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Voltammetric determination of trace mercury at a sonogel–carbon electrode modified with poly-3-methylthiophene

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Abstract

The sonogel–carbon electrode is a new class of sol–gel electrode that exhibit favourable mechanics and electrics properties to be used as electrochemical sensor. In this paper, a modified sonogel–carbon electrode is proposed to determine mercury at trace levels. The modified electrode is obtained by electropolymerization of 3-methylthiophene on the surface of a bare sonogel–carbon electrode. This electrode shows high selectivity and sensitivity and linear response towards Hg(II), with a detection limit of $1.4 \times 10^{-3}\,\mathrm{mg\,l^{-1}}$. The electrode is reusable by a simple chemical cleaning procedure. No deterioration was observed in the electrode response during at least 1 week of successive measurements.

Keywords: Modified electrode; Conducting polymer; Poly-3-methylthiophene; Mercury(II); Sonogel–carbon electrode

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1. Introduction

Heavy metals are attracting more attention in environmental, toxicological, pharmaceutical and biomedical analysis [1–3]. Among those, the detection of mercury is of particular interest [4], due to the toxicity of its derivatives responsible for a widespread public concern, as a result of several environmental disasters [5,6]. Some analytical techniques have been employed in metal analysis, such as atomic absorption spectrometry (AAS) [7], X–ray fluorescence [8] or UV spectrophotometry [9]. Electrochemical techniques, in particular differential pulse anodic stripping voltammetry (DPASV), have been extensively used for metal ion analysis [10,11] and they compete very well with the usual techniques. Non-stationary voltammetric methods have been introduced in an attempt to improve the sensitivity and selectivity of the electroanalytical measurements [12], in conjunction with the use of chemically modified electrodes [13,14]. Other forms of modern electroanalysis of heavy metals include the use of self-assembled monolayer modified electrodes, nanotube-modified electrodes and sonoelectroanalysis [15–17]. Many modifiers have been employed which are generally based on two types of interaction: ion exchange [12] and complexation [18]; in the former case, cation–exchangers like Nafion [19] are capable of preconcentrating metallic ions, whereas the analysis based on complexing interaction is more selective due to the specific interaction between specially designed ligands and metal ions. Sulphur containing complexing agents are mostly used as modifiers for mercury determination due to their high affinity for different species of mercury [20]. Usually, these modifiers are covalently bonded on the electrode surface or physically entrapped in a polymer matrix [21].

Recently, some of us have developed a new type of graphite-based sol–gel electrode, the sonogel–carbon

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electrode, which is obtained using high-energy ultrasounds. Classical procedures for the synthesis of acid catalysed sol–gel-based electrode materials include the addition of an alcoholic solvent to the initial precursor mixture to make it homogeneous and the employment of an ultrasound bath for several minutes to promote the hydrolysis. On the contrary, by means of sonocatalysis, high-energy ultrasounds are applied directly to the precursors, and ultrasonic cavitation is achieved so that hydrolysis with acidic water is promoted in a few seconds and in the absence of any additional solvent. Thanks to the phenomenon of ultrasonic cavitation, sol–gel reactions occur in a unique environment, leading to gels with special characteristics. These so-called sonogels are mainly of high density, with a fine texture and homogeneous structure. The mix of sonogel with spectroscopic grade graphite leads to the sonogel–carbon electrode [22,23].

These electrodes show very favourable electroanalytical properties for their use as amperometric sensors and, furthermore, they can easily permit the incorporation of numerous receptor molecules at the sonogel–carbon materials [24–26], which can notably improve the selectivity. In the present paper, we propose a new application of sonogel–carbon electrodes based on the incorporation of poly-3-methylthiophene (P3MT) as selective receptor for mercury. The developed electrode shows a good amperometric response versus mercury and also a great power to preconcentrate the ion, due to the affinity of poly-3-methylthiophene versus mercury.

2. Experimental

2.1. Reagents and materials

Methyltrimethoxysilane (MTMOS), tetrabutylamoniumhexafluorophosphate (TBAHFP) and all the reagents for the Britton–Robinson buffer solution (*ortho*-phosphoric acid, boric acid, acetic acid and sodium hydroxide) were from Merck (Darmstad, Germany). HCl was from Panreac (Barcelona, Spain). Thiophene, pyrrol, 3-methylthiophene, Nafion and dithizone, were from Aldrich (Milwaukee, WI). Graphite powder (spectroscopic grade RBW) was from SGL Carbon (Ringsdorff, Germany). $HgSO_4$ (Merck) was used to prepare the standards Hg(II) solutions. All other chemicals were of reagent grade and used as received. Nanopure water was obtained by passing twice-distilled water through a Milli-Q system (18 MΩ cm, Millipore, Bedford, MA). Glass capillary tubes, i.d. = 1.15 mm, were used as bodies for the composite electrodes.

