A disposable electrochemical sensor based on bifunctional periodic mesoporous organosilica for the determination of lead in drinking waters

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Abstract A new bifunctional disulfide- and tetrasulfide-bridged periodic mesoporous organosilica (PMO) with mercaptothiazoline ligand was synthesized and employed to prepare chemically modified carbon paste electrodes for Pb(II) detection in aqueous media by square wave adsorptive stripping voltammetry. To demonstrate the real interest of bifunctionalization, carbon paste electrodes were prepared with disulfide- and tetrasulfide-bridged PMO without mercaptothiazoline ligand. Results showed the importance of bifunctionalization of PMOs to improve the sensitivity for the determination of Pb(II) in water samples. To achieve the most accurate and sensitive Pb(II) measurements, optimization of the operating parameters in preconcentration and detection steps was performed. Finally, the modified carbon paste electrode prepared with bifunctional disulfide-bridged PMO with mercaptothiazoline ligand was applied to determine Pb(II) in different water samples without any pre-treatment. Using this electrode, the optimal operating conditions were 120 s of electrolysis time in HCl 0.4 M. In these conditions, the voltammetric signal increased linearly with the preconcentration time from 1 to 10 min. Under optimized conditions, the linear range was 2 - 100 µg/L (R^2 = 0.9943) with a detection limit of 0.5 µg/L (for 5 min preconcentration time). Good reproducibility was achieved on both single and equally prepared electrodes. The accuracy of the method was validated by analysing Pb(II) in different drinking and natural water samples, with spiked recoveries in the range of 95 – 105 ± 10%. The results demonstrated that the prepared electrochemical sensor exhibited selectivity, fast response time and exceptional long-time stability.

Keywords Bifunctional periodic mesoporous organosilica . Disulfide- and Tetrasulfide-bridged . Modified carbon paste electrode . Voltammetric analysis . Lead . Drinking waters

Introduction

Contamination of the environment by heavy metals remains a serious problem because of their high toxicity, at very low concentrations, and their non-biodegradability. Heavy metals are incorporated into the whole environment where they can enter into human body via drinking water and foods. Pb(II) is classified as prevalent hazardous heavy metal, which constitutes a major environmental health problem. Accumulation of Pb(II) can cause poisoning, cancer and damage of several organs, particularly kidneys, liver and central nervous system. In 2014, the European Union has set the maximum allowable concentration of lead to be 10 μg L^{-1} in water for human consumption [1]. Therefore, efforts to develop rapid, robust and highly sensitive methods for the determination of ultra-trace Pb(II) in these samples are extremely important.

Electrochemical techniques, including anodic stripping voltammetry (ASV) have been used extensively for the determination of trace heavy metal ions, because of its low instrumentation cost, high sensitivity, high selectivity, easy operation and the ability of portability [2, 3]. In the past years, most electrodes in ASV were mercury electrodes. Nowadays, due to the toxicity of mercury, numerous attempts have been made to develop "environmentally friendly" solid state electrodes. Among these mercury-free solid state electrodes, carbon paste electrodes (CPEs) which have the advantage of low cost, facile fabrication, porous surface, low background current, wide potential range and easy renewal of its surface, have become an attractive new subject of electroanalytical investigations as a potential replacement for mercury and mercury film electrodes. In that respect, novel types of CPEs are continuously developed, testing new modifiers and mediators for traditional carbon paste mixtures or using new carbon paste mixtures, in which both graphite and binders are replaced by alternative materials.

The applicability of this kind of electrochemical devices may expand in the near future and will have a substantial impact in disciplines such as green electroanalytical chemistry, among others [4].

In order to enhance the sensitivity and selectivity of the electrochemical analysis of Pb(II) by using CPEs, the development of new chemically modified CPEs have received increasing attention in the past decades. For example, CPEs have been chemically modified, among others, with cyclodextrins [5], bismuth modified zeolite [6], multi-walled carbon nanotubes [7, 8], titanium/zirconium dioxide [9], double-stranded DNA and ferric oxide nanoparticles [10], metal-organic framework [11] and functionalized ordered mesoporous silicas (OMSs) [12, 13] for the determination of Pb(II) in different samples. Functionalized OMSs are a particular group of chemical modifiers whose use in the preparation of this type of electrodes is of continuing interest, as a result of its unique properties to improve sensitivity owing to fast mass transport processes [14]. These materials combine the chemical reactivity of the organic ligand, immobilized via covalent binding onto the silica surface, with the mechanical stability of the inorganic silica framework. For these reasons, these electrodes represent a subclass of chemically modified CPEs with widespread applicability, for example, to the determination of heavy metals [15]. Pre-concentration step in open-circuit with this kind of electrodes enable selective recognition of toxic metals, after a fine tuning of the nature of the organo-functional groups in the silica. Therefore, the use of functionalized OMSs as modifiers in the preparation of CPEs allows achieving better sensitivity, reproducibility, detection limits, etc., as a result of its large surface area, specific porous networks, narrow pore-size distribution and tuneable pore sizes over a wide range [16]. Recently, considerable work has proved the fact that modification of electrodes with functionalized OMSs can enhance the analytical performance of methods for heavy

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metal detection [17]. However, the use of new types of functionalized OMS in electrochemical sensors is yet an attractive strategy in this sense. A recent review of Bellido-Milla et al. [4] summarizes recent trends in CPEs development, with special attention in the use of emergent materials as new binders and to the development of other composite electrodes, including the use of OMSs.

An important breakthrough in the area of materials science was the preparation of the so-called periodic mesoporous organosilicas (PMOs) [18]. A recent review by Mizoshita et al. [19] highlights the unique structural features of PMOs and their expanding potential applications. PMOs are a class of mesoporous organic-inorganic silicas formed by hydrolytic condensation of bridged organosilane precursors of the general formula $[(R'O)_3Si]_nR$ ($n \geq 2$) in the presence of a structure-directing agent. PMO materials contain covalent Si-C bonds in the framework of the mesoporous silica (organic groups are an integral part of the pore walls). Thus, changing the nature of the organic bridges induces different properties in the material. One of the main interests in locating organic groups in the framework is the possibility to functionalize the channel pores by employing mixtures of bridged silsesquioxanes and terminal trialkoxysilyorganosilanes $[(R'O)_3SiR'']$. This leads to bifunctional PMOs (BPMOs) with distinct locations of the functional groups, a combination of bridging organic units inside the framework and terminal organic groups whose ends point into the channels. BPMOs prepared by co-condensation were first reported by Asefa et al. [20]. Post-modification of PMOs by grafting reaction to obtain BPMOs is also feasible [21].

