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Development of a carbon nanotubes paste electrode modified with crosslinked chitosan for cadmium(II) and mercury(II) determination

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ABSTRACT

A functionalized carbon nanotubes paste electrode modified with cross-linked chitosan for the determination of trace amounts of cadmium(II) and mercury(II) by linear anodic stripping voltammetry is described. Under optimal experimental conditions, the peak current was linear in the Cd(II) concentration range from 5.9×10^{-8} to 1.5×10^{-6} mol L⁻¹ with a detection limit of 9.8×10^{-9} mol L⁻¹ and, for Hg(II) from 6.7×10^{-9} to 8.3×10^{-8} mol L⁻¹ with a detection limit of 2.4×10^{-9} mol L⁻¹. The proposed method was successfully applied for the determination of Hg(II) in natural and industrial wastewater samples, and Cd(II) in sediments, human urine, natural, and industrial wastewater samples.

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1. Introduction

Cadmium is a highly toxic and carcinogenic substance for humans. It has been listed as the sixth most poisonous substance jeopardizing human health [1–3]. The exposition of humans to lower amounts of cadmium may cause renal dysfunction, bone degeneration, lung insufficiency, liver damage, and hypertension [4]. Consequently, the quantification of trace levels of cadmium is a challenging analytical problem of long-standing interest. Several analytical approaches have been applied for the determination of trace amounts of cadmium in biochemical and environmental resources, such as spectrophotometry [1], atomic absorption spectrometry [1], stripping voltammetry [2–7], and X-ray fluorescence [2]. The common methods adopted for the concentration assessment of the metal ions are mainly focused on the use of atomic absorption or inductively coupled plasma (ICP) atomic emission spectroscopy, ICP-mass spectrometry, and electrochemistry (EC) techniques. However, owing to the ponderous and sophisticated instrumentation the spectroscopy methods are fairly cumbersome and not suitable for the *in situ* measurements. On the contrary, the electrochemical techniques have attracted increasing levels of interest. This is owing to the fact that electrochemical methods possess high sensitivity, good selectivity, low cost, simplicity, and

easy data read-out [2,4–10]. Thus, various electrochemical methods, utilizing different modified electrodes have been reported for the determination of Cd(II). Among all the EC methods, stripping voltammetry provides a powerful tool for the determination of metal ions [11,12].

Since the 20th century, after the disaster at Minamata Bay [13] mercury-based compounds has been widely studied, which were observed bioaccumulation, biomagnification to the gravity of its effects on health, being more visible symptoms related to nervous system, kidney, immune, and reproductive systems.

Several analytical methods have been applied for the determination of mercury in biological and environmental samples, such as spectrophotometry [13,14], atomic absorption spectrometry [15,16], stripping voltammetry [17–20] using a different electrodes as gold, glassy carbon, nanoparticles, and carbon paste electrodes.

In general, the performance of anodic stripping voltammetry (ASV) is strongly affected by the electrode material. An ideal electrode should possess qualities such as low ohmic resistance, chemical and electrochemical inertness, good mechanical properties, high hydrogen and oxygen overpotential (wide potential window), low background current and ease of reproduction of the electrode surface. The high sensitivity of ASV [21] is mainly specified by the first step involving the pre-concentration of the analyte species.

The metal adsorption capacity of several low-cost adsorbents, such as biopolymers, has been investigated in the present study. These biopolymers, which are obtained from renewable sources,

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can selectively adsorb several metallic ions [22]. Among these biopolymers, chitosan has proved to be an extremely promising material. Chitosan is a natural biopolymer produced by the alkaline N-deacetylation of chitin, the most abundant natural polymer after cellulose [23–28]. Chemical modifications of chitosan may include chemical cross-linking (to increase polymer stability in acidic solutions) or grafting of new functional groups (to increase the adsorption sites), which can increase the adsorption capacity and selectivity toward the metal ions in the solution [29–32]. Cross-linking agents like glyoxal (GO), epichlorohydrin (ECH), glutaraldehyde (GA), and 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide together with N-hydroxysuccinimide (EDC-NHS) are examples of chemical modifications on chitosan [33,34].

Since the discovery of Carbon Nanotubes (CNTs) by Iijima in 1991 [36], they have attracted increasing attention owing to their extraordinary structural, mechanical, and electrical properties as well as their assurance in the field of material science. The subtle electronic properties indicate that this material has the ability to promote a more effective electronic transfer, resulting in wider applications in electrochemistry [35–39]. Numerous applications of CNTs have also been investigated. For example, they were widely used as scanning probes [40], electron field emission sources [41], nanoelectronic devices [42], batteries [43], potential hydrogen storage material [44] and chemical sensors [45].

In the present study, a simple and effective carbon nanotube paste electrode modified with cross-linked chitosan was developed, and the electrode was applied to the determination of Cd(II) and Hg(II) by anodic stripping voltammetry (ASV). The modifier, chitosan cross-linked with GA can pre-concentrate Cd(II) or Hg(II) from an aqueous solution on its surface and thereby significantly increase the analytical signal. In addition, the high stability and electrical conductivity of carbon nanotubes enables the proposed electrode to have a wide linear range of concentrations, high sensitivity, good selectivity and reproducibility for the determination of these metal species in many samples.

