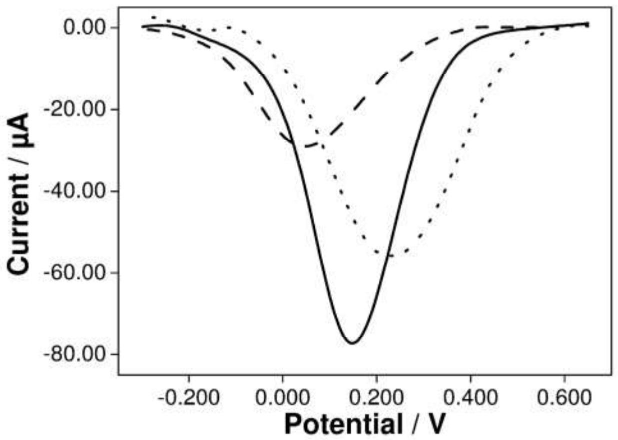

Fig. 2. Differential pulse voltammograms at GCE/MWCNT–Polyhis obtained in different supporting electrolytes IS 0.150 M pH 5.00: HCl solution (dotted line), phosphate buffer solution (dashed line), and acetate buffer solution (solid line), after 10.0 min accumulation at open circuit potential from a 5.00×10^{-5} M Cu(II) solution with medium exchange. Pulse height: 0.004 V; pulse amplitude: 0.050 V; period: 200 ms.

3.2 Optimization of Cu(II) Reduction at GCE/MWCNT–Polyhis

Figure 2 displays differential pulse voltammograms for the reduction of 5.0×10^{-5} M Cu(II) solutions prepared in HCl, phosphate buffer and acetate buffer solutions IS 0.150 M pH 5.00 at GCE/MWCNT-Polyhis. The corresponding peak potentials (E_{pc}) and peak currents (I_{pc}) values are summarized in Table 1. The reduction of Cu(II) occurs at different potentials and the associated currents are also different depending on the supporting electrolyte. Considering that the most adequate pH for the complex formation between histidine and Cu(II) is 5.00 [17] and that for further analytical applications it is important to have a peak as high and well-defined as possible, the acetate buffer solution pH 5.00 was chosen as supporting electrolyte for his-Cu(II) reduction analysis. Under these conditions is possible to improve the detection limit and avoid overlapping with other possible reducing signals from concomitant cations present in the sample.

The effect of the IS on the preconcentration/reduction of his-Cu (II) was evaluated using 0.200 M acetate buffer solution pH 5.00. Figure 3A shows the variation of the cathodic peak current as a function of the IS. The signal increases with the increment in the IS up to 0.150 M, to

Table 1. DPV parameters obtained from recordings shown in Figure 2.

Supporting electrolyte	E_p	I_p
Acetate buffer	0.150 V	77.2 µA
HCl	0.230 V	55.7 µA
Phosphate buffer	0.046 V	29.0 µA

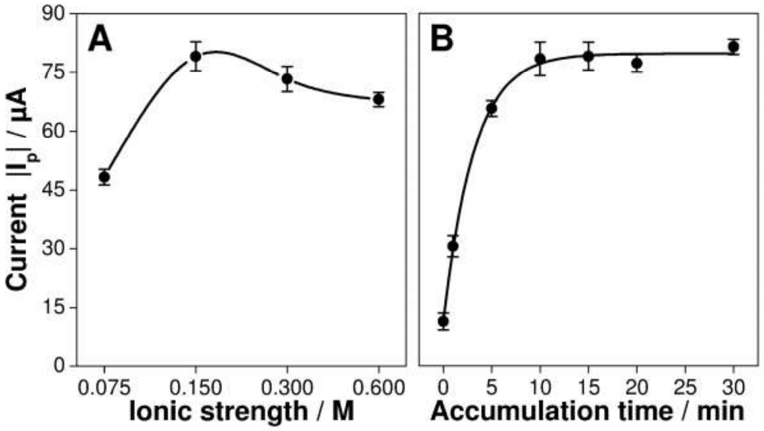

Fig. 3. Influence of the ionic strength (A) and the accumulation time (B) on the DPV response at GCE/MWCNT–Polyhis for the reduction of 5.00×10^{-5} M Cu(II) solution in 0.200 M acetate buffer solution pH 5.00. The experiments were performed at open circuit potential with medium exchange. DPV parameters as in Figure 2.

slightly decrease thereafter. Therefore, 0.200 M acetate buffer IS 0.150 M pH 5.00 was selected for further studies.