Thioether groups show strong affinity for metal ions and are ideal functional sites on mesoporous materials to achieve efficient adsorbents to remove heavy metal ions in waters. In these sense, disulfide- and tetrasulfide-bridged PMOs have demonstrated very high adsorption capacity for heavy metals, mainly mercury, which

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was possible as the synthesis of this type of materials allows for the incorporation of a high percentage of multifunctional groups into the silica mesostructure [22-24]. However, despite these advantages, using BPMO as modifier in carbon paste electrodes for the determination of heavy metals has not been reported in the literature.

In this paper we report for the first time the application of disulfide- and tetrasulfide-bridged BPMOs as modifiers in CPEs for Pb(II) determination. To demonstrate the real interest of bifuntionalization, CPEs were prepared using the same procedure with disulfide- and tetrasulfide-bridged PMOs. Finally, employing a disulphide-bridged BPMO a new electrochemical sensor was development coupled with a small portable instrument to create a simple and environmental friendly assay for rapid analysis of Pb(II) in drinking waters. The prepared sensor gave an excellent stripping response to Pb(II) and possessed some advantages such as wide linear range, fast response time, long-time stability, reproducibility and relative low detection limit.

Experimental

Reagents and materials

Poly(ethylene glycol)- block-poly(propylene glycol)- block-poly(ethylene glycol) Pluronic 123 (M_{av} = 5800; d = 1.019 Kg/m^3) and tetraethyl orthosilicate (TEOS) 99% (M = 208.33, d = 0.933 Kg/m^3) were purchased from Fluka (Spain). Bis(triethoxysilylpropyl)disulfide (BTSPDS) (M = 474.82; d = 1.024 Kg/m^3), bis(triethoxysilylpropyl)tetrasulfide (BTSPTS) (M = 538.94; d = 1.069 Kg m^{-3}), 2-mercaptothiazoline (MTZ) 98% (M = 119.21), 3-chloropropyltriethoxysilane (CPTS) 95% (M = 240.81, d = 1007 Kg/m^3) and triethylamine (TEA) (M = 101.19, d = 726

Kg/m^3) were purchased from Sigma-Aldrich (Germany). Hydrochloric acid 37% ($M =$ 36.46, d = 1190 Kg/m^3) and ethanol (M = 46.07, d = 789 Kg/m^3) were purchased from Scharlau (Spain). Organic solvents (toluene, dimethylformamide, diethyl ether and hexane) were purchased from SDS (France). These solvents were distilled and dried before use according to conventional literature methods. Milli-Q water (resistance 18 MΩ/cm) used in the preparation of standard solutions was obtained from a Millipore Milli-Q-System (Waters, USA). All manipulations were performed under dry nitrogen gas using standard Schlenk techniques.

Synthesis of mercaptothiazoline ligand

The mercaptothiazoline ligand was prepared according to the procedure described in literature [25]. MTZ (5.00 g, 41.10 mmol) was dissolved in 50 mL of dimethylformamide. CPTS and TEA were added in a 1:2:1 stoichiometry (MTZ:CPTS:TEA). The mixture was heated for 48 h at 110 ºC with magnetic stirring under a nitrogen atmosphere using standard Schlenk-tube techniques. The mixture was filtered to eliminate the precipitate of triethylamine chloride. The dimethylformamide was evaporated and the excess of CPTS was distilled under vacuum (150 ºC and 0.75 mm Hg). The resulting viscous oil (dark-orange colour, yield 96%) was characterized by ^{1}H NMR, ^{13}C NMR, and IR spectroscopy.

Synthesis of bifunctional periodic mesoporous organosilica

20 g of Pluronic P123 were completely dissolved in 600 g of 2.0 M HCl and 152 mL of H$_2$O at 35 ºC. To this solution, 36.2 g of TEOS were added with vigorous stirring. After

stirring for 10 min, 9.16 g of BTSPDS or 10.40 g of BTSPTS were added to the above solution (BTSPDS/TEOS or BTSPTS/TEOS molar ratio = 10:90). The reaction mixture was stirred at the same temperature for 24 h, and then transferred into a Teflon-lined autoclave and heated for 24 h at 100 ºC without stirring. After filtering, the sample was washed with water, and dried in air at 40 ºC. The rest of surfactant was removed by heating the solid at reflux in a solution of ethanol/HCl (97/3%, v/v) with a Soxhlet for 48 h. Finally the solid was filtered, washed with water and dried at 40 ºC for 24 h.

MTZ ligand was covalently bonded to the disulfide- or tetrasulfide-bridged PMO (PMO-S-S and PMO-S-S-S-S, respectively) previously synthesized using the homogenous method. 12.00 g of the MTZ ligand (prepared as indicated in section 2.2) was reacted with 12.00 g of activated PMO-S-S or PMO-S-S-S-S (24 h at 90 ºC under high vacuum) in 50 mL of dry toluene with mechanical stirring (48 h under reflux conditions under a nitrogen atmosphere). The resulting bifunctional organosilica (MTZ-PMO-S-S or MTZ-PMO-S-S-S-S) was filtered off and washed with toluene (2 x 30 mL), ethanol (2 x 30 mL) and diethyl ether (2 x 30 mL). Finally, the product was dried for 8 h at room temperature under vacuum.

Characterization

X-ray diffraction (XRD) pattern of the silicas were obtained on a Philips Difractometer model PW3040/00 X'Pert MPD/MRD at 45 KV and 40 mA, using a wavelength Cu Kα (λ = 1.5418 Å). N_2 gas adsorption-desorption isotherms were performed using a Micromeritics ASAP 2020 analyzer. Infrared spectra were recorded on a Thermo Nicolet 380 FT-IR spectrophotometer in the region 4000 to 400 cm^{-1} by using spectra quality KBr powder. Elemental analysis (% N and % S) were performed in the Centro

de Microanálisis Elemental de la Universidad Complutense de Madrid (Spain) using a microanalyser model LECO CHNS-932. Scanning electron micrographs and morphological analysis were carried out on a XL30 ESEM Philips with an energy-dispersive spectrometry system (EDS). The samples were treated with a sputtering method with the following parameters: sputter time 100 s, sputter current 30 mA, and film thickness 20 nm using sputter coater BAL-TEC SCD 005. Conventional transmission electron microscopy (TEM) was carried out on a TECNAI 20 Philips microscope operating at 200 kV, with a resolution of 0.27 nm and $\pm$ 70º of sample inclination, using a BeO sample holder. The thermal stability of the modified nanostructured silicas was studied using a Setsys 18 A (Setaram) thermogravimetric analyzer with a 100 mL platinum crucible. A synthetic air atmosphere was used and the temperature increased from 25 to 800 ºC at a speed of 10 ºC per minute.