2. Experimental

2.1. Reagents and solutions

The multiwalled carbon nanotubes of diameter 60–70 nm and length 5–9 μm were purchased from Sigma (St. Louis, MO, USA), which submitted to a chemical pre-treatment for 12 h using a mixture of concentrated sulfuric and nitric acids in a proportion of 3:1 v/v, respectively. Subsequently, the mixture was filtered, washed with deionized water until a pH level of 6.5–7.0 was reached, and then dried at 120 °C for 5 h.

The chitosan was obtained by N-deacetylation of chitin in a multi-step process by means of the freeze–thaw cycles, as previously described [46]. The chemical modification of chitosan with epichlorohydrin (ECH) or GA was carried out as previously de-

scribed [33]. The chitosan was immersed in a solution of 0.01 mol L⁻¹ ECH and 0.07 mol L⁻¹ NaOH at 40 °C and maintaining under magnetic stirring for 2 h. Subsequently, the mixture was filtered, rinsed with water until a pH level of 6.5–7.0 was reached, and then dried at room temperature. The chemical modification of chitosan with (GA) was carried out by dissolving chitosan in a solution of 2.5% v/v GA and maintaining under constant agitation at room temperature for 12 h. Subsequently, the chitosan was filtered, rinsed with water to remove the unreacted GA residue, and then dried at room temperature.

All solutions were prepared with ultra-pure water of resistivity not less than 18 M Ω cm obtained with a Millipore Milli-Q system. All other chemical reagents were used as received. A stock solution of 1.0×10^{-2} mol L⁻¹ Cd(II) and 1.0×10^{-3} mol L⁻¹ Hg(II) was prepared by dissolving Cd(NO₃)₂ or HgCl₂ in deionized water. It was later diluted to desired concentrations using deionized water.

2.2. Apparatus

The voltammetric measurements were performed using a three-electrode system, including the modified carbon nanotubes paste electrodes as the working electrode, a platinum plate as the counter electrode, and Ag/AgCl (3.0 mol L⁻¹ KCl) as the reference electrode. A potentiostat/galvanostat Autolab model PGSTAT12 (Ecochemie, Netherlands) controlled by the GPES 4.9 software was used.

The surface electrode morphology was characterized by a field-emission gun scanning electron microscopy FEG/STEM mode (Supra 35-VP, Carl Zeiss, Germany).

The comparative method for Cd(II) determination was carried out by SpectraAA-640 flame atomic absorption spectrometer (Varian, Mulgrave, Australia) equipped with a deuterium lamp background corrector. The measurements were performed at 228 nm, using a cadmium hollow cathode lamp.

The comparative method for Hg(II) determination was performed by a VISTA AX simultaneous inductively coupled plasma optical emission (ICP OES) spectrometer with axial view configuration (Varian, Mulgrave, Australia).

2.3. Preparation of CNPE modified with chitosan and cross-linked chitosan (ECH) or GA

Initially, chitosan was crosslinked with ECH or GA as described elsewhere [33]. Thus, the chemically modified electrodes were prepared by mixing chitosan or cross-linked chitosan with ECH or GA, functionalized multi-walled carbon nanotubes, and mineral oil in different proportions. The mixture was then manually homogenized for at least 30 min. Then, paste was packed into an electrode body, consisting of plastic cylindrical tube (o.d. 8 mm, i.d. 6 mm) with a copper wire for electric contact and the surface was smoothed against clean paper. The unmodified carbon nanotubes

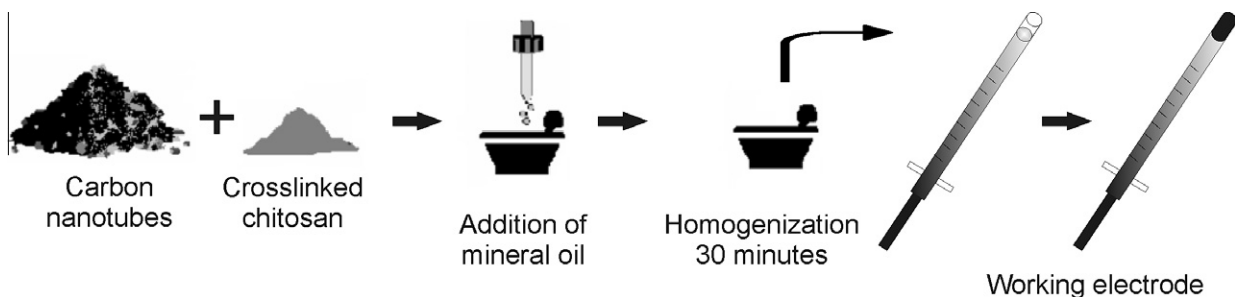


Fig. 1. Schematic construction of the working electrode.

