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Abstract

A new simple chronoamperometry methodology was developed for the ultrasensitive determination of mercury ions using a PEDOT: PSS {Poly (3,4-ethylenedioxythiophene) poly(styrenesulfonate)} coated graphite carbon electrode. The polymer was coated carbon electrode was optimized using simple cycle voltamerometric measurement, that gives in the presence of 5×10^{-3} $mol.L^{-1}$ mercury ions a cathodic peak started at +(600±50) mV vs. Ag/AgCl, and an anodic peak started at +(100±10) mV vs. Ag/AgCl. Electro accumulation of mercury ions onto the PEDOT: PSS modified electrode was performed at +100 mV vs. Ag/AgCl for 30 sec in a pH 2.25 nitric acid solution. Chronoamperometry measurements were carried out at +600 vs. Ag/AgCl allowing the oxidation of accumulated mercury. Using this method, mercury ions were detected for concentrations ranging between 0.1 $\mu mol.L^{-1}$ to 8.0 $\mu mol.L^{-1}$ (R^2= 0.998). The detection limit was calculated to be 0.01 $\mu mol.L^{-1}$ and the quantification limit of 0.04 $\mu mol\ L^{-1}$. The method was shown to be highly precise and sensitive, negligible interference was detected from other metal ions. The proposed method was successfully applied for the detection of mercury ions in vegetables.

Keywords: Mercury determination, Cyclic voltammetry, chronoamperometric, carbon electrode, PEDOT: PSS modified electrode, Poly (3.4-ethylenedioxythiophene)

1 Introduction

Mercury toxicity and ubiquity have withdrawn major public attention with great health concerns to emphasis the impotent of this material monitoring. Although many regulations have been set worldwide, banding or controlling the spread of mercury containing products, accumulation of the material in soil or river basin stile represent major source for crops contamination (Pujol *et al.*, 2014) (Seco-Reigosa *et al.*, 2014). Standard methods for Hg analysis include: cold vapor atomic absorption spectrometry (CV-AAS) (Lobring and Potter, 1992) and inductively coupled plasma-mass spectrometry (ICP-MS) (Palmer *et al.*, 2006). Some Hg-monitoring applications, without requiring sample pretreatment, depend upon point-of-use sensors that are simple, rapid, stable, reliable, and inexpensive. Accordingly, various methods have been developed such as colorimetric (Liu *et al.*, 2010), fluorometric (L. Wang *et al.*, 2014), magnetic (Najafi *et al.*, 2013), electrochemical (Mart'\in-Yerga, González-Garc'\ia and Costa-Garc'\ia, 2013), etc. Electrochemical techniques have the superior potential to meet this demand via chemically modified electrodes or sensors that provided characteristic such as sensitivity and reliability. Many works on the development of chemically modified electrodes for mercury ion sensing have been reported, e.g. in recent 10 years, more than 150 papers have been published dealing with new electrodes that have been fabricated for mercury determination (Alizadeh, Ganjali

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and Zare, 2011). As for electrochemical applications, the utilization of PEDOT:PSS; Poly (3,4-ethylenedioxythiophene) poly(styrenesulfonate), for electrode modification and the detection of toxic metal ions was seldom reported (Vacca *et al.*, 2008). The material, PEDOT:PSS, is one of the most promising conducting polymers because of its high conductivity, excellent environmental stability, and simple acid/base doping/dedoping chemistry (Z. Wang *et al.*, 2014). In addition, PEDOT contains sulfur which can endow two unpaired electrons. This thiol-functionalized polymer is readily conjugated with positively-charged heavy metal ions, the property which utilized in the present work for selective and sensitive detection of mercury ions (Mart'\in-Yerga, González-Garc'\ia and Costa-Garc'\ia, 2013). In brief, simple and direct PEDOT:PSS graphite carbon electrode coating, that is coupled with basic and new chronoamperometric monitoring methodology for mercury determination is developed. The possibility for method application for mercury determination in environmental sample was also reported (Yasri *et al.*, 2011) (Rattan, Singhal and Verma, 2013).