Instrumentation

Anodic stripping square-wave voltammetry (SW-ASV) measurements were performed in an battery-powered Bipotentiostat µSTAT200 (Dropsens, Spain) using a conventional voltammetry cell equipped with three electrodes: a modified carbon paste electrode, as working electrode, a saturated Ag/AgCl electrode, as reference electrode, and a platinum wire (Metrohm), as auxiliary electrode. A PC with DropView software for Windows was used to control the instrument, plot the measurements and perform the analysis of results. All measurements were made at room temperature and under an atmospheric environment.

Preparation of working electrode

Modified CPEs were prepared by mixing 0.100 g (20% w:w) of BPMOs (MTZ-PMO-S-S or MTZ-PMO-S-S-S-S) with 0.300 g (60% w:w) of carbon paste (Metrohm). Then, 0.100 g (20% w:w) of mineral oil (Aldrich) were added to the carbon paste/BPMO mixture and mixed for 2 h until obtain a uniform paste. The so obtained materials were packed into the end of a 5.0 cm long polyethylene tube (i.d. 3 mm), with a metallic wire as inner electrical contact. Appropriate packing was achieved by pushing the electrodes surfaces against a sheet of paper (this procedure also helps to eliminate the excess of mineral oil). Smoothing of the electrodes surfaces were made by hand-polishing on a filter paper. When necessary, news electrodes surfaces were obtained by replacing the wetted paste by freshly prepared product and polishing them again on a filter paper. All freshly-made electrodes were activated by performing 2–3 cycles of electrolysis/stripping in 0.3 M HNO_3 (SW-ASV was operated at a frequency of 100 Hz with pulse amplitude of 50 mV and a potential step height of 5 mV). CPEs were also prepared using the same procedure with disulfide- and tetrasulfide-bridged PMOs.

Voltammetric measurements

During preconcentration step, the modified CPE was immersed in 100 mL of Pb(II) solution efficiently stirred for a time of 5 min (300 rpm) at open-circuit. The modified CPE was then rinsed with Milli-Q water and transferred to the voltammetric cell containing 100 mL of electrolyte solution (HCl 0.3 or 0.4 M). For cathodic electrolysis, a negative potential (-1.0 V) was applied to the electrodes immediately after immersing into the electrolyte solution for a period of 120 s, to reduce the adsorbed metal into

elemental form. Square wave ASV (SW-ASV) was performed by sweeping a potential toward positive values (from -1.0 V to +0.4 V). SW-ASV was operated at a frequency of 100 Hz with pulse amplitude of 50 mV and a potential step height of 5 mV. No stirring conditions were used in both cathodic electrolysis and stripping steps. After each measurement, to ensure that no metal was still left on the electrodes surfaces, a regeneration of the electrodes was performed by electrolysis and stripping steps in 0.3 M HNO_3. If the electrode surface is clean, no peak will be detected in the second step. Each measurement was performed in triplicate and the average value was reported.

Results and discussion

Characterization of bifunctional periodic mesoporous organosilica

XRD pattern of MTZ-PMO-S-S and MTZ-PMO-S-S-S-S exhibited one intense well-resolved diffraction peak at $2\theta \sim 1.13°$ and 1.27 ° (d_{100} = 78.05 and 69.72 Å, respectively) in addition to very less intense broader peaks, which can be indexed as the (100), (110) and (200) reflections, respectively. These patterns demonstrated 2D ordered hexagonal mesostructure with the space group P6*mm* for the material. A unit cell parameter, a_0, of 90.12 and 80.5 Å, respectively, was calculated.

More detailed structural information of MTZ-PMO-S-S and MTZ-PMO-S-S-S-S was achieved by TEM (Fig. 1a and 1b). TEM images for this material showed aligned mesopores that were regular in diameter with a long-range packing order, confirming that the material possessed a well-ordered 2D hexagonal mesoporous structure. TEM also reveals that the whole material displayed an ordered mesoporous framework and

there were not disordered domains in it. On the other hand, SEM images of these materiasl showed mainly particles with irregular morphology (Fig. 1c and 1d).

Nitrogen adsorption-desorption isotherms of the MTZ-PMO-S-S and MTZ-PMO-S-S-S-S materials exhibit representative type IV curves, according to the IUPAC classification that were characteristics of mesoporous materials with a high surface area and a narrow pore-size distribution. The isotherms presented an H1-type-like hysteresis loop with a capillary condensation step at a relative pressure (P/P_0) of 0.35, approximately, suggesting uniform cylindrical mesopores. The synthesized materials possessed very high Brunauer-Emmett-Teller (BET) surface area (S_{BET} = 1,032 and 935 m^2/g), a total pore volume of 0.83 and 0.84 cm^3/g and a Barret-Joyner-Halenda (BJH) average pore diameter of 30.3 and 25.8 Å, respectively, typical of surfactant-assembled mesostructures. The wall thickness calculated was 59.8 and 58.4 Å, respectively.

FTIR spectra of the MTZ-PMO-S-S and MTZ-PMO-S-S-S-S (Fig. 2) showed a large broad band at 3,400 cm^{-1} attributed to O-H bond stretching of the surface silanols groups. Centered at 1,090 cm^{-1} appeared a broad peak due to the siloxane vibrations of (SiO). The band at 956 cm^{-1} was assigned to Si-OH stretching. The bands at 802 and 472 cm^{-1} were assigned to Si-O-Si stretching and Si-O-Si bending vibrations, respectively. The presence of –S-S- and –S-C- bonds was confirmed with bands at 696 and 566 cm^{-1}, respectively. Around 3,000-2,800 cm^{-1} the material presented bands due to aliphatic C-H stretching vibrations for pendant alkyl chains. Characteristic bands appeared at 1,475 cm^{-1} for C=N stretching vibrations of the attached MTZ groups. The presence of these peaks demonstrated the introduction of organic groups into the silica framework. On the other hand, the %S and %N obtained by elemental analysis for these materials also confirmed the successful introduction of disulfide- and tetrasulfide-

bridged groups in the silica (1.02 and 3.48 mmol S/g) and the presence of the MTZ ligand (1.46 and 0.59 mmol/g) onto the pore surface. These results showed that much more reactive silanol groups on the surface of PMO-S-S can be functionalized by with MTZ ligand by grafting method, so MTZ-PMO-S-S showed a high bi-functionalization degree, which provided to this material with a great number of active sites towards heavy metals.