The interaction time of Cu(II) at GCE/MWCNT-Polyhis is another important parameter in the optimization of the working conditions of the sensor. Figure 3B shows the I_{pc} values as a function of the accumulation time at GCE/MWCNT-Polyhis in 5.00×10^{-5} M Cu(II) solutions and stripping in acetate buffer solution IS 0.150 M previous medium exchange. I_{pc} increases with the accumulation time up to 10 minutes, to level off thereafter due to the saturation of the histidine residues available for complexation. According to these results, the selected conditions for Cu(II) determination are the following: 10 minutes interaction of GCE/MWCNT-Polyhis at open circuit potential using Cu(II) solutions prepared in 0.200 M acetate buffer solution IS 0.150 M pH 5.00 and stripping in the acetate buffer solution.

3.3 Characterization of Cu(II) Reduced at GCE/MWCNT–Polyhis

Figure 4A shows SEM images of a the GCE/MWCNT-Polyhis surface after reduction of his-Cu(II) accumulated for 10 min from a 5.00×10^{-5} M Cu(II) solution (prepared in 0.200 M acetate buffer solution IS 0.150 M pH 5.00). From this image it is possible to see the distribution of MWCNT in the whole electrode surface. To confirm the presence of copper, EDS measurements were performed in the same electrode region than the one shown in Figure 4A and the results are displayed in Figure 4B. The picture clearly demonstrates the distribution of copper in the whole surface. The Inset shows the EDS spectrum where a Cu peak (K line) appears at 8.05 KeV, clearly evidencing the presence of Cu after its reduction on the electrode surface. The other inset displays the EDS elemental map for Cu on a GCE/MWCNT surface (control experiment). The amount of Cu(II) available for reduc-

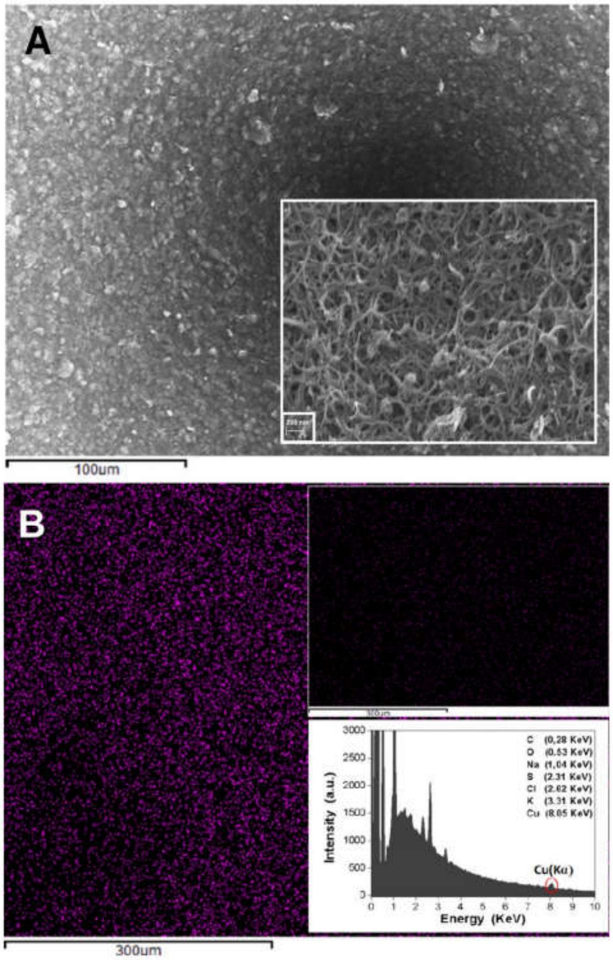

Fig. 4. (A) SEM image and magnification (inset) of a GCE/MWCNT–Polyhis surface after Cu(II) reduction from a 5.00×10^{-5} M Cu(II) solution in 0.200 M acetate buffer solution IS 0.150 M pH 5.00 after 10 min of accumulation at open circuit potential. (B) EDS map for Cu of the same electrode area than A. The insets show the spectrum showing the presence of Cu (K line) at 8.05 KeV and the EDS map after Cu(II) reduction on a GCE/MWCNT surface.

tion on this platform was considerably lower than on GCE/MWCNT-Polyhis, demonstrating the importance of his-Cu(II) complex formation for the analytical determination of Cu(II).

3.4 Analytical Application of GCE/MWCNT–Polyhis

Figure 5 shows the calibration plot obtained at MWCNT-Polyhis modified GCE from the DPV response for increasing concentrations of Cu(II) between 5.00×10^{-7} M and 2.00×10^{-5} M. The calibration plot shows a linear relationship between 5.00×10^{-7} M and 1.25×10^{-5} M with an average sensitivity of $(3.6\pm0.3)\times10^{6}$ µA M^{-1}, and a correlation coefficient of 0.996 (values obtained from four different sensors and four different MWCNT–Polyhis dispersions). Well-defined DPV peaks are obtained for the reduction of his-Cu(II) at 0.170 V for all the studied concentrations range (Inset). The detection limit was 75 nM or 4.8 µg L^{-1} (taken as $3.3\sigma/S$, where σ is the standard deviation of the blank signal and S, the sensitivity) and the quantification limit was 0.23 µM (taken as $10\sigma/S$). Therefore, taking into account that the limit for Cu(II) in drinking water suggested by the World Health Organization is 2 mg L^{-1} (31.5 µM) [6,7], the proposed sensor allows the determination a Cu(II) at a level almost 420 times smaller than this value. The reproducibility, obtained with four different electrodes and four different dispersions was 6.6%.