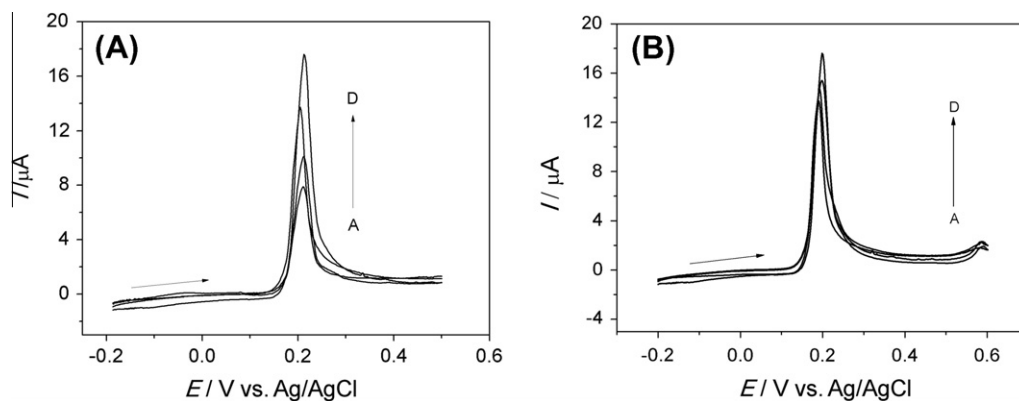


Fig. 2. (A) LSASV of CNPE, CNPE-CTS, CNPE-CTS-ECH and CNPE-CTS-GA in presence of $1.0 \times 10^{-7} \text{ mol L}^{-1} \text{ Cd(II)}$. (B) LSASV of CNPE, CNPE-CTS, CNPE-CTS-ECH and CNPE-CTS-GA in presence of $9.0 \times 10^{-7} \text{ mol L}^{-1} \text{ Hg(II)}$. The experimental conditions were $0.1 \text{ mol L}^{-1} \text{ NaNO}_3$ supporting electrolyte (pH adjusted with conc. HNO_3 to 6.1), accumulation potential of -0.2 V for 270 s and scan rate of 25 mV s^{-1} .

paste electrodes were also prepared using the same procedure as shown in Fig 1.

2.4. Analytical procedure

The Cd(II) and Hg(II) determinations were evaluated by linear sweep anodic stripping voltammetry (LSASV). The parameters used in the LSASV for both analytes measurements were evaluated. The modified CNPE was applied for Cd(II) determination in samples of industrial wastewater, natural water, urine, and sediments and Hg(II) determination was applied in industrial wastewater and natural water.

The samples of sediments were collected from the Jundiá river (São Paulo, SP, Brazil) and dried in an oven at $65 \text{ }^\circ\text{C}$ up to a constant mass. Later, the sediments were softened and drizzled in a mesh of $212 \text{ }\mu\text{m}$. A sample mass of 100 mg was digested with 2.0 mL of aqua regia and 1 mL of concentrated H_2O_2 , in a closed microwave oven for 34 min. After cooling the microwave vessels, 1.0 mL of $1.0 \text{ mol L}^{-1} \text{ HF}$ was added for the attack of the silicate fractions and $0.5 \text{ g H}_3\text{BO}_3$ for the complexation reaction of the remaining fluorides [47]. Finally, the sediments samples A ($1.37 \times 10^{-5} \text{ mol L}^{-1}$), B ($1.47 \times 10^{-5} \text{ mol L}^{-1}$), C ($1.48 \times 10^{-5} \text{ mol L}^{-1}$) and D ($17.6 \times 10^{-5} \text{ mol L}^{-1}$) determined by FAAS were diluted in 0.1 mol L^{-1} acetic acid solution (pH = 3.0) for measurements.

3. Results and discussion

3.1. Study of the CNPE and CNPE modified with chitosan and cross-linked chitosan for metallic ions determination

Initially, the functionalization of carbon nanotubes was evaluated. Carbon nanotubes paste electrodes were prepared using functionalized and non-functionalized carbon nanotubes. As expected, the functionalized carbon nanotubes exhibit a higher analytical signal, which can be related to the introduction of polar hydrophilic surface groups, mainly carboxyl group at the ends or at the sidewall defects of the nanotubes structure that can increase the conduction of electrons as observed in a previous work of our group [33]. The SEM images proved appearance of sidewall in functionalized carbon nanotubes when compared with non-functionalized carbon nanotubes (see Fig. 4).

It was performed the peak current response for Cd(II) and Hg(II) by LSASV evaluation for the functionalized carbon nanotubes paste electrode (CNPE). This contained 60% m/m of functionalized carbon nanotubes and 40% m/m of mineral oil. It also contained functionalized carbon nanotubes paste electrode modified with chitosan

(CNPE-CTS), chitosan cross-linked with ECH (CNPE-CTS-ECH) or GA (CNPE-CTS-GA) containing respectively 60% m/m of functionalized carbon nanotubes, 20% m/m of modifier, and 20% m/m of mineral oil. The measurements were carried out separately for both analytes ($1.0 \times 10^{-7} \text{ mol L}^{-1} \text{ Cd(II)}$) and $9.0 \times 10^{-7} \text{ mol L}^{-1} \text{ Hg(II)}$) in $0.1 \text{ mol L}^{-1} \text{ NaNO}_3$ (pH = 6.1 adjusted with conc. HNO_3) solution using an accumulation potential of -0.2 V applied for 270 s, in a potential range from -0.2 to 0.6 V vs. Ag/AgCl ($3.0 \text{ mol L}^{-1} \text{ KCl}$) raised at a scan rate of 25 mV s^{-1} . The CNPE (A), the electrodes modified with chitosan (B), the cross-linked chitosan with ECH (C), and the GA (D) are all shown in Fig. 2. It was observed that the CNPE-CTS-GA presented a higher analytical signal for Cd(II) and Hg(II) detection in comparison to the modified electrodes with CTS-ECH and CTS. However, at present, the role of CTS cross-linked in the enhanced current is not sufficiently clear. Nevertheless, the crosslinking of chitosan can improve the ion transportation by a mechanism involving pore and membrane diffusion, as recently described [48,49]. This could be responsible for the enhanced analytical response of the electrode for metallic cations.