Finally, thermal stability of the MTZ-PMO-S-S and MTZ-PMO-S-S-S-S material was established by thermogravimetric analysis. As it can be seen in Fig. 3a and 3b, the TGA curves and heat flow showed between 250 and 600 ºC and 11 and 14% weight loss and two exotermic peaks, respectively, that were attributed to the oxidative decomposition of the thioether functionality and MTZ ligand. These results confirmed that disulfide- and tetrasulfide-bridged groups and MTZ ligand can be stable up to 250 ºC in air that imply very good thermal stability of the materials.

Voltammetric measurements optimization

Modified CPEs prepared with both BPMOs (MTZ-PMO-S-S or MTZ-PMO-S-S-S-S) were applied to determine Pb(II). To demonstrate the real interest of bifunctionalization, CPEs were prepared with PMO-S-S and PMO-S-S-S-S. To achieve the most accurate and sensitive Pb(II) measurements, optimization of the operating parameters in preconcentration and detection steps was performed. Factors affecting the preconcentration of Pb(II) onto the electrode surface include preconcentration time. Factors affecting the detection of Pb(II) onto the electrode surface include electrolysis/stripping solution composition and electrolysis time. Other parameters affecting Pb(II) preconcentration step as ionic strength or pH have not been studied in

order to reduce water samples pre-treatment. Finally, the modified CPE prepared with MTZ-PMO-S-S was applied to determine Pb(II) in different water samples without any pre-treatment

Electrochemical performance of CPEs modified with PMOs

The electrochemical behaviors of different electrodes in the absence and presence of Pb(II) were investigated after open-circuit accumulation. Figure 4a and 4b shows the voltammograms obtained with CPEs modified with MTZ-PMO-S-S-S-S-CPE and MTZ-PMO-S-S-CPE, respectively. As can be seen, in both cases there is an anodic peak at -0.45V, related to the oxidation of Pb(0) to Pb(II). To prove the importance of bifunctionalization, CPEs modified with PMO-S-S-S-S and PMO-S-S, without the MTZ ligand, were also prepared and used for voltammetric measurements of Pb(II). As shown in Figure 4a and 4b, using these modified CPEs relatively smaller peaks were obtained. These results show that the BPMOs have two different active sites in their union with the Pb(II), the sulfide bridges and the MTZ ligand and confirm the interest of bifunctionalization in order to improve the sensitivity in the Pb(II) determination. Moreover, no redox peaks were observed on CPEs modified with BPMOs in absence of Pb(II) in the accumulation step, indicating that the BPMOs were non-electroactive in the selected potential window.

Electrolysis/stripping solution

Desorption of previously accumulated Pb(II) ions from the electrode surface to the electrode/solution interface must take place to enable the voltammetric detection.

Subsequent to the desorption process, an electrolysis was performed by applying a negative potential of -1.0 V to reduce the Pb(II) ions to Pb(0), followed by the quantification of lead via SW-ASV, which oxidizes the previously reduced Pb(0) to Pb (II). Thus, as electrolysis and stripping media HNO_3 (0.2 M) and HCl (0.2 M) solutions were tested. The experiments were performed with a 100 and 25 µg/L Pb(II) solution for MTZ-PMO-S-S-CPE and MTZ-PMO-S-S-S-S-CPE, respectively, with 5 min of preconcentration time and 120 s of electrolysis time. As it can be seen, when MTZ-PMO-S-S-S-S was used to prepare the modified CPE (see inset in Fig. 5b), the use of HCl as electrolysis/stripping media improved the sensitivity of the electrode to Pb(II) ions compared with the HNO_3. In fact, HCl is a better medium for electrolysis/stripping of the Pb(II) previously absorbed in the silica surface because the $PbCl_2$ formed is more stable than the $Pb(NO_3)_2$. Similar results were obtained for CPE modified with MTZ-PMO-S-S. In consequence, different concentration of HCl (0.1, 0.2, 0.3, 0.4 and 0.5 M) were tested as electrolysis/stripping medium. Results obtained with CPE modified with MTZ-PMO-S-S indicated that a significant increase in the signal was produced increasing the HCl concentration from 0.1 to 0.4 M (Fig. 5a), while with CPE modified with MTZ-PMO-S-S-S-S the increase in the signal was only observed from 0.1 to 0.3 M (Fig. 5b). Therefore, 0.4 and 0.3 M HCl were chosen as electrolysis/stripping media for quantitative purposes, because good signal and reproducibility was achieved in the voltammetric responses.

Preconcentration time

The effect of preconcentration time (1, 2, 5 and 10 min) on the voltammetric response for Pb(II) detection was studied. The experiments were performed using 100 µg/L Pb(II)

solutions for preconcentration step, and 120 s of electrolysis time in 100 mL of 0.3 M

HCl for MTZ-PMO-S-S-CPE and 0.2 M HCl for MTZ-PMO-S-S-S-S-CPE. Results

obtained for MTZ-PMO-S-S-CPE, shown in Fig. 6a, indicated that peak currents

increased with time (from 1 to 10 min) in all cases. For a rapid analysis of lead, one min

preconcentration time was found to be enough for higher concentration (100 µg/L), but

longer time (≥ 5 min) may be required in samples with lower Pb(II) concentration. This

short preconcentration time can be attributed to a fast adsorption rate, due to the pore

structure of MTZ-PMO-SS silica that enhances the diffusion rate of the Pb(II) ions into

the electrode surface. Results obtained for CPE modified with MTZ-PMO-S-S-S-S (Fig.

6b) showed a different trend. In this case, the peak current increased when the

preconcentration time increased from 1 to 5 min and then remained almost constant.

These results suggest that this CPE was saturated by Pb(II) ions when the

preconcentration time was higher than 5 min, that could be due to the lower

functionalization degree of the MTZ-PMO-S-S-S-S material and its lower pore size that

difficult the diffusion of Pb(II). Moreover, for 1 min of preconcentration time the peak

current obtained with this CPE was smaller than that obtained with the CPE modified

with MTZ-PMO-S-S. These results indicated that the CPE modified with the

tetrasulfide-bridged PMOs presented a lower diffusion rate of the Pb(II) ions into the

electrode that could be attributed to its pore structure.