2 Material and methods

2.1 Reagents

Poly (3,4-ethylenedioxythiophene) (PEDOT) was synthesized by Cidetec (San Sebastian, Spain) according to a previously described method. A stock mercury solution of 5×10^{-2} mol.L^{-1} was prepared from reagent grade mercury nitrate $Hg(NO_3)_2$ (Merck chemicals). To investigate the mercury ion level in different media, the stock solution was diluted to the requested level for working voltammetric investigations in the indicated medium. Supporting electrolytes were prepared in bidistilled water using Hydrochloric acid (HCl,37%), nitric acid (HNO_3,65%), sodium chloride (NaCl,99.8%), sodium acetate (CH_3COONa,99.6%), acetic acid (CH_3COOH,99.5%), sulfuric acid (H_2SO_4,98%), Phosphoric acid (H_3PO_4,98%), all purchased from Merck chemicals.

Interference studies of cationic ions were made by adding an indicated quantity of the corresponded nitrate salts and all salts were purchased from Merck chemicals.

2.2 Carbon electrode preparation and modification

Graphite carbon electrode rods with diameter of (Ø=0.945cm) was purchased from (Thermadyne, Arcair, Tweco Inc.). The electrode rod was molded in surround with (50% w/v) self curing copolymer acrylic resin (RESPAL, Type II - class I, Italy) allowing the crosscutting of the uncovered graphite rod as a contact surface area for the carbon electrode. Electrodes prepared in this way were used for both purposes, as a counter carbon electrode and for modified working electrodes. In a mean that the working and counter electrodes were of (Ø=0.945cm) diameter circle.

Prior to each experiment, the carbon electrode was first polished, rinsed with deionized water, and ultrasonicated successively in a 1:1 aqueous solution of HCl and an Ethanol solution for 2 min, the process then followed with electrodes air drying.

A modified carbon electrode was prepared by direct coating of the working electrode with 80 µL of the PEDOT: PSS dispersion, then the electrode was left to dry for 30 min at 60°C.

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2.3 Apparatus and measurement

Electrochemical measurements were performed with a VOLTALAB potentiostat (model PGP 201, Radiometer, France), driven by the general-purpose electrochemical systems data processing software (VOLTALAB master 4 software) connected with proper computation system. The electrolysis vessel with volume capacity of 100 mL, was connected to a three electrode system consisting of a PEDOT: PSS modified carbon electrode, a carbon counter electrode and an Ag/AgCl double junction reference electrode (model, AG 9101, Metrohm, Switzerland, with 3M KCl filling). The modified electrode was tested in 25 mL electrolyte under constant magnetic stirring (400 rpm) and was kept in a thermostatic at 25°C (any modification of these conditions should be otherwise stated).

A Hitachi Atomic Absorption Spectrophotometry (AAS), Z-2000 Series, was also used to validate the mercury determination method. The AAS system was provided with Hallow cathod lamp (Hitachi) for mercury determination, and the instrument run under the following measuring conditions: wavelength 283.3 nm, lamp current 6 mA, acetylene fuel at flow rate 2.0 L min^{-1}, and burner height 7.5 mm.

A digital pH-meter from (Wissenschaftlich Techmische Werkstatten, Inolab level 1, Germany), was used for pH values reading. Micropipette continuously adjustable that can be covering a volume range from 10 to 5000 µl (model FAA, Isolab) was used for preparing the experimental solutions.

2.4 Cyclic voltammetry measurements

Cyclic voltammetry measurements were performed by scanning the potential from +0.80 V to -0.1V vs. Ag/AgCl at a scan rate of 10 mv sec^{-1}, with third cycle number illustration. The oxidation peak generated upon injection of mercury ions to the final concentration of 5×10^{-3} mol.L^{-1}.