The crosslinking reactions are usually carried out in order to prevent chitosan dissolution in acidic solutions or to improve the metal adsorption properties, i.e., to increase the capacity or to enhance the selectivity. Since glutaraldehyde binds to the amino

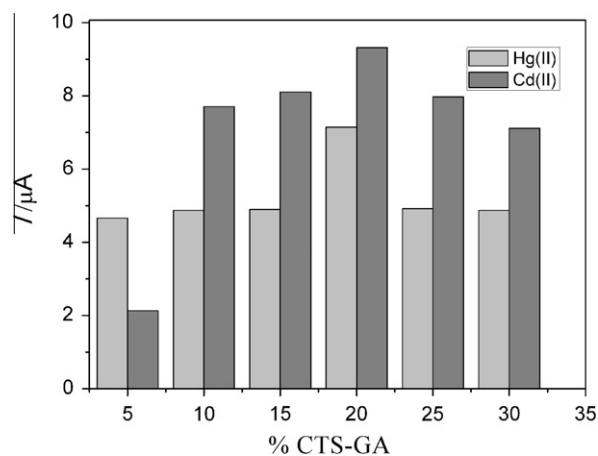


Fig. 3. Anodic peak currents obtained by LSASV as function of the amount of CTS-GA in the CNPE for $1.0 \times 10^{-7} \text{ mol L}^{-1} \text{ Cd(II)}$ or $9.0 \times 10^{-7} \text{ mol L}^{-1} \text{ Hg(II)}$ solution. The experimental conditions were $0.1 \text{ mol L}^{-1} \text{ NaNO}_3$ supporting electrolyte (pH adjusted with conc. HNO_3 to 6.1), accumulation potential of -0.2 V for 270 s and scan rate of 25 mV s^{-1} .

groups, it is necessary to identify the chemical functionality that is responsible for metal–chitosan interaction [50]. When comparing the types of cross-linking, it was observed that the use of the GA reagent yielded the highest current response. This could be related to the presence of the free hydroxyl groups that would be able to complex with Cd(II) cations. Therefore, the CNPE-CTS-GA electrode was selected for further studies owing to the best performance responses for Cd(II) and Hg(II).

The influence of the concentration of CTS-GA in the paste composition on the peak current of Cd(II) and Hg(II) was studied for a 1.0×10^{-7} Cd(II) or 9.0×10^{-7} mol L⁻¹ Hg(II) solution. The influence was investigated by altering the mass ratio of CTS-GA to the functionalized carbon nanotubes in the electrode, the peak currents increased with the increase of the CTS-GA mass up to 20% (m/m) in the paste, as observed in Fig. 3. When the amount of CTS-GA was higher than 20% (m/m) the capacitive current was enhanced, the peak becoming broad and the peak currents decreasing significantly. The best functionalized carbon nanotubes paste composition was found with an electrode composition of 60% (m/m) CNTs, 20% (m/m) CTS-GA, and 20% (m/m) mineral oil. Moreover, this composition presented the best anti-fouling resistance, repeatability of signals and the reproducibility of the electrodes.

The image was performed in order to verify the electrode surface of the CNPE-CTS-GA, as observed in the FEG-SEM image presented in Fig. 4. Subsequently, it was observed that the cross-linked chitosan particles were densely dispersed in the electrode surface.

The electrochemical responses of CNPE-CTS-GA electrode in various supporting electrolytes such as HCl, NaNO₃, KNO₃, NaCl, KClO₄, KCl at 0.1 mol L⁻¹ concentration and acetate buffer solution (at 0.1 mol L⁻¹ and pH ~ 5.0) were also investigated. The best re-

sults in terms of sensitivity (slope of the analytical curve) and voltammetric profile or behavior were found with a 0.1 mol L⁻¹ acetate buffer solution, which was used in further studies to evaluate the effect of the pH in the range from 2.5 to 5.5. The 0.1 mol L⁻¹ acetic acid solution (pH = 3.0) presented the best peak shape and higher anodic stripping peak current for the detection of Cd(II). In the same way, it was studied the best electrolyte for Hg(II) determination using the supporting electrolytes, however, for this metallic ion it was chosen 0.1 mol L⁻¹ HCl. Therefore, a 0.1 mol L⁻¹ acetic acid solution was used for Cd(II) determination and 0.1 mol L⁻¹ hydrochloric acid was used for Hg(II) determination in further studies.

The dependence of the anodic peak currents with the scan rate in LSASV was appraised in the range from 10 to 120 mV s⁻¹. An increase in the magnitude of the peak current with the increase in the scan rate up to 80 mV s⁻¹ was observed and remaining constant after this value. Thus, it was chosen a scan rate of 80 mV s⁻¹ for subsequent studies.