Electrolysis time

The effect of the electrolysis time on the voltammetric response for Pb(II) detection was

also tested with both modified CPEs. The experiments were performed with a 1,000

µg/L Pb(II) solution, 5 min of preconcentration time and 0.3 M HCl as electrolysis and

stripping media. Similar results were obtained in both cases; the peak current increased as the electrolysis time increased from 60 to 120 s, and leveled off after this time to 180 s. This effect is probably due to the generation of the hydrogen bubbles in the electrode surface that affected the stability of the voltammetric response. In consequent, 120 s of electrolysis time was chosen as the optimal for lead deposition.

Interferences and detection of multi-component metals ions

Cations may be considered as interferences to the voltammetric detection of Pb(II) if they compete with this metal for the binding sites on the MTZ-PMO-S-S material during the preconcentration step or if its peak response overlaps the Pb(II) peak in the detection step. On the other hand, some anions present in waters have the capability to complex with many metals ions. Consequently, these anions may compete with the thioether and/or MTZ binding sites for Pb(II) ions, reducing the voltammetric detection of lead. Consequently, the selectivity of the developed electrode was evaluated by intentionally introducing some cations and anions into the Pb(II) solution during the preconcentration step. The experiments were performed under the optimized conditions with a solution containing 25 µg/L of Pb(II) and 100 µg/L or 1,000 µg/L of the interference. The tolerance concentration was taken as the measured signal variation $\pm$ 5% relative error. Based on the results obtained, 100 µg/L of Ca^{2+}, Mg^{2+}, Cl^- and 1,000 µg/L of SO_4^{2-}, NO_3^- and HCO_3^- have negligible effect on the lead signal. On the other hand, when Ca^{2+} or Mg^{2+} concentration was 1,000 µg/L, the Pb(II) signal was reduced to 67 and 61%, respectively. Moreover, the ion influence can easily be eliminated by applying the standard addition method for the evaluation of the concentration of lead in water samples.

Pb(II) determination by SW-ASV involves a first step were the Pb(II) cations are adsorbed on the electrode surface at open circuit potential. This preconcentration step reduces interferences during the stripping step because many species can be left in the sample solutions in function of the affinity between the organic ligand and the specie. On the other hand, it is possible to adsorb on the electrode surface some species which have high affinity against the organic ligand. As the redox potential of Hg(II) is different from Pb(II), but this metal possess a high affinity to the thioether and MTZ functionalities, the CPE modified with PMO-SS-MTZ was tested for simultaneous detection of both metal ions. Fig.7 shows a representative voltammogram of 500 µg/L of Hg(II) and 500 µg/L of Pb(II) (5 min of preconcentration time, 0.4 M HCl as electrolysis and stripping media, 120 s of electrolysis time). As shown in this figure, well-defined, sharp and separated stripping peaks for both Pb(II) and Hg(II) were detected, which can be attributed to the very high number of active sites on MTZ-PMO-S-S that minimizes the competition among both metals in the preconcentration step. These results confirmed that it could be possible to be detected simultaneously Hg(II) and Pb(II) with the modified electrode without sacrificing the Pb(II) voltammetric signal. Similar study was carried out for simultaneous detection of 500 µg/L of Pb(II) and 500 µg/L or 1,000 µg/L of Cd(II) with MTZ-PMO-S-S-CPE, but for this metal not redox peak were found in the concentration studied.

Analytical performance

Signal stability was first studied as a key parameter to test the practical usability of the developed CPE. Results obtained indicated that analytical signals for a single CPE surface, modified with MTZ-PMO-S-S, were stable for at least 500 measuring cycles

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whereas for a single CPE surface modified with MTZ-PMO-S-S-S-S the analytical signals were only stable for 25 measuring cycles. This fact indicates that the CPE modified with the disulfide-bridged PMO had long-term stability for dealing with the preconcentration and stripping procedure. For a single electrode surface using a preconcentration time of 5 min, the RSD of three replicate measurements of a solution containing 25 µg/L of Pb(II) was less to 7% and 9% for CPE modified with MTZ-PMO-S-S and MTZ-PMO-S-S-S-S, respectively. Using the same electrode surface for three consecutively days, the RSD was less to 11% and 25% (three determinations for each day) for CPE modified with MTZ-PMO-S-S and MTZ-PMO-S-S-S-S, respectively. To test the reproducibility of the electrode modification procedure, three different electrodes were prepared with MTZ-PMO-S-S and assayed in different days. The RSD obtained was 14% (three determinations for each electrode). These results indicated a very good and better reproducibility for Pb(II) detection with the developed CPE modified with MTZ-PMO-S-S with respect to the CPE modified with MTZ-PMO-S-S-S-S, so the first was selected to carry out the analysis of lead in water samples.

Fig. 8 shows calibration curves obtained with CPE modified with MTZ-PMO-S-S for the voltammetric response measure (peak current) versus the metal ion concentration under the optimized conditions (5 min of preconcentration time, 0.4 M HCl as electrolysis and stripping media, 120 s of electrolysis time). The voltammetric response was linear to the Pb(II) concentration with a R^2 of 0.995 in the range of 2 to 100 µg/L. The limits of detection (LOD) and quantification (LOQ) were calculated as the concentration of Pb(II) that provides a signal/noise (S/N) ratio of 3 and 10, respectively. The background noise was measured in a voltamogram obtained for 5 µg/L under the optimized conditions. Values obtained for LOD and LOQ were 0.5 and 1.8 µg/L after 5 min of preconcentration time.

Sample analysis

To test the proposed methodology, different dinking (mineral and tap water) and natural (groundwater) samples were assayed without any pre-treatment with CPE modified with MTZ-PMO-S-S. Water samples were spiked with Pb(II) to obtain a measurable level of 10 µg/L (according the European Regulation). To compensate matrix effects, Pb(II) was determined in the water samples by standard addition method and accuracy was assessed by recovery test (Fig. 9a and 9b). In this conditions, Table 1 show recovery values between $95 \pm 10\%$ and $105 \pm 10\%$ (n = 3) using 5 min of preconcentration time. These results suggest that methodology developed can be used for rapid analysis of Pb(II) in these waters.