2.5 Chronoamperometric measurements

Chronoamperometric measurements was performed by applying a reduction voltage at +100 mV vs. Ag/AgCl for 30 second, allowing a maximum deposition of mercury ions on the working electrode, and then performed by automatically switching the applied potential to a cathodic value of +600 mV vs. Ag/AgCl. The time necessary to reach oxidation current density plateau was 3-15 seconds. The peak response for the current intensity at the voltage corresponded to the anodic values are concentration dependent. A calibration curve for mercury ion concentration (µmol.L^{-1}) against the peak current density (mA/cm^2) was then constructed.

2.6 Pretreatment of the vegetable samples

Vegetables of chard (white beet), spinach and Lettuce were collected from the countryside area of Quweiq river mouth (Aleppo, Syria). The vegetable was collected washed, dried for 24 hours at 60˚C and then 25 grams of each vegetable were placed into Teflon vessels, and 10 mL of HNO_3 was added , then The digestions process was completed by heating it at 125 °C for 6 hours (AGENCY., 1998). The solution was then filtered and the filter was washed with 10 mL of 6 mol.L^{-1} nitric acid, finally the filtrates were combined and adjusted to a final volume of 25 mL The obtained solution was analyzed by atomic absorption spectroscopy. Chronoamperometric measurements were carried out using 10 mL of the

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obtained solution diluted to 100 mL with 0.05 mol L^{-1} HNO_3. The measurements were performed using 10 mL of the same solution diluted to 100 mL with mercury solutions of known concentrations.

3 Results and discussion

3.1 Cyclic voltammetry experiments

The cyclic voltammograms of Hg^{2+} on bare carbon electrode, and on PEDOT: PSS modified carbon electrodes were examined in 0.05M HNO_3 medium, Fig.1. Shows a small oxidation peak without corresponded with reduction peak when used bare carbon electrode (curve c), whereas on PEDOT: PSS modified carbon electrodes (curve a) Hg^{2+} exhibits a narrow, well-defined oxidation peak corresponded with broad reduction peak, started at +(600±50) mV and +(100±10) mV vs. Ag/AgCl, respectively. No detectable signal was observed in the absence of Hg^{2+} using the same electrolyte (curve b). These results showed the potential application of PEDOT: PSS modified electrode for detecting of mercury ions. It was confirmed by studying the response of PEDOT: PSS modified carbon electrodes towards mercury at various concentrations Fig. 2.I. The calibration curve demonstrated that the response was linear for all the Hg^{2+} concentrations tested, i.e. from 2.0 to 14.0 µmol.L^{-1} (R^2 =0.995) Fig. 2.II.

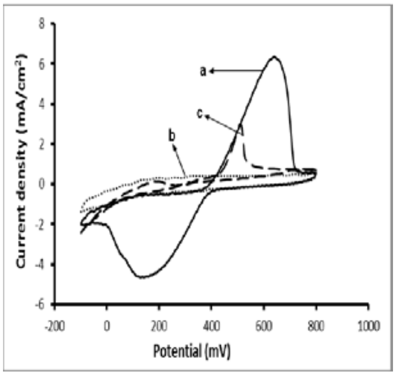

Fig.1 Cyclic voltammograms for Hg^{2+} 5.0×10^{-3} mol.L^{-1} in 0.05 mol.L^{-1} HNO_3 on: (a) PEDOT:PSS modified carbon electrode, and (c) bare carbon electrode, comparing with (b) mercury free electrolyte on PEDOT:PSS modified carbon electrode. Potential ramp +0.8 V to -0.1V vs. Ag/Ag Cl, scan rate 10 mv sec^{-1}.