2.2. Instrumentation

All electrochemical measurements were performed with an Autolab PGSTAT20 (Ecochemie, Utrecht, The Netherlands). The experiments were carried out in a three-electrode cell at room temperature (25 ± 1 °C) under nitrogen atmosphere; the counter electrode was a platinum wire and a Ag/AgCl, 3M KCl electrode was used as the reference; the composited filled capillary tubes were used as working electrode. Differential pulse anodic stripping voltammetry, square wave voltammetry (SWV) and cyclic voltammetry (CV) were the electrochemical techniques applied to study the behaviour of the sonogel–carbon electrodes. Instrumental parameters were as follows: pulse amplitude ±60 mV; pulse repetition time, 0.4 s; initial potential, 0 V; end potential, 0.5 V; pretreatment at −0.5 V for 12 s; frequency for SWV, 10 Hz. CV measurements were carried out at a scan rate of $100\,mV\,s^{-1}$.

A 600-W Model, 20 kHz ultrasonic processor (Kontes, Dusseldorf, Germany) equipped with a 13 mm titanium tip was used. The ultrasonic processor was enclosed inside a sound-proof chamber during operation.

Atomic absorption spectroscopy measurements were performed using a Unicam 929 AA spectrometer.

2.3. Preparation of the sonogel electrode

To prepare the sonogel–carbon, 500 μl of MTMOS and 100 μl of 0.2 M HCl were mixed and then insonated during 5 s; next, 1 g of graphite powder was added and homogeneously dispersed in the sonosol obtained. By applying ultrasonic cavitation to favour the sol–gel process to begin, we have avoided the use of alcoholic solvent and reduced drastically the time needed to get a unique phase; the mixture was insonated during 5 s to promote cavitation and thus hydrolysis. The complete procedure has been described previously [22,23]. Before modification, the electrodes were polished with No. 1200 emery paper to remove extra composite material, wiped gently with weighing paper, thoroughly washed with deionised water and allowed to dry at room temperature; electrical contact was established by inserting a copper wire.

2.4. Preparation of the sonogel–carbon electrode modified with poly-3-methylthiophene

The electropolymerization of P3MT was carried out as described by Mark et al. [27], with the following modifications: the polymer electrosynthesis was realized at 0 °C in a cell containing deaerated acetonitrile, 0.01 M TBAHFP and 0.1 M 3-methylthiophene (corresponding to an injection of 220 μl from the monomer stock solution). The synthesis was initiated by cyclic voltammetry, scanning towards positive potentials from 0 to 1.6 V at a scan rate of $100\,mV\,s^{-1}$. After electrosynthesis, the P3MT films were kept for a few minutes at a reducing potential, in contact with the original electrolyte anion, for undoping.

2.5. Scanning electron microscopy (SEM) measurements

To carry out these measurements, the microscope, a JSM 5400 type (JEOL, Japan), was coupled to the analyser, a link type with a Si/Li detector and an ultra thin window. The P3MT film and Sonogel electrode were washed, then dried; the films were then introduced into a high vacuum system before application of electron beam.

2.6. Electrochemical impedance spectroscopy (EIS) measurements

The electrochemical impedance spectroscopy measurements were performed with a Voltalab 10 type PGZ 100 from Radiometer. The impedance spectra were set up as described previously [28]. The initial frequency used was 10 kHz, and the final one was 10 mHz with an ac amplitude from 5 to 10 mV. In order to insure the inert effect of P3MT electrode during the experiment, a potential of 1000 V was chosen. All other conditions were as described in the voltammetric procedure.

2.7. Procedure for determination of Hg(II)

The determination of Hg(II) is carried out by the following four-step procedure:

(a) *Accumulation step*: The electrode is immersed in the sample solution for 30 min at open circuit.
(b) *Reduction step*: A reduction potential is applied for 12 s; after this, the electrode is rinsed thoroughly with deionised water and transferred to a clean stripping media.
(c) *Stripping step*: The anodic stripping of the reduced metal is performed.
(d) *Cleaning after stripping*: The electrode is cleaned by immersing it in 6 M HNO_3 for 2 min; so, the electrode is ready for a next experiment.