The anodic stripping peak currents for 1.0×10^{-7} mol L⁻¹ Cd(II) or 9.0×10^{-7} Hg(II) solution after an accumulation time of 270 s under different accumulation potentials are shown in Fig. 5. It can be seen that when the accumulation potential shifts negatively from -0.1 to -0.8 V, the stripping peak currents for Cd(II) solution increase up to potential of -0.4 V and do not change for potentials from -0.4 to -0.8 V. The experiments also demonstrated that a further negative shift of the accumulation potential could not obviously increase the peak current. However, it could cause a relatively higher background current, which is mainly attributed to the hydrogen evolution at such negative potentials. Therefore, an accumulation potential of -0.4 V was chosen for further studies. In the Hg(II) case, similarly the anodic peak currents increase until

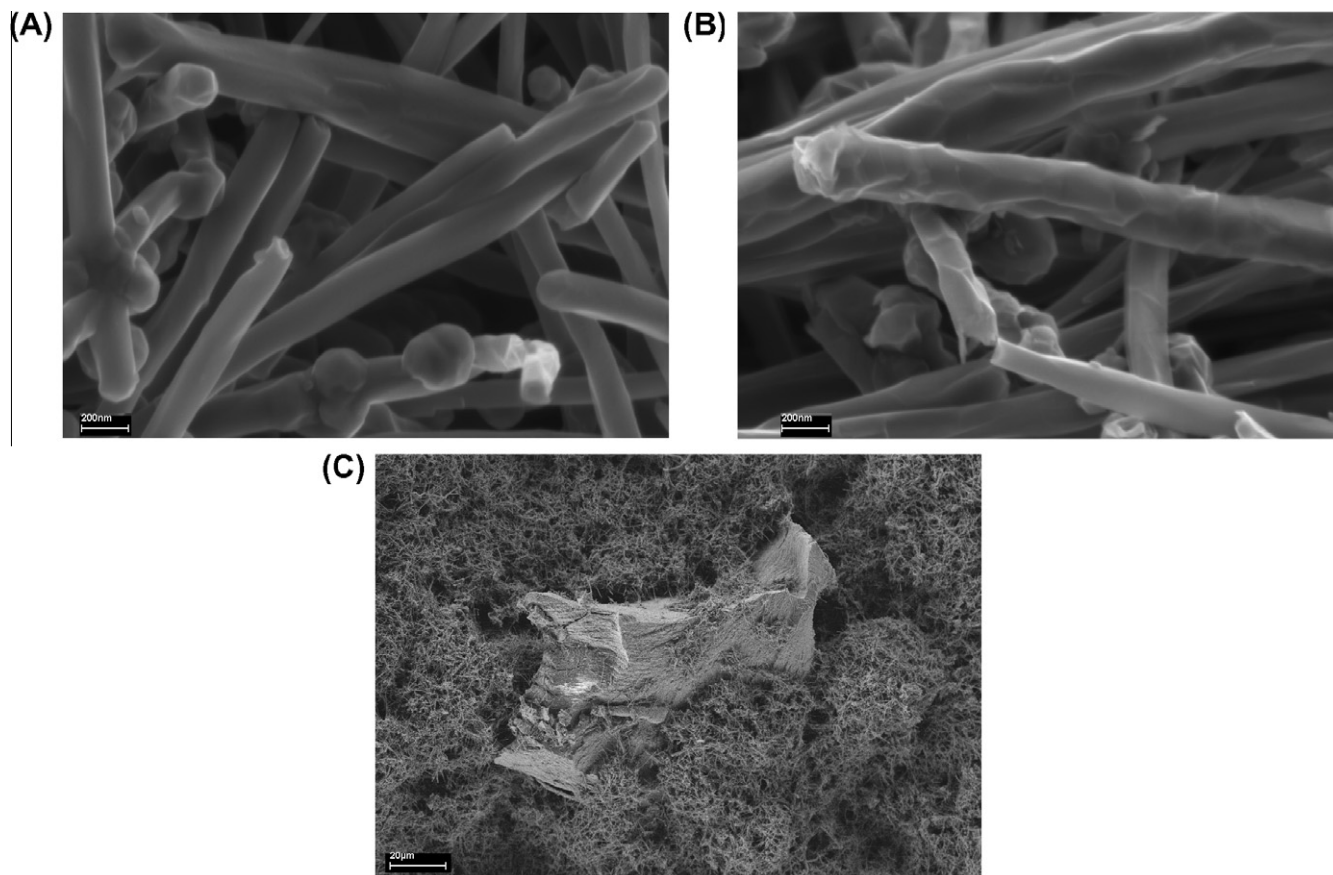


Fig. 4. SEM image of (A) non-functionalized carbon nanotubes, (B) functionalized carbon nanotubes, and (C) CNPE-CTS-GA.

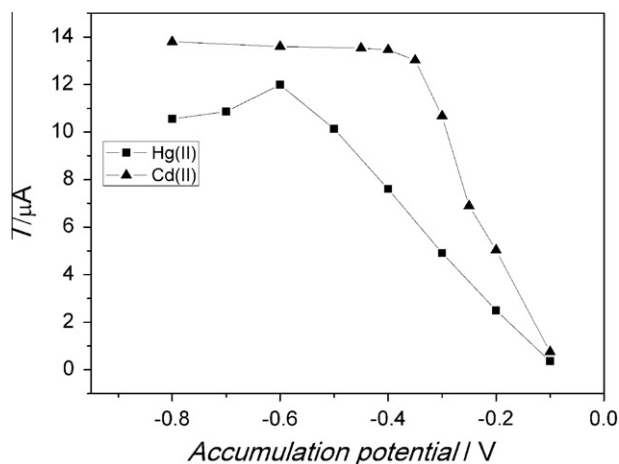


Fig. 5. Study of the anodic peak currents obtained by LSASV as function of the accumulation potential in presence of $1.0 \times 10^{-7} \text{ mol L}^{-1} \text{ Cd(II)}$ or $9.0 \times 10^{-7} \text{ mol L}^{-1} \text{ Hg(II)}$. The experimental conditions were supporting electrolytes: 0.10 mol L^{-1} acetic acid for Cd(II) and 0.1 mol L^{-1} hydrochloric acid for Hg(II) at a scan rate of 80 mV s^{-1} .