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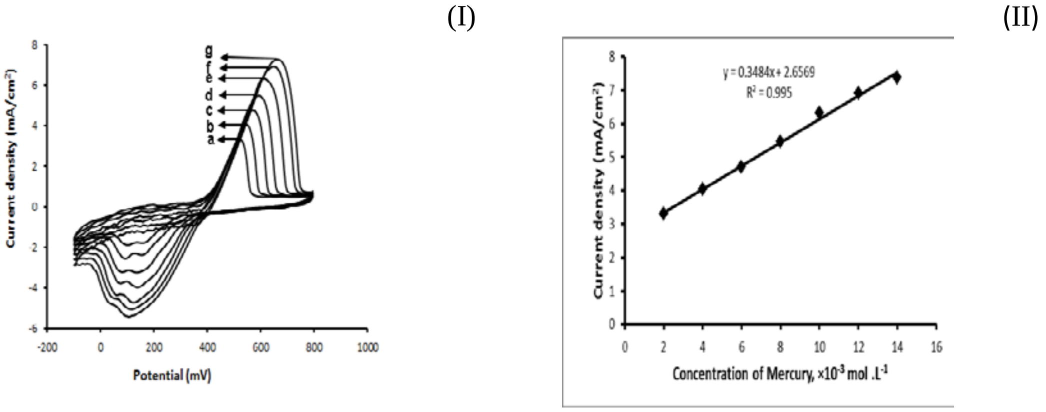
(I) (II)

Fig.2 (I) Cyclic voltammogram and, II) the corresponded calibration curve, in 0.05 mol.L^{-1} HNO_3 medium, using PEDOT:PSS modified carbon electrode for Hg^{2+} concentration at: (a) 2.0, (b) 4.0, (c) 6.0, (d) 8.0, (e) 10.0, (f) 12.0 and (g) 14.0 mmol.L^{-1}**.** The potential ramp from +0.8V to -0.1V vs. Ag/Ag Cl at a scan rate of 10 mv sec^{-1}.

3.2 Optimization of experimental conditions

Optimum conditions for the electrochemical response of PEDOT: PSS modified carbon electrode were established by measuring the anodic current density peak in dependence on supporting electrolyte, pH optimum, and the stability of PEDOT: PSS coating material in the supporting electrolyte.

3.2.1 The effect of supporting electrolyte

A sweep voltammograms extracted from cyclic voltammograms in the presence of 5×10^{-3}mol.L^{-1} Hg^{2+} in 0.05 mol.L^{-1} of various electrolytes of HNO_3, H_2SO_4, H_3PO_4, HCl, CH_3COOH, NaCl, and CH_3COONa, are presented in Fig.3. The highest and narrowest peak was surprisingly observed for mercury ion in HNO_3 medium (pH=2.25). Similar results with lower anodic current were obtained with H_2SO_4 and H_3PO_4, whereas CH_3COOH reduce the analytical signal dramatically with no sign was observed with HCl, NaCl, and CH_3COONa. The best response was obtained with HNO_3.

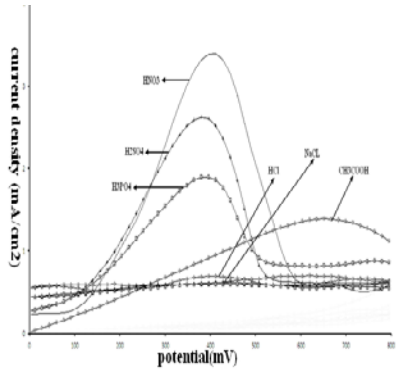

Fig.3 A sweep voltammograms extracted from cyclic voltammograms on PEDOT: PSS modified carbon electrode for 5.0×10^{-3} mol.L^{-1} Hg^{2+}in: a) HNO_3,b) H_2SO_4, c) H_3PO_4, d) CH_3COOH, e) NaCl, f) HCl, g) CH_3COONa all at concentration of 0.05 mol.L^{-1}. The potential ramp from +0.6V to 0.0V vs. Ag/Ag Cl at a scan rate of 10 mv sec^{-1}

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3.2.2 The effect of pH

Varying the pH of nitric acid within the range of (1×10^{-4} to 4×10^{-1}) mol.L^{-1}, Fig.4. exhibits maximum anodic current response at 0.05M HNO_3, with sharp and reproducible analytical signals. This electrolyte concentration was used in the later optimization study. The best response was obtained at (pH=2.25).