Comparison with others CPEs modified with OMSs

Determination of Pb(II) using the developed method was compared with some other reported studies using different OMSs as CPE modifiers. Results are shown in Table 2. It can be seen that the liner range, reproducibility and limit of detection of the present method are higher to or at the same level as the published methodologies [12, 13, 26 – 29]. Moreover, the stability of the electrode prepared in this work has been shown to be much higher than that of other CPE modified with OMS, since peak current was not significantly reduced after 500 cycles. From these results, it is clear that the organic-inorganic framework of the PMO provided the electrode surface with remarkable long-term stability. In addition, the modified electrode prepared with MTZ-PMO-S-S exhibited improved signal responses compared with other OMS modifiers. This fact can be attributed to the exceptional characteristic of BPMOs that could make them as

promising modifiers in electrochemical analysis and extend the scope of applications on electrochemistry sensors.

Concluding remarks

Bifunctional periodic mesoporous organosilicas are interesting modifiers to prepare chemically modified carbon paste electrodes because its high surface area, high porosity, controllable and narrowly distributed pore size, ordered pore arrangement and very high functionalization degree. In this study, we have demonstrated that a carbon paste electrode modified with MTZ-PMO-S-S is a good option to determine Pb(II) by anodic stripping voltammetry in waters. The electrode prepared has three main advantages: a low LOD (0.5 µg/L after 5 min preconcentration time), a good reproducibility and a exceptional long-time stability, thus has a great potential to be used in the development of portable analyzers for monitoring heavy metal ions in water samples.

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Fig. 1 TEM images of **a** MTZ-PMO-S-S, **b** MTZ-PMO-S-S-S-S. SEM images of **c** MTZ-PMO-S-S, **d** MTZ-PMO-S-S-S-S

Fig. 2 FT-IR spectra of **a** MTZ-PMO-S-S and **b** MTZ-PMO-S-S-S-S

Fig. 3 Thermogravimetric curves and heat flow of **a** MTZ-PMO-S-S and **b** MTZ-PMO-S-S-S-S

Fig. 4 Voltammograms obtained by SW-ASV after 5 min preconcentration time and 120 s of electrolysis time at -1.0 V in 0.2 M HCl as electrolysis/ stripping media using **a** CPE modified with tetrasulfide-bridged PMO after and before of bifunctionalization with MTZ ligand for 25 µg/L Pb(II) solution and **b** CPE modified with disulfide-bridged PMO after and before of bifunctionalization with MTZ ligand for 100 µg/L Pb(II) solution

Fig.5 Effect of HCl concentration as electrolysis/ stripping media on the voltammetric response (peak current) measured by SW-ASV after 5 min preconcentration from 100 µg L^{-1} Pb(II) solution and 120 s of electrolysis time at -1.0 V using **a** CPE modified with MTZ-PMO-S-S and **b** CPE modified with MTZ-PMO-S-S-S-S; inset shows peak response in HNO$_3$ and HCl 0.2 M

Fig. 6 Effect of the preconcentration time on the voltammetric response (peak current) measured by SW-ASV after preconcentration from 100 µg/L Pb(II) solution and 120 s of electrolysis time at -1.0 V in 0.3 M HCl using **a** CPE modified with MTZ-PMO-S-S; inset shows representative voltammograms in ascending order of preconcentration time and **b** CPE modified with MTZ-PMO-S-S-S-S

Fig. 7 Representative voltammograms obtained using CPE modified with MTZ-PMO-S-S for the simultaneous detection of 500 µg/L of Hg(II) and 500 µg/L of Pb(II) measured by SW-ASV after 5 min preconcentration and 120s electrolysis in 0.4 M HCl

Fig. 8 Calibration curve obtained using CPE modified with MTZ-PMO-S-S for Pb(II) measured by SW-ASV after 5 min preconcentration time and 120 s of electrolysis time in 0.4 M HCl

Fig. 9 a Matrix effect in Pb(II) determination in laboratory tap water measured by SW-ASV after 5 min preconcentration time and 120 s of electrolysis time in 0.4 M HCl obtained using CPE modified with MTZ-PMO-S-S. **b** Representative voltammograms of laboratory tap water spiked with different amounts of Pb(II) solution in ascending order of concentration
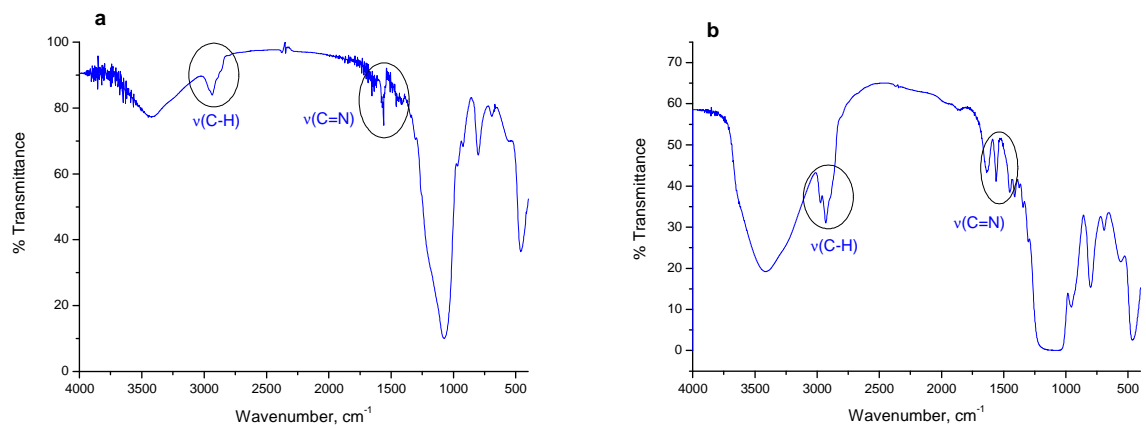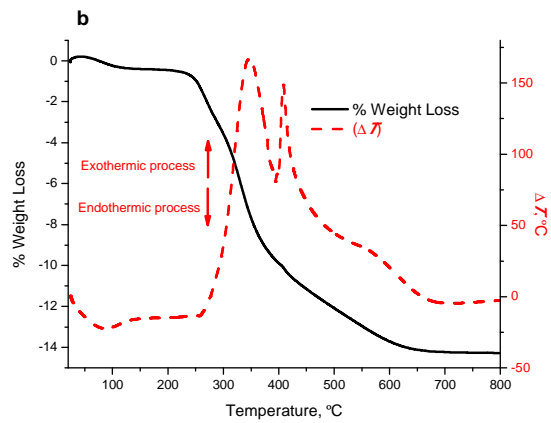
Fig. 1.