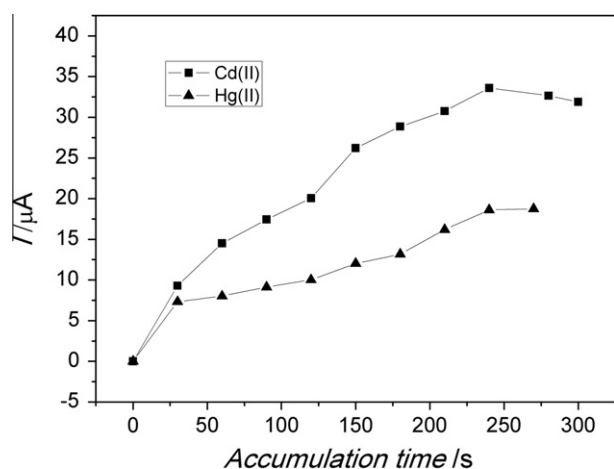


Fig. 6. Study of the anodic peak currents obtained by LSASV as function of the accumulation time in presence of $9.0 \times 10^{-7} \text{ mol L}^{-1} \text{ Hg(II)}$. The experimental conditions were 0.1 mol L^{-1} hydrochloric acid supporting electrolyte, scan rate of 80 mV s^{-1} . Inside the study of accumulation time for $1.0 \times 10^{-7} \text{ mol L}^{-1} \text{ Cd(II)}$ in 0.1 mol L^{-1} acetic acid supporting electrolyte, scan rate of 80 mV s^{-1} .

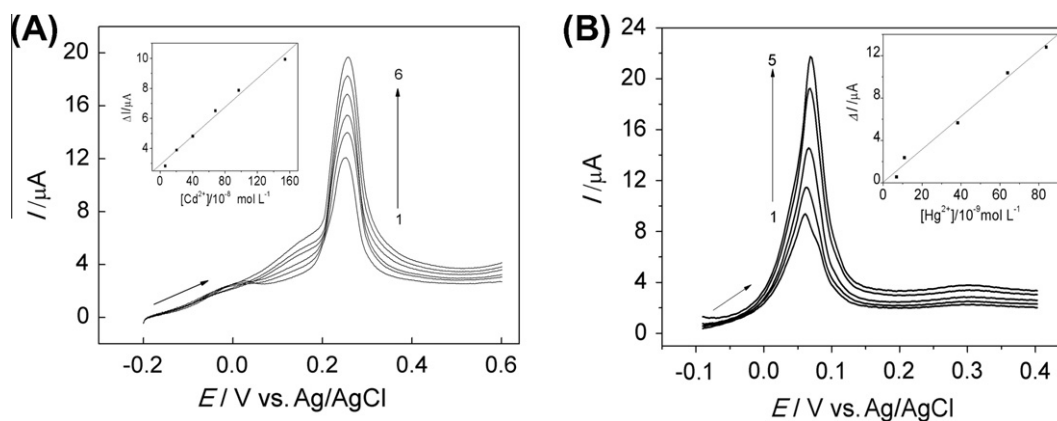


Fig. 7. Voltammograms and calibration curve obtained with CNPE-CTS-GA in different Cd(II) (A) and Hg(II) (B) concentrations. The experimental conditions were supporting electrolyte: 0.1 mol L^{-1} acetic acid for Cd(II) and 0.1 mol L^{-1} HCl for Hg(II), accumulation potential of -0.4 V for Cd(II) and -0.6 V for Hg(II), accumulation time of 240 s and scan rate of 80 mV s^{-1} for both metallic cations.

-0.6 V for Hg(II), and more negative accumulation potentials, from -0.6 to -0.8 V , the stripping peak current for Hg(II) remains almost unchanged.

The influence of the accumulation time on the anodic stripping peak current for $1.0 \times 10^{-7} \text{ mol L}^{-1} \text{ Cd(II)}$ or $9.0 \times 10^{-7} \text{ mol L}^{-1} \text{ Hg(II)}$ solution is shown in Fig. 6. Accumulation time is the most important factor for determination of the detection limit in stripping voltammetric analysis. At the same accumulation potential, a longer accumulation time would cause metallic ions to be reduced more completely. Subsequently, this would lead to a higher peak current. However, when the accumulation time is extremely long the reduced ions covers the entire effective electrode surface, and the peak current does not change with the increasing accumulation time. Experiments with different accumulation times ranging from 0 to 350 s were performed. The best definition and maximum peak current were obtained at a time accumulation of 240 s for both metallic cations. After this time, the signal it started to level off, which could be attributed to the fact that the amount of Cd(II) or Hg(II) on the modified electrode surface had greatly increased. If the accumulation time increases from 240 to 350 s, the peak current of analytes remains almost unchanged and the plot becomes a straight line, thereby revealing that the amount accumulated at the modified electrode surface tends to a limiting value. Therefore, an accumulation potential of -0.4 V for Cd(II) and -0.6 V for Hg(II) within the accumulation time of 240 s for both metallic cations and were selected for the accumulation time.