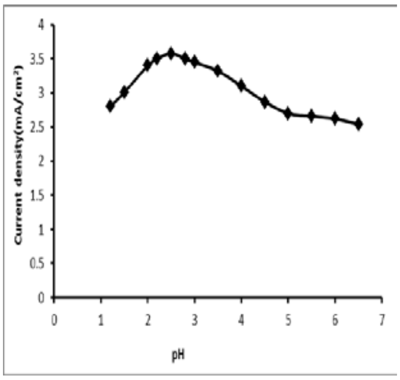

Fig.4 Anodic current density response for 5.0×10^{-3}mol.L^{-1} Hg^{2+} on PEDOT: PSS modified carbon electrode in various pH of supporting electrolyte HNO_3.

3.2.3 Stability of PEDOT: PSS modified carbon electrode

A good stability of chemically modified electrodes is a key condition for the reliability of the sensors. The stability of the PEDOT: PSS modified carbon electrodes described in this work was studied by keeping the electrode immersed in 0.05 mol.L^{-1} HNO_3 solution for several days, at room temperature (25°C). During this time, the electrode was tested daily using 5×10^{-3} mol.L^{-1} of mercury ions Fig.5. In these conditions, the peak response for the anodic current density showed a good stability during the first 13 days (3.466 ± 0.172 mA/cm^2), with RSD values in day 10 is 4.96% (n=5). The response decreased slightly at day 14 (RSD = 5.9%; n =5).

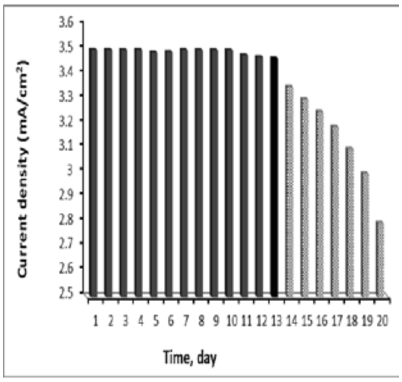

Fig.5 The corresponded current density for 5.0 x 10^{-3} mol.L^{-1} Hg^{2+} detection on PEDOT:PSS modified electrode that is kept in 0.05 mol.L^{-1} HNO_3 solution for several days.

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3.2.4 The effect of reduction time on chronoamperometric measurement

A various of Reduction Time were studied by Apply Reduction potential Corresponding to completion of mercury deposition. Fig.6. shows the response of the current density value to different Reduction times for 5.0×10^{-6} mol.L^{-1} mercury ions in 0.05 mol.L^{-1} nitric acid. It was observed that the current density increases with the reduction time and reaches a maximum value for a reduction time of 30 sec. and the stability of current density was observed using longer reduction time

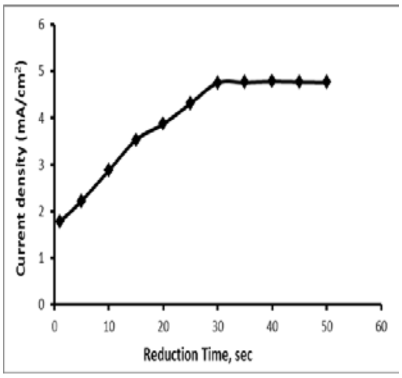

Fig.6 Different reduction time against the anodic current density peaks for 5.0×10^{-6} mol.L^{-1} Hg^{2+} detection.