3. Results and discussion

3.1. Cyclic voltammetry

The modified sonogel–carbon electrode showed no electroactivity in a potential range between 0.5 and 1 V. Under the experimental conditions used, in a 0.2 M Britton–Robinson buffer media, the obtained signal was stable, without peaks and with a low residual current. Previously to the study of the mercury response, the P3MT-modified electrode was immersed in the Britton–Robinson buffer and a scan between 0 and 0.5 V was carried out. For the next step, cyclic voltammograms were recorded after 30 min of preconcentration at open circuit inside a solution of a 5 mg l^{-1} of $HgSO_4$. Fig. 1 shows an anodic peak with a peak potential value, $E_P = 0.179$ V (at 100 mV s^{-1}); the peak current increased with the increase of concentration of Hg(II) in the accumulation media. These results indicate the accumulation of Hg(II) on the surface of the modified electrode, as a consequence of complexing interaction. There is a cathodic peak at around 0.075 V, but it is broader than the anodic one; this is consistent with the fact that mercury, like other 3d metal, such as copper, cadmium or zinc [29], has poorly defined reduction waves, but they show sharp and intense reoxidation stripping waves. The comparison between the two voltammetric patterns (modified electrode and unmodified electrode) shows relevant differences, both in peak sharpness as well as in peak potential. In fact, at the modified electrode, the peak is sharper and significantly shifted towards a less negative potential value than the peak recorded at an unmodified electrode.

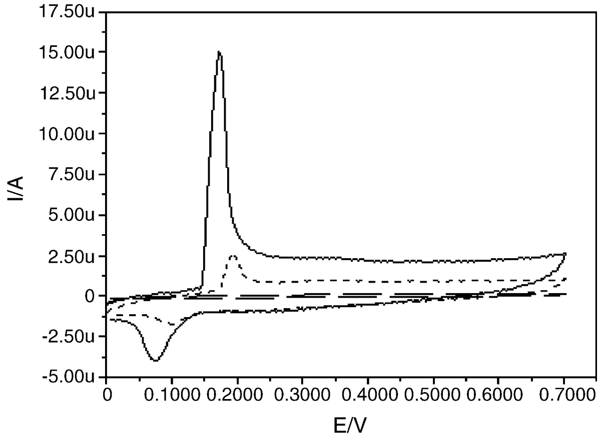

Fig. 1. Cyclic voltammetry after incubating at open circuit during 30 min. Scan rate, 100 mV s^{-1}; (- - -) background response; (. . .) bare sonogel–carbon electrode; (—) sonogel–carbon electrode modified with poly-3-methylthiophene.

3.2. Stripping voltammetry

The voltammograms of Fig. 2A and 2B show the responses of the electrode when applying DPASV and SWV, respectively. As can be seen the response for DPASV is better than for SWV. In DPASV, the oxidation peak is sharp and it is function of the concentration; it clearly appears that this method gives a good result in order to detect mercury. In both types of experiments, the electrode was immersed in a solution of Hg(II) during 30 min at open circuit, then rinsed with deionised water and put in a cell containing 0.2 M of Britton–Robinson buffer; finally, DPASV or SWV mode was immediately applied.

Different accumulation potentials were tested with the aim to found the best reduction potential for Hg(II). Potentials from 0 to −1.1 V were applied. The peak current increases when reduction potentials were changed from 0 to −0.5 V; from this value, the peak current stabilizes, although the best defined peak was obtained for −0.5 V. So, −0.5 V was used for further studies.

3.3. Electrode cleaning

Two cleaning methods were tested: an electrochemical method and a chemical one. The electrochemical method involves an electrolysis process after each measurement by applying DPASV from 0 to 0.5 V for five cycles; the chemical one involves an immersion in 6 M HNO_3 solution for 2 min.