3.2. Interference studies

A systematic study was carried out to evaluate the interference under the optimum conditions of foreign cations, anions, and organic substances on the determination of Cd(II) or Hg(II). The examined ions, such as Fe(III), Cu(II), Zn(II), Mn(II), Pb(II), Ni(II) in a 100-fold excess did not interfere. Anions, such as Cl^- , CO_3^{2-} , SO_4^{2-} , PO_4^{3-} (and urea for Cd(II)) in a 100-fold also showed no interference. Fortunately, the presences of most examined ions in water samples are very low and the tolerance limit was defined as the maximum concentration of the interfering species which caused an error lower than 3% in the analysis.

3.3. Quantitative aspects

The relationship between the anodic peak current and the Cd(II) concentration was also studied. Well-defined peaks were observed by applying an accumulation potential of -0.4 V for 240 s following the LSASV with a scan rate of 80 mV s^{-1} in a concentration

range from 5.9×10^{-8} to 1.5×10^{-6} mol L⁻¹. The calibration curve for Hg(II) was studied in the potential interval from -0.1 to 0.4 V vs. Ag/AgCl, scan rate of 80 mV s⁻¹ after an accumulation time of 240 s, applying a potential of -0.6 V.

In addition, the calibration curves were observed in Fig. 7. It can be seen that the peak current increased proportionally with the concentration of Cd(II) ranging from to yield the linear regression equation of $\Delta I_{pa} (A) = 2.92 + 0.05[Cd(II)] (10^{-8} \text{ mol L}^{-1})$, with a cor-

relation coefficient of 0.995 and a detection limit of 9.8×10^{-9} mol L⁻¹ ($3 \times SD/m$, where SD is the standard deviation of blank and m is the slope of the analytical curve). A relative standard deviation of 2.0% for 1.0×10^{-7} mol L⁻¹ Cd(II) solution ($n = 10$) under optimized conditions was also obtained. The anodic peak current was linearly dependent on the Hg(II) concentration ranging from 6.7×10^{-9} to 8.3×10^{-8} mol L⁻¹ in 0.10 mol L⁻¹ HCl. The voltammograms and the respective calibration curve are shown in Fig. 7. In accordance with the calibration curve the linear regression equation was $\Delta I_{pa} (\mu A) = 0.53 + 0.15 [Hg(II)] (10^{-9} \text{ mol L}^{-1})$, correlation coefficient of 0.995 and a detection limit of 2.4×10^{-9} mol L⁻¹. A relative standard deviation of 1.7% for 1.0×10^{-7} mol L⁻¹ Hg(II) solution ($n = 10$) under optimized conditions was also obtained. Relative standard deviations of 4.0% and 2.0% was obtained for 1.0×10^{-8} mol L⁻¹ Hg(II) solution and 1.0×10^{-7} mol L⁻¹ Cd(II) solution respectively using four different electrodes prepared in the same way.

Table 1
Recovery studies of Cd(II) or Hg(II) in different samples.

Metallic ion	Sample	Added	Found	Recovery
Cd(II) concentration ($\mu\text{mol L}^{-1}$)	Human urine	0.50	0.49 ± 0.03	98.0
		5.0	5.1 ± 0.1	102
		10.0	9.9 ± 0.1	99.0
	Natural water	0.50	0.49 ± 0.03	98.0
		5.0	5.1 ± 0.1	102
		10.0	9.9 ± 0.1	99.0
Industrial wastewater	0.50	0.52 ± 0.09	104	
	1.0	1.0 ± 0.1	100	
	5.0	4.9 ± 0.1	98.0	
Hg(II) concentration (nmol L ⁻¹)	Natural water	8.0	7.8 ± 0.1	97.5
		10.0	10.3 ± 0.1	103
	Industrial wastewater	15.0	15.1 ± 0.2	100
		8.0	7.9 ± 0.1	99.0
	Industrial wastewater	10.0	10.2 ± 0.1	102
		15.0	14.7 ± 0.2	98.0

3.4. Application

The proposed method was employed in different samples to determine Cd(II) or Hg(II) in water samples and verify its potential application. To evaluate the applicability of the proposed electrode, the recovery of metallic ions was realized in the spiked samples of industrial wastewater, natural water for both metallic cations and human urine for Cd(II), as shown in Table 1.

Table 2
Determination of Cd(II) in sediments and Hg(II) in natural water.

Sample	Cd(II) concentration (10^{-7} mol L ⁻¹)			Sample	Hg(II) concentration (nmol L ⁻¹)				
	Comparative method ^a	Proposed method	Relative error%		Comparative method ^b	Proposed method	Relative error%		
Sediments	A	0.50 ± 0.03	0.52 ± 0.09	4.0	Natural water	A	8.4 ± 0.2	8.6 ± 0.2	2.4
	B	2.4 ± 0.2	2.3 ± 0.1	-4.1		B	10.4 ± 0.3	10.2 ± 0.2	-1.9
	C	3.5 ± 0.2	3.6 ± 0.1	1.0		C	12.2 ± 0.2	12.0 ± 0.5	-1.6
	D	10.7 ± 0.2	11.1 ± 0.1	3.6		D	15.3 ± 0.1	15.8 ± 0.2	3.4

^a Determined by TS-FF-AAS.