3.3 Chronoamperometric measurement

Chronoamperometric measurements of PEDOT-PSS modified sensors were carried out in the conditions optimized by voltammetry measurements, i.e. using 0.05 mol L^{-1} HNO_3 as supporting electrolyte and value pH=2.25. Prior of measurements, an electrodeposition step was performed for 30 seconds, allowing an optimal deposition of mercury ions on the working electrode. The chronoamperometric response of the sensor achieved using various mercury ions concentrations is presented in Fig.7. A strictly linear variation of the anodic peak current was observed for concentrations ranging from (0.1×10^{-6} to 8.0×10^{-6}) mol.L^{-1} ($y = 0.5392x + 1.8594$, R^2 0.998). The limit of detection (LOD) and limit of quantification (LOQ) were calculated using the formula LOD= 3.3 SD/b and LOQ= 10 SD/b, respectively, where SD is the standard deviation of five reagent blank determinations and b is the slope of the calibration curve (Meier and Zünd, 2005). In these conditions, the LOD and LOQ of the developed sensor were calculated to be 0.01 µmol.L^{-1} and 0.04 µmol.L^{-1}, respectively. It was observed that mercury concentrations higher than 8 µmol.L^{-1} induced the formation of multilayers on the working electrode surface, resulting in a slight decrease of the peak current and therefore affecting the detection procedure.

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The precision and accuracy of the method towards mercury determination was assessed by analyzing 9 standard solutions of mercury ions with concentrations ranging from (0.1×10^{-6} to 8.0×10^{-6}) mol.L^{-1} in 0.05 mol.L^{-1} HNO_3 Table.1. Whatever the value of tested concentration is, a very accurate quantitative recovery was obtained, with rates ranging from 99.62 to 103.00%, intra-day RSD values ≤4.90 % (n= 5), and inter day RSD values ≤4.85 % (n = 5). The inter variability of the sensors responses was studied by measuring the response of 10 different electrodes to 5 μmol.L^{-1} mercury ions. In these conditions, a very satisfying RSD value of 2.2% was obtained. These results showed excellent reproducibility of PEDOT: PSS modified carbon electrodes.

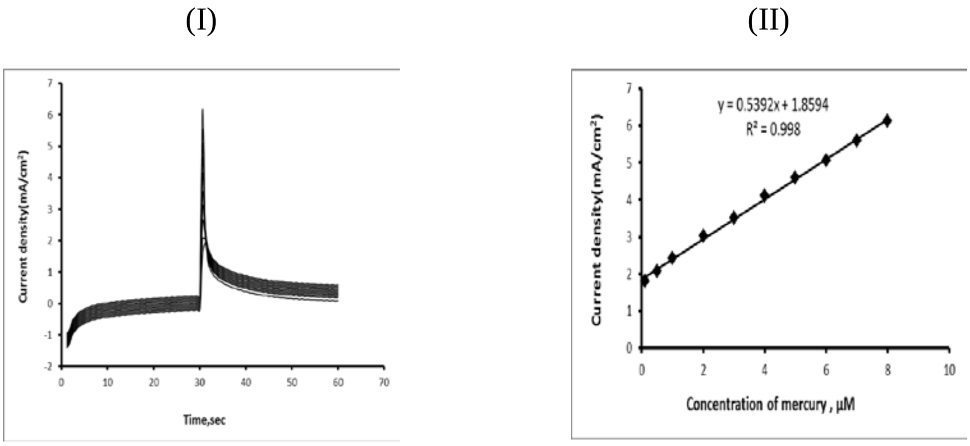

Fig.7 (I) Chronoamperometric diagram and, II) the corresponded calibration curve, in 0.05 mol.L^{-1} HNO_3 medium, using PEDOT:PSS modified carbon electrode for mercury ions concentration at: (a) 0.1, (b) 0.5, (c) 1.0, (d) 2.0, (e) 3.0 , (f) 4.0 , (g) 5.0, (h) 6.0 , (g) 8.0 µmol.L^{-1}**.** The reduction voltage +100 mV vs. Ag/AgCl for 30sec then switched to an oxidation voltage of +600 mV vs. Ag/AgCl .

Table 1: Chronoamperometric determination of Hg^{2+} on PEDOT: PSS modified carbon electrode in HNO_3 0.05 mol.L^{-1} media.