To evaluate the selectivity, the sensor was challenged with solutions containing different cations, even in concentrations one order of magnitude higher than that of Cu(II), both, individually and mixed with other cations. Figure 6 depicts differential pulse voltammograms obtained in 0.200 M acetate buffer solution IS 0.150 M pH 5.00 at GCE/MWCNT-Polyhis after 10 min accumulation at open circuit potential in a 1.00×10^{-5} M Cu(II) solution (solid line) and in a solution containing 1.00×10^{-5} M Cu(II) plus 1.00×10^{-4} M of Cd(II), Zn(II), Co(II), Fe(III), Fe(II), Al(III), Ni(II), Pb(II),Cr(III), Mn(II) (dotted line). The peak current obtained in the presence of Cu (II) alone or in the presence of the other cations was almost the same, indicating that there is no interference. It is important to remark that the stability constant for Polyhis with Cu(II) in solution is considerably higher than those with other cations [18], being the metal binding trend with Polyhis as follows: Cu(II) $\gg$ Cd(II) $\approx$ Ni(II) $>$ Co(II) $>$ Pb(II) $\gg$ Na(I) $\approx$ Ca(II) $\approx$ Mg(II) $\approx$ Cr(III) $\approx$ Mn(II). These results demonstrate that the accumulation of Cu (II) at open circuit potential through the complexation with the histidine residues present at GCE/MWCNT-Polyhis, prevents the reductive accumulation of other metallic ions and avoids the interference in the reduction of Cu(II) [19]. Another potential interference is the dissolved organic matter (DOM) since it contains some ligands that could compete by Cu(II) in the complex formation. However, the significant difference between the stability constant for Polyhis-Cu(II) and DOM-Cu(II) (10^{19} [20] and 10^{5} [21], respectively) provides clear evidence that the histidine residues have stronger binding affinity than DOM, suggesting a negligible interference by DOM under our experimental conditions.

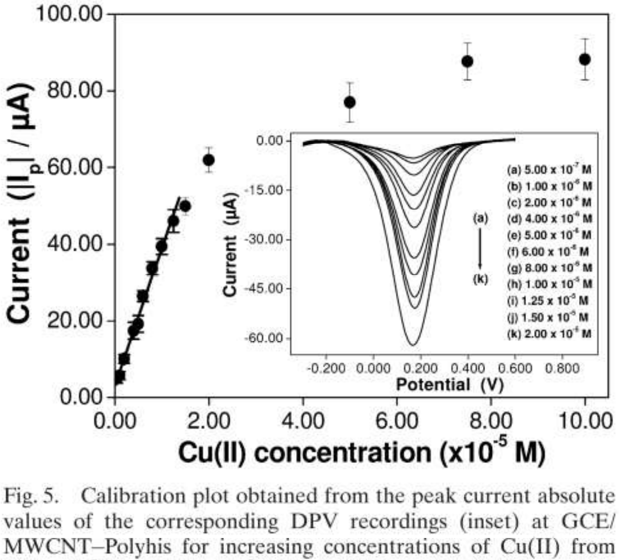

Fig. 5. Calibration plot obtained from the peak current absolute values of the corresponding DPV recordings (inset) at GCE/MWCNT–Polyhis for increasing concentrations of Cu(II) from 5.00×10^{-7} M to 2.00×10^{-5} M in 0.200 M acetate buffer solution IS 0.150 M pH 5.00. Accumulation time: 10.0 min at open circuit potential with medium exchange. DPV parameters as in Figure 2.

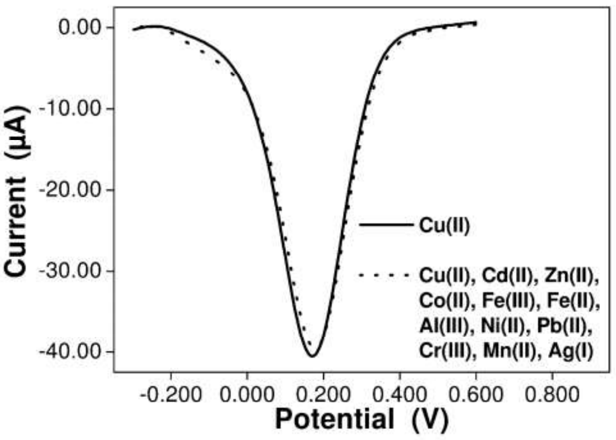

Fig. 6. DPV reduction signal for 1.00×10^{-5} M Cu(II) solution (solid line) compared to the reduction signal obtain in a mixed solution (dotted line) containing 1.00×10^{-5} M Cu(II) and eleven cations (10.00×10^{-5} M each) at GCE/MWCNT–Polyhis in 0.200 M acetate buffer solution IS 0.150 M pH 5.00 after 10 min of accumulation at open circuit potential with medium exchange.