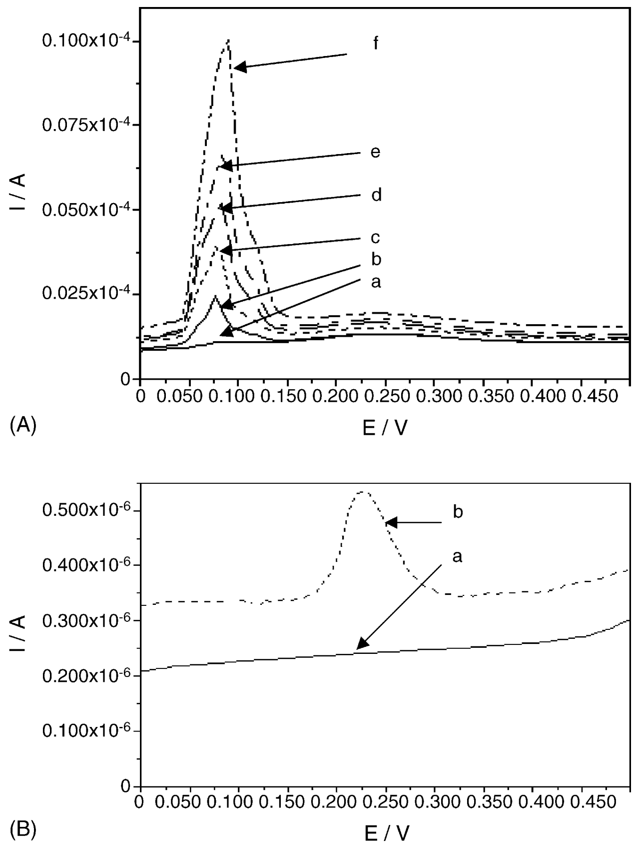

Fig. 2. (A) DPASV on a P3MT-modified electrode of several Hg(II) concentrations, after incubation at open circuit during 30 min.: (a) background response; (b) 0.13 mg l^{-1}; (c) 0.26 mg l^{-1}; (d) 0.39 mg l^{-1}; (e) 0.52 mg l^{-1}; (f) 0.78 mg l^{-1}. (B) SWV on a P3MT-modified electrode after accumulation for 30 min in a Hg(II) solution of 0.78 mg l^{-1}: (a) background response and (b) response for a Hg(II) concentration of 0.78 mg l^{-1}.

Fig. 3 shows the DPASV voltammograms at the modified electrode after electrochemical and chemical cleanings, respectively. The results show that the second method is more efficient than the first one, considering the cleaning efficiency. Therefore, the chemical cleaning method was used after each measurement.

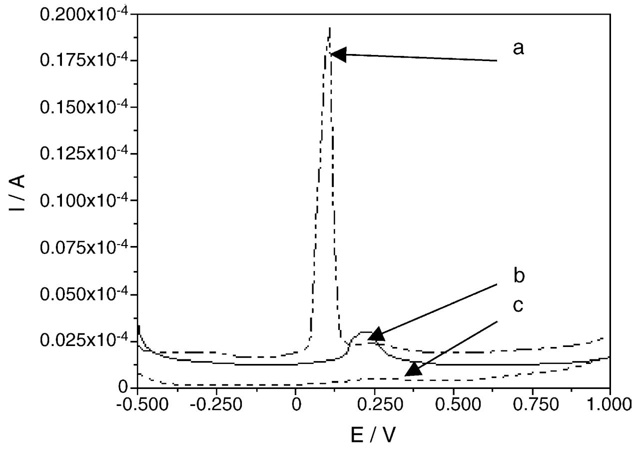

Fig. 3. DPASV on a P3MT-modified electrode: (a) after accumulation for 30 min in a solution of 1.30 mg l^{-1} of Hg(II); (b) after electrochemical cleaning; (c) after chemical cleaning; scan rate, 100 mV s^{-1}; accumulation, 12 s at 0.5 V.

Table 1
Voltammetric parameters of Hg(II) in the P3MT films under different pH conditions

pH	I_{p1} (A)	I_{p2} (A)	E_1 (V)	E_2 (V)
1.5	8.7×10^{-6}	0	0.100	–
2	8.8×10^{-6}	0	0.076	–
4	2.4×10^{-6}	2.3×10^{-6}	0.160	−0.120
6	2.7×10^{-6}	4.7×10^{-6}	0.176	−0.138
8	1.0×10^{-6}	9.0×10^{-6}	0.074	−0.250
10	1.7×10^{-6}	0	0.074	–
12	0	0	–	–
13	0	0	–	–

3.4. Effect of the supporting electrolyte and pH

The effect on the determination of Hg(II) of several experimental conditions and parameters were explored. First of all, several supporting electrolytes, such as KCl, KNO_3, $LiClO_4$, NaCl, TBAHFP and Britton–Robinson were tested. Among those, the Britton–Robinson buffer was found to be the most suitable.