Hg^{2+} (10^{-6} mol.L^{-1})	Intra-day accuracy and precision			Inter-day accuracy and precision		
	Hg^{2+} (10^{-6} mol.L^{-1}) (n=5)			Hg^{2+} (10^{-6} mol.L^{-1}) (n=5)		
	Found ± SD	R%	RSD%	Found ± SD	R%	RSD%
0.1	0.102 ± 0.005	102.00	4.90	0.103 ± 0.005	103.00	4.85
0.5	0.502 ± 0.016	100.40	3.18	0.498 ± 0.017	99.620	3.35
1.0	1.006± 0.043	100.60	4.27	1.005 ± 0.028	100.50	2.78
2.0	2.004 ± 0.087	100.22	4.34	1.995 ± 0.029	99.750	1.45
3.0	2.997± 0.078	99.910	2.60	3.030 ± 0.049	100.99	1.60
4.0	3.993± 0.076	99.820	1.90	3.997± 0.057	99.922	1.42
5.0	5.024 ± 0.075	100.49	1.49	5.061± 0.063	101.22	1.24
6.0	6.093 ± 0.112	101.54	1.83	6.058± 0.062	100.97	1.03
8.0	8.146± 0.078	101.83	0.97	8.088 ± 0.053	101.10	0.66

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3.4 Study of interferences due to other metallic ions

The influence of other metal ions (Mg^{2+}, Fe^{3+}, Co^{2+}, Ca^{2+}, Ni^{2+}, K^{+}, Cd^{2+}, Cu^{2+}, Zn^{2+} and Pb^{2+}) on the determination of 5.0 $\times 10^{-6}$ $mol.L^{-1}$ Hg^{2+} in 0.05 $mol.L^{-1}$ Nitric acid (pH 2.25) was investigated. The experiment data are listed in Table.2. A relative error of ±5% on the concentration of Hg^{2+} was considered tolerable. The results indicated that in our working conditions most of the metal ions do not interfere on the determination of Hg^{2+}, except Cu^{2+} that displayed an oxidation peak at +75 mV vs. Ag/AgCl for high concentration levels, up to 270-fold higher than Hg^{2+} concentration. The same behavior was observed for Fe^{3+} ions at concentration levels exceeding 550-fold. It was shown that the peak current of Hg^{2+} oxidation was not significantly varied in the presence of more than 750-fold higher concentrations of Mg^{2+}, Fe^{2+}, Co^{2+}, Ca^{2+}, Ni^{2+}, K^{+}, Cd^{2+}, Zn^{2+} and Pb^{2+} ions. The above results demonstrate that at optimum working conditions the PEDOT: PSS modified carbon electrode showed good sensitivity for the detection of Hg^{2+} as well as very good selectivity towards other metallic ions.

Table 2: Determination of 5 $\times 10^{-6}$ $mol.L^{-1}$ by chronoamperometric on PEDOT:PSS Modified Carbon Electrode in the presence of other ions.

Added ions	**Hg^{2+} Concentration**			**Variation%***	**Tolerable limit [cation]/[Hg^{2+}]**
	Mean $5\times10^{-6} mol.L^{-1}$	**S.D** $5\times10^{-6} mol.L^{-1}$	**RSD%**		
Alone	4.98	0.15	3.01	0.0	0
with Pb (II)	5.23	0. 24	4.58	+5.0	850
with Fe (III)	4.72	0.19	4.02	-5.2	550
with Fe (II)	4.74	0.20	4.21	-4.8	950
with Co (II)	4.70	0.22	4.68	-5.6	750
with Mg (II)	4.71	0.21	4.45	-5.4	980
with K (I)	4.73	0.18	3.80	-5.0	1030
with Ca (II)	4.74	0.19	4.00	-4.8	800
with Ni (II)	5.22	0.20	3.83	+4.8	900
with Cd (II)	5.24	0.18	3.52	+5.2	1000
with Cu (II)	5.25	0.17	3.24	+5.4	270
with Zn (II)	5.20	0.19	3.87	+4.4	800

* Variation % at 5×10^{-6} $mol.L^{-1}$ = 100 × [{(peak current of pure mercury)-(peak current of mercury with each cations)}/(peak current of pure mercury)].