^b Determined by ICP OES.

Table 3
Comparison of the figures of merit for the present work and some recently reported electrodes for Cd(II) determination.

Electrode	Modifier	Method	Deposition time (s)	L.D. (nmol L ⁻¹)	Refs.
GC	Nafion-Graphene	DPASV	500	0.044	[57]
MWCNTs	-	PSA	180	74.7	[58]
BDD	Sb-NPs	LSASV	120	1334	[59]
Pt	Kaolin	SWASV	1500	54.0	[60]
MWCNTs	CTS-GA	LSASV	270	9.8	This work

GC – Glassy Carbon; MWCNTs – Multi-walled Carbon Nanotubes; BDD – Boron-Doped Diamond; CNTs – Carbon Nanotubes; Sb-NPS – Antimony Nanoparticles; CTS-GA – Chitosan with Glutaraldehyde; DPASV – Differential Pulse ASV; PSA – Potentiometric Stripping Analysis; LSASV – Linear sweep ASV; SWASV – Square Wave ASV.

Table 4
Comparison of the figures of merit for the present work and some recently reported electrodes for Hg(II) determination.

Electrode	Modifier	Method	Deposition time (s)	L. D. (nmol L ⁻¹)	Refs.
Au	-	SWASV	60	1.9	[17]
MWCNTs	DHP	SWASV	300	32.0	[18]
GC	Au-NPs	DPASV	120	0.2	[19]
CPE	SG-NPorous	DPASV	450	8.0	[20]
MWCNTs	CTS-GA	LSASV	240	2.4	This work

Au – Gold Electrode; MWCNTs – Multi-walled Carbon Nanotubes; GC – Glassy Carbon; CPE – Carbon Paste Electrode; DHP – Dihexadecyl Hydrogen Phosphate; Au-NPS – Gold Nanoparticles; SG-NPorous – Silica Gel Nanoporous; CTS-GA – Chitosan with Glutaraldehyde; DPASV – Differential Pulse ASV; LSASV – Linear sweep ASV; SWASV – Square Wave ASV.

The concentration of Cd(II) in sediments was also determined by Thermospray Flame Furnace Atomic Absorption Spectrometry (TS-FF-AAS) [47,51] to verify the accuracy of the voltammetric method. It was found that the results obtained by CNPE-CTS-GA are in good agreement with the comparative method, as shown in Table 2. This indicates that the method has good accuracy and potential application for the determination of Cd(II). Also, it was found that the results obtained by the proposed method were not statistically different from the comparative method values at a 95% confidence level.

Table 2 also presents the Hg(II) concentrations determined in spiked water samples. Aliquots of Hg(II) was added in the collected water from river of the region (Monjolinho – São Carlos – SP – Brazil) and the results were compared with those obtained by ICP OES technique. Each sample was analyzed in triplicate and the results obtained by the proposed method were not statistically different from the comparative method values, at a 95% confidence level.

According to the National Oceanic and Atmospheric Administration (NOAA) [52] the maximum level allowed of Cd(II) and Hg(II) in natural waters in the USA are 0.02 mg L^{-1} ($1.8 \times 10^{-7} \text{ mol L}^{-1}$) and 0.0014 mg L^{-1} ($7.0 \times 10^{-9} \text{ mol L}^{-1}$), respectively. For Canadian [53] and Brazilian [54] agencies, the allowed levels are 0.005 mg L^{-1} ($4.5 \times 10^{-8} \text{ mol L}^{-1}$) for Cd(II) (in both countries) and 0.001 mg L^{-1} ($5.0 \times 10^{-9} \text{ mol L}^{-1}$) or 0.002 mg L^{-1} ($1.0 \times 10^{-8} \text{ mol L}^{-1}$) for Hg(II), respectively. The proposed method is able to detect the heavy metals tested at the regulatory level without any further pretreatment of the samples.

Adsorption capacity of crosslinked chitosan towards Hg(II) and Cd(II) are different, once that CNPE-CTS-GA electrode presents different linear ranges and detection limit for these analytes. A similar electrode for Cu(II) determination was developed by our group [33], using as crosslinker epichlorohydrin instead of glutaraldehyde. Moreover, some research groups have been proposed electrodes for heavy metal determination using crosslinked chitosan with different crosslinker agents [55,56], which present different selectivity. Moreover, the accumulation potential, the supporting electrolyte and the structure of crosslinked chitosan with GA may influence selectivity and/or detection limit.

The response characteristics of the proposed method were compared with those reported in the literature with different electrodes developed for Cd(II) and Hg(II) (Tables 3 and 4). It can be seen that the proposed CTS-GA carbon nanotube paste electrode system has a good detection limit with a low deposition time as compared to most of the other methods for the electrochemical determination of Cd(II) and Hg(II).

4. Conclusions

The functionalized carbon nanotubes and chitosan cross-linked with glutaraldehyde can be used in the development of modified electrodes for the determination of Cd(II) or Hg(II). Thus, the chitosan cross-linked with glutaraldehyde exhibits a higher accumulation ability for the studied metallic ions. The CNPE-CTS-GA, which can be easily prepared, has proved to be a selective electrode for Cd(II) or Hg(II) analysis in urine, natural water, and industrial wastewater samples using linear scan anodic stripping voltammetry with satisfactory results.

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