We have studied the influence of the pH of the supporting electrolyte on the voltammetric behaviour of the P3MT films preconcentrated with Hg(II) species. Table 1 summarizes the voltammetric parameters of the P3MT films under different pH conditions. It clearly appears that the pH of the supporting electrolyte plays a key role in the voltammetric behaviour. As it is shown in Table 1, at pH values from 4 to 8, there are two oxidation peaks for mercury, whereas in more acidic media there is a unique and greater peak. At pH 10, there is also a unique but lower peak. No peaks were observed at pH values from 12 to 13.

3.5. Effect of the number of electropolymerization cycles

The effect of the number of cycles of electropolymerization on the observed peak intensity, resulting from incorporation of mercury into P3MT films, has been examined by applying cyclic voltammetry from 0 to 1.6 V. The results in Table 2 show that the peak intensity increases as a function of the number of cycles up to 10 cycles and then starts to de-

Table 2
Effect of the number of electropolymerization cycles on Hg(II) peak intensities

Number of cycle	I_p (A)	E_P (V)
0	7.7×10^{-7}	0.083
2	8.2×10^{-6}	0.152
5	8.3×10^{-6}	0.152
10	9.0×10^{-6}	0.075
15	2.1×10^{-6}	0.152
20	1.6×10^{-6}	0.152
25	0	–
30	0	–

Table 3
Influence of several modifiers on Hg(II) signal

Polymer/modifier system	I_p (A)	E_p (V)
Sonogel–carbon	7.7×10^{-7}	0.087
Sonogel–carbon–polythiophene	2.8×10^{-6}	0.095
Sonogel–carbon–polypyrrol	2.3×10^{-6}	0.095
Sonogel–carbon–poly-3-methylthiophene	8.8×10^{-6}	0.075
Sonogel–carbon–nafion	1.3×10^{-6}	0.180
Sonogel–carbon–dithizone	3.8×10^{-6}	0.217
Sonogel–carbon–P3MT–pyrrol	0	–
Sonogel–carbon–P3MT–β-cyclodextrine sulfat	0	–

crease. The thickness of the film at sonogel–carbon electrode surface seems to play a key role in the response of the sensor. Ten cycles have been consequently chosen as the optimal condition for P3MT electropolymerization.

3.6. Effect of preconcentration time

AAS has been employed to determine the optimal incubation time for the Hg(II) preconcentration on the electrode surface. A P3MT-modified electrode was dipped in a 0.78 mg l^{-1} nitric acid solution of Hg(II); every 5 min, the absorbance of the remaining solution was measured. The results show a rapid and linear decrease of Hg(II) as a function of incubation time, up to 30 min; after this time, no significant variation in concentration was noticed. This result indicates that Hg(II) can be preconcentrate quite rapidly on the P3MT film until a saturation of the host sites on the conducting polymer was reached. Thus, an incubation time of 30 min was chosen as the optimum.

3.7. Influence of the modifier

Table 3 shows the peak intensity and peak potential values for an unmodified sonogel–carbon electrode and those for several modified sonogel–carbon electrodes. The modified electrodes contained one of the following modifiers: Nafion, P3MT, polythiophene, polypyrrol or dithizone. Surprisingly, P3MT showed the highest oxidation peak and, consequently, was the selected modifier to continue the studies.

3.8. Sensor calibration, detection limit, reproducibility and stability

A calibration plot was drawn for the chosen conditions, i.e., pH 2 Britton–Robinson buffer, 30 min incubation time at open circuit; reduction at −0.5 V for 12 s and stripping in 0.2 M Britton–Robinson from 0 to 0.5 V at 100 mV s^{-1}. The sensor exhibits a linear response between 0.01 and 0.78 mg l^{-1}, with a regression equation of I_P (A) = 10^{-5} C (mg l^{-1}) -2×10^{-7} and a correlation coefficient, R^2, of 0.999. Furthermore, there was no visible deterioration in the response of the electrodes during at least 1 week of successive operation. The detection limit, calculated as the blank signal plus three times the blank standard deviation [30], was 1.4×10^{-3} mg l^{-1}; this detection limit is under the mercury level reported by the U.S. Environmental Protection Agency for ground water and drinking water, 2×10^{-3} mg l^{-1} [31]. The reproducibility was measured by the analysis of eleven solutions with a Hg(II) concentration of 0.13 mg l^{-1}; a relative standard deviation of 2.5% was obtained. The mean peak current value was 1.13 μA; this mean value compare well with that obtained by the regression equation (relative error, 2.9%). Such performance indicates that this cheap and very simple procedure to prepare modified electrodes is a stable and reliable procedure.