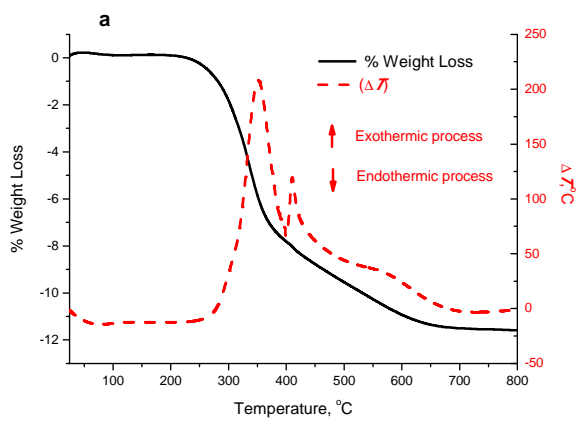**Fig. 2**.

Fig. 3.

Fig. 4.

a

Current, µA (y-axis)
Concentration HCl, mol/L (x-axis)

b

Current, µA (y-axis)
Concentration HCl, mol/L (x-axis)

HCl 0,2M
HNO3 0,2M

Fig. 5

a

y = 0,175x + 0,4169
R² = 0,9882

b

Fig. 6.

Fig. 7.

Fig. 8.

y = 0,0292x + 0,0817
R² = 0,9952

a

Current, μA (y-axis: 0,0 to 4,0)
Pb concentration, μg/L (x-axis: 0 to 150)

y = 0,0291x + 0,3224
R² = 0,9943

b

Current, μA (y-axis: 0 to 7)
Potential, V (x-axis: -1 to -0,2)