3.5 Application to real samples

The PEDOT:PSS modified carbon electrode was used for the determination of mercury ions in three different vegetables (chard, spinach, and Lettuce) that have been cultivated in an area well-known to be contaminated by mercury (Ramadan and Mandil, 2009). The results shown in Table.3. clearly demonstrate the presence of mercury in the three different vegetable samples. The analytical results obtained from a series of mercury standard solutions spiked with unknown samples gave quantitative recoveries in the range of 98.0–101.0 %. The amount of mercury in unknown samples was also determined and was expressed as the mass fraction of dried vegetable Table.4. The test of significance showed that Student's t test values

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and F-values at 95% confidence level were less than the theoretical values, indicating that there is a good agreement between the results obtained by the proposed method and the reference AAS method. These results prove that the PEDOT:PSS modified carbon electrode developed in this work has practical significance and is able to determine Hg^{2+} in real samples.

Moreover, the concentration levels of Hg^{2+} in the three vegetable samples analyzed indicate high levels of contamination that demand more attention and control of the pollution in the region.

Table 3: Chronoamperometric determination of mercury in different vegetable samples spiked with known concentrations of Hg^{2+}.

Sample	Hg^{2+} added ($\times 10^{-6}$ mol.L^{-1})	Hg^{2+} found ± S.D ($\times 10^{-6}$ mol.L^{-1}) (n=5)	R (%)
Chard	-	0.120 ± 0.003	-
	0.1	0.101* ± 0.004	101.0%
	0.5	0.498 ± 0.010	99.60%
	1.0	0.997 ± 0.020	99.70%
Spinach	-	0.115 ± 0.004	-
	0.1	0.099* ± 0.005	99.00%
	0.5	0.499 ± 0.017	99.80%
	1.0	1.002 ± 0.022	100.2%
Lettuce	-	0.107 ± 0.002	-
	0.1	0.098* ± 0.004	98.00%
	0.5	0.503 ± 0.021	100.6%
	1.0	0.999 ± 0.028	99.90%

* The value here is some subtraction of the mercury concentration value found in the vegetable samples.

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Table 4: Determination of Hg^{2+} ions in vegetable samples, comparison of chronoamperometric and Atomic Absorption Spectrometry methods. The tabulated t and F values at 95% confidence level and for five degrees of freedom were respectively 2.57 and 6.05

Sample	Chronoamperometric Method (n=5)	Atomic Absorption Spectrometry Method (n=5)
	Hg^{2+} (mg/Kg) ± SD	Hg^{2+} (mg/Kg) ± SD
Chard	0.2407 ± \7*-0.010	0.2520 ± 0.009 F=1.23 *t* = -2.52
Spinach	0.2306 ± 0.009	0.2217 ± 0.011 F=1.49 *t* = +2.21
Lettuce	0.2146 ± 0.011	0.2088 ± 0.009 F=1.49 *t* = +1.17

4 Conclusion

Fast and effective analyses of mercury ions in vegetable samples have been performed using a novative chronoamperometric monitoring method involving PEDOT:PSS modified carbon electrodes. The cyclic voltammetry results clearly showed the advantages of PEDOT:PSS coated electrodes as compared with bare carbon electrodes. The polymer coating allows avoiding problems of irreversible adherence, which otherwise could mercury to blocking and fouling of the electrode surface. The PEDOT:PSS modified carbon electrode showed excellent responses with LOD values in the micromolar ($mg.L^{-1}$) level. The suitability of the proposed method was demonstrated by determining the concentration of mercury in vegetable samples grown in a mercury contaminated area, the validation of the results was performed by atomic absorption spectroscopy measurements.

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