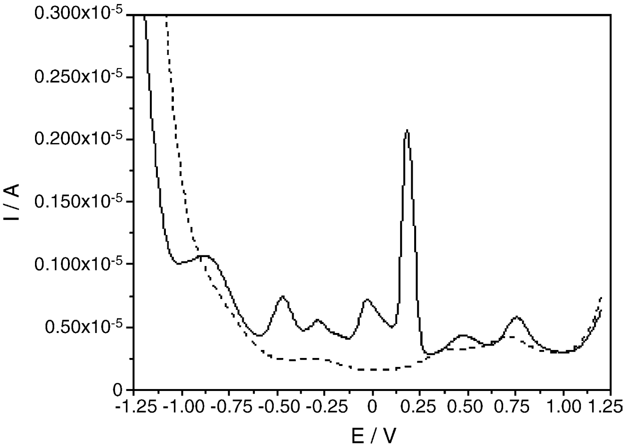

Fig. 4. DPASV of Hg(II) (0.2 mg l^{-1}) on a P3MT-modified electrode after exposure to a solution containing a mixture of Cd(II), Cr(III), Cr (VI), Zn(II), Ni(II), Pb(II) and Cu(II) (4 mg l^{-1} each one).

3.9. Study of interferences

Several common metal ions were subjected to DPASV under the optimal conditions described previously. All cations were submitted to the same open circuit preconcentration procedure described above. The electrode was immersed in a mixture of Hg(II), Cr(III), Cd(II), Cu(II), Zn(II), Pb(II), Cr(VI) and Ni(II) at a 4 mg l^{-1} concentration for the interferents and 0.2 mg l^{-1} for Hg(II) (1:20 analyte:interferent mass ratio). The voltammogram in Fig. 4 shows one oxidation peak at a potential of about 0.15 V attributed to mercury (according to previous experiences). Although other minor signals are detected, the peak height for Hg(II), 1.89 μA, compare well with that obtained by the regression equation. When a 1:1 analyte:interferent mass ratio is used, only the Hg(II) signal is observed. These results allow us to conclude that the proposed sensor is able to determine mercury even in the presence of the principal metallic ions that can exist in natural waters.

3.10. EIS measurements

In order to confirm the mechanisms suggested in the voltammetric part of this work regarding the P3MT/Hg(II) interaction, we have performed some EIS measurements.

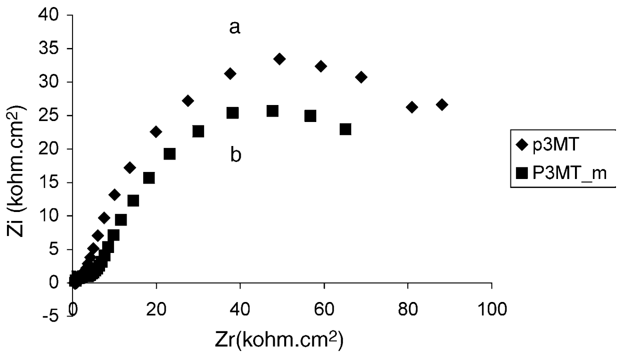

Fig. 5. Nyquist plot for: (a) the mercury-free P3MT-modified electrode and (b) Nyquist plot for the P3MT/Hg(II) system.

The impedance spectra were collected at 1000 mV (versus SCE) in a frequency range from 10 kHz to 10 mHz with an ac amplitude of 5 mV. The potential of 1000 V was chosen in order to insure the stability of the P3MT/Hg(II) films during the measurements. Fig. 5a shows the Nyquist plot for the mercury-free P3MT-modified electrode. The high frequency arc observed may be associated to charge transfer at the P3MT/solution interface. If we admit the Randles equivalent circuit model, the calculated (Voltamaster® 4.0 software) charge-transfer resistance R_{ct} and the double layer capacitance C_d are successively: 28.70 Ω cm² and 46.78 µF cm⁻². These data are typical of metal electrodes covered with polymeric films.