In order to evaluate the practical application of the proposed electrochemical sensor, we determined the recovery of Cu (II) in tap water and groundwater samples (by triplicate) using the MWCNT–Polyhis-modified GCE. The obtained results are summarized in Table 2. For the concentrations evaluated the recuperation assay ranged between 96 and 102% from the most diluted to the most

Table 2. Recovery assay for Cu(II) from spiked tap water and groundwater. Comparison between values obtain with GCE/MWCNT–Polyhis and ICP-MS. ND: not detected. ICP-MS: inductively coupled plasma-mass spectrometry.

Samples	Cu(II) added ($\times 10^{-6}$ M)	Our sensor Cu(II) found	Recovery (%)	ICP-MS Cu(II) found
Tap water	0.00	ND	–	0.028 ± 0.002
	5.00	4.9 ± 0.2	98.1	4.95 ± 0.06
	10.00	10.2 ± 0.5	102.2	10.03 ± 0.05
Groundwater	0.00	ND	–	0.064 ± 0.001
	5.00	4.9 ± 0.3	97.7	5.02 ± 0.09
	10.00	10.0 ± 0.6	100.4	9.7 ± 0.3

concentrated samples, respectively. The proposed sensing platform was validated using ICP-MS (Table 2). The excellent agreement obtained between our data and the ICP-MS results demonstrates that GCE/MWCNT-Polyhis can be successfully used for the quantification of Cu(II) in a simple, fast, sensitive, and selective way without the need of expensive equipments, opening the way for further potential applications of our sensor for Cu(II) determination in water and industrial effluents.

GCE/MWCNT-Polyhis presents several advantages compared to other reported Cu(II) sensors based on CNT modified GCEs [19,22–26] and CNT modified carbon paste electrodes [27]. In most cases, the detection of Cu was focused on the preconcentration of Cu(II) by reducing it on the electrode surface at negative potentials (−1.00 V or −0.60 V) followed by the quantification of the deposited material by anodic stripping voltammetry [22,27]. In those cases, the selectivity to discriminate copper against other cationic metals that can be co-deposited under the same preconcentration procedure depends exclusively on the peak potential separation and resolution of the anodic stripping voltammetry signal. Therefore, the number of cationic species that can be determined without interference is quite limited. Some authors have also done the preconcentration of Cu(II) at open circuit potential [19,23–26] based on Cu(II) complexation with some chelating agents like L-cysteine [19,23], poly(2-amino-4-thiazoleacetic acid) [24], poly(2-aminothiazole) [25], or tripeptide Gly-Gly-His [26], although the determination was done from anodic stripping analysis previous reduction of the complexed Cu(II) [19,23–25]. At variance with those methods for Cu(II) determination, the proposed sensor presents the advantage of better selectivity than other platforms [19,22–27]. Moreover, the sensitivity of our sensor is better than those obtained with GCE/MWCNT-poly(1,2-diaminobenzene) [22] and Cu-ion imprinted polymer-MWCNT-modified carbon paste electrode [27], and comparable to the ones obtained with GCE/MWCNT-poly(2-amino-4-thiazoleacetic acid) [24] and GCE/MWCNT-poly(2-aminothiazole) [25]. It is smaller than the sensitivities obtained using a GCE modified in a more complex way using an hybrid material (GCE/SWCNT-gold nanoparticle-L-cysteine) [19].

4 Conclusions

The combination of the unique and outstanding catalytic properties of MWCNTs with the efficiency of Polyhis to disperse these nanostructures, the stability and reproducibility of the GCE modified with the dispersion, the huge increase in the electroactive area of the resulting electrode, and the selective chelating properties of histidine towards Cu(II) was successfully used for the sensitive and selective quantification of Cu(II) from the reduction of the complexed Cu(II) by differential pulse voltammetry. This new strategy is not interfered by other metallic ions and produces an intelligent sensing layer for the quantification of Cu(II) without sample pretreatment. Thus, we are proposing here a simple, fast, sensitive and highly selective electrochemical sensor for the quantification of Cu(II), with LOD that allows the quantification of Cu(II) at levels considerable smaller than those established by WHO, offering interesting possibilities for further quality control and environmental monitoring applications.

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