un   μg/L
10   μg/L
30   μg/
50 ppb
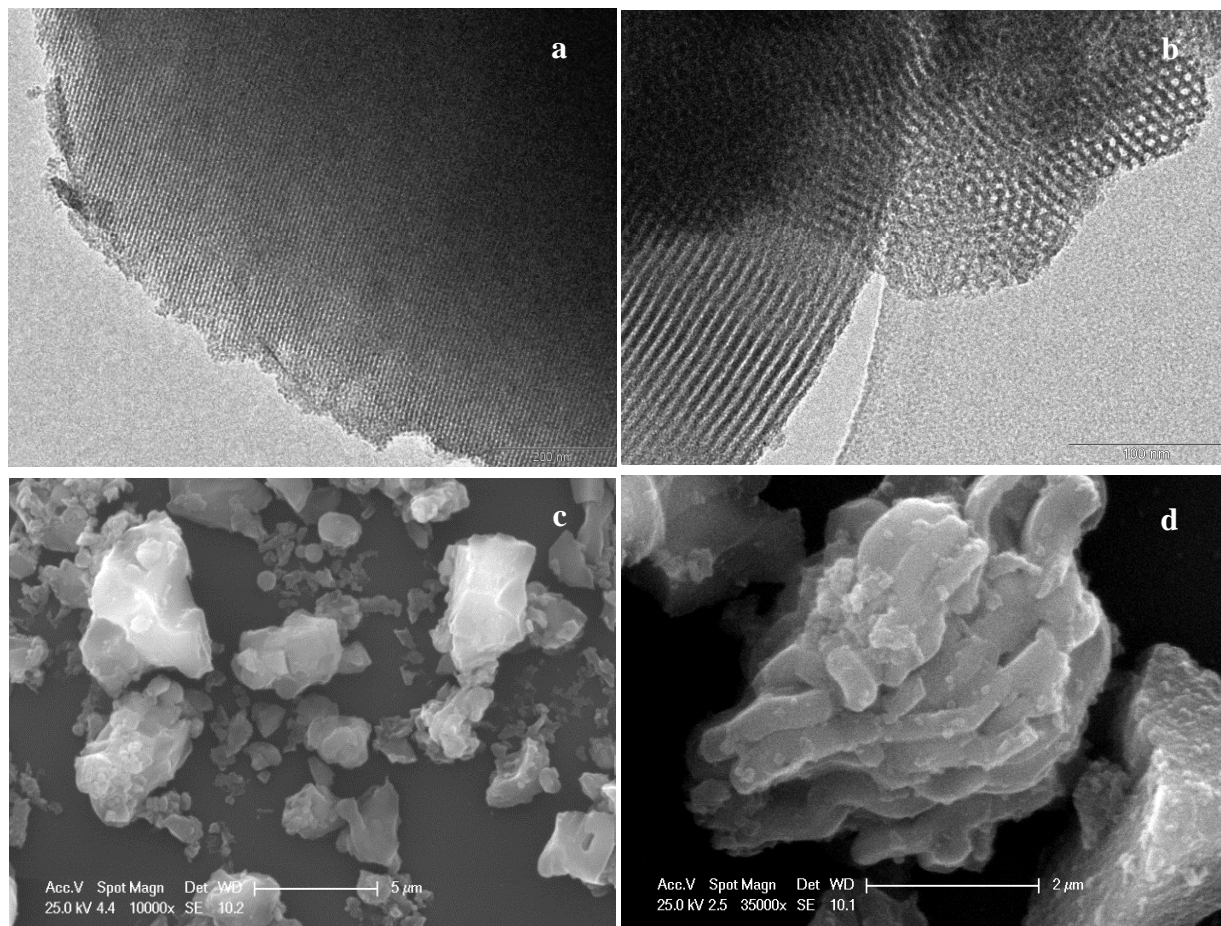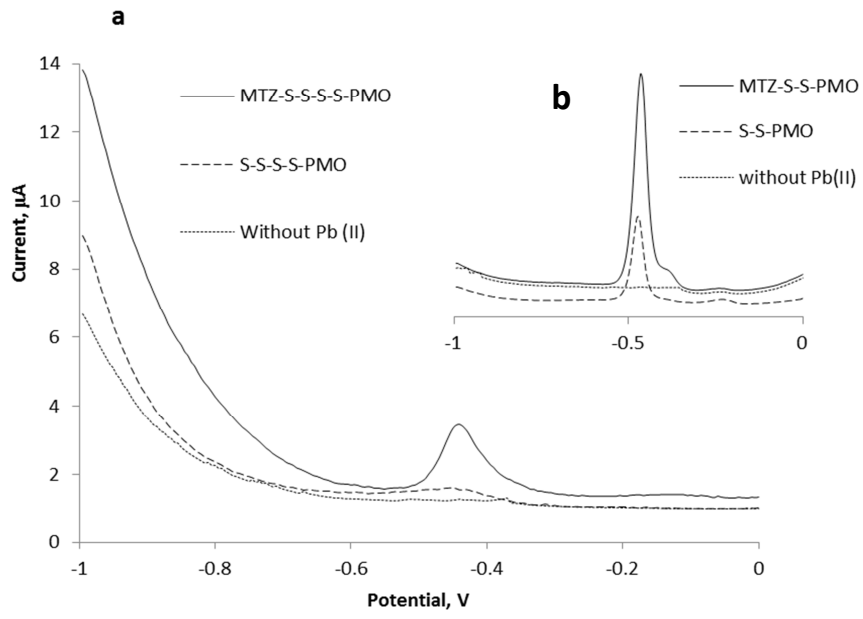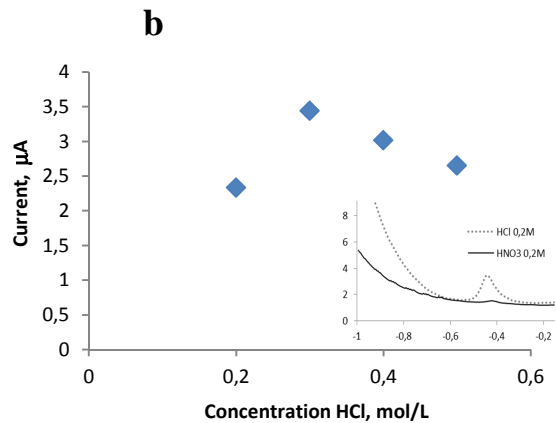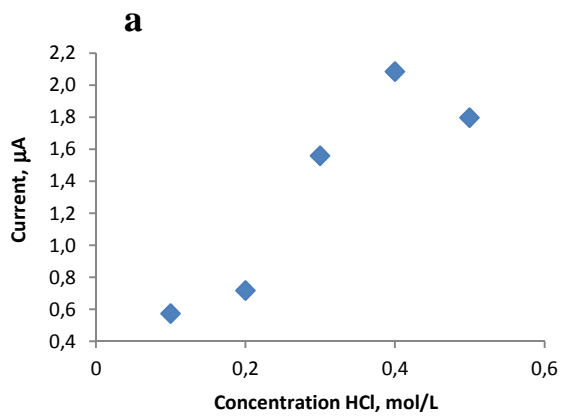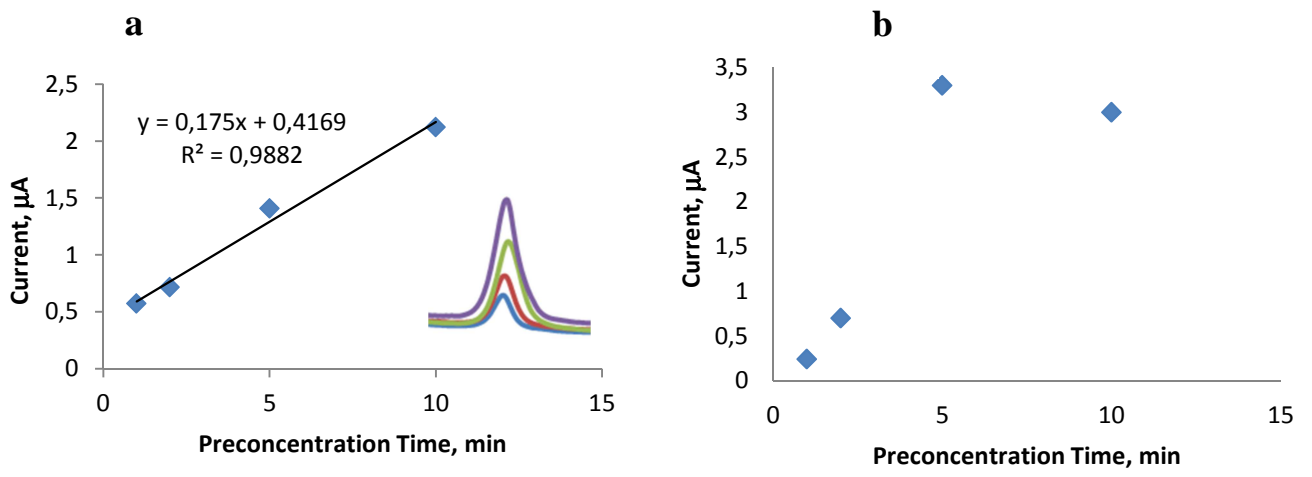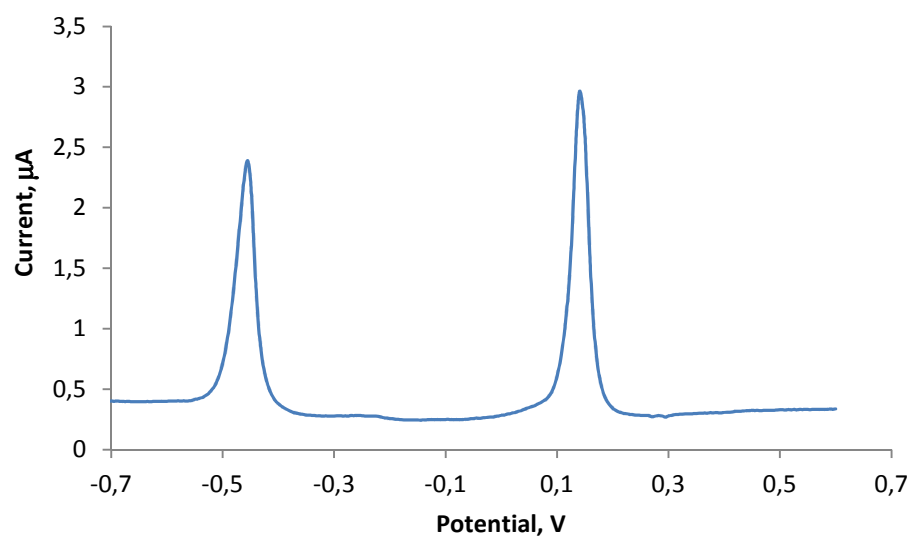