On the other hand, Fig. 5b also exhibits a arc like Nyquist plot for the P3MT/Hg(II) system. The electrical parameters calculated were: $R_{ct} = 21.92\ \Omega\ \mathrm{cm}^2$ and $C_d = 89.09\ \mu\mathrm{F\ cm}^{-2}$. It appears clearly from these data that the capacitance at the interface increases when the P3MT film is exposed to Hg(II). This observation is in agreement with the literature in the case of adsorption phenomenon at the electrode surface. Our result, give another evidence for Hg(II) adsorption on the P3MT film as part of an integrated process leading to the electrolytic reduction of the heavy metal at the polymer surface. The observed decrease of the charge-transfer resistance means also that the modified electrode becomes more conductive, which can be explained by the presence of mercury on the electrode surface.

The reproducibility of the measurements from several P3MT electrodes was good thanks to a rigorous control of the experimental conditions leading to the electrode preparation.

3.11. SEM measurement

Fig. 6 present the picture of a P3MT-modified electrode after exposition to a Hg(II) solution, obtained at 30.00 KV with a 1000× zoom. It clearly shows that the polymer film maintains its regular and typical (cauliflower) structure which confirms that the Hg(II) do not alter the mechanical stability of the sol–gel electrode.

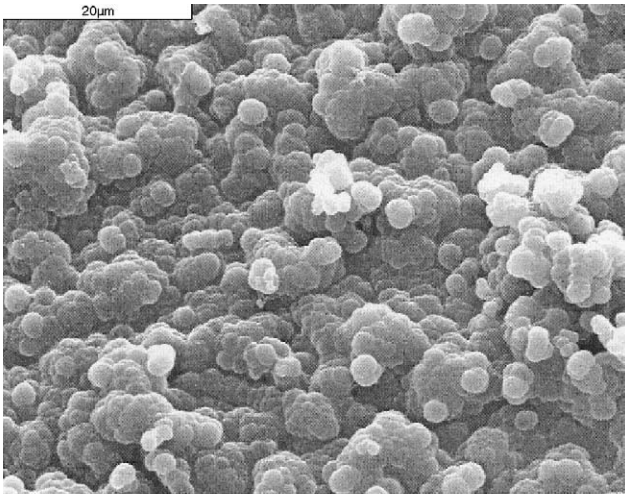

Fig. 6. Scanning electron microscopy (SEM) of a P3MT-modified electrode after exposition to a mercury(II) solution obtained at 30.00 KV with a 1000× zoom.

Table 4
Determination of mercury in waste waters samples

Wastewater sample	E_p (V)	Hg(II) concentration (mg l^{-1})
S1	–	n.d.[a]
S2	–	n.d.[a]
S3	0.080	0.13
S4	0.080	0.20
S5	0.080	0.10
Industrial reject	0.090	0.60
Home reject	0.100	0.40

See text for the source of water samples.
[a] n.d., no detected.

3.12. Analysis of real samples

The analytical performance of the method was assessed by determination of mercury in wastewaters, where possible interference due to complexity of the matrix can occurs. The results of the determination of mercury in these samples are given in Table 4. Samples were collected from Martiel river (Tetouan, Morocco). S1, S2, S3, S4 and S5 are sampling places established by the Laboratoire Regional de l‘Environnement of Tetouan; industrial and home rejects samples were collected near to the place where the wastes were dumped to Martiel river.

The results were compared with those obtained by AAS; no Hg(II) was detected for samples S1 and S2, as in electrochemical analysis. The other Hg(II) concentration values obtained by AAS were similar than those by electroanalysis, with deviations below 2.9% for all samples.

4. Conclusions

The results discussed above probe that sonogel–carbon materials are very appropriate to deposit P3MT films. The great capability of the polymer to preconcentrate mercury, in conjunction with the good electrical and mechanical properties of the sol–gel basis, becomes the proposed P3MT film modified sonogel–carbon electrode in a promising sensor to mercury species. Adsorption/chemical reaction/electrolytic reduction are the primary means for incorporation of Hg(II) species on the P3MT film. Our results also show that the incorporation process was related to the thickness and oxidation state of P3MT films. Mercury species were found to be readily preconcentrated onto P3MT film without chemically active counter ions. We are actually further investigating the mechanisms governing the Hg(II) selective interaction with P3MT by means of some accurate spectroelectrochemical techniques. The study of the performances of our sensor for field and on site applications is also under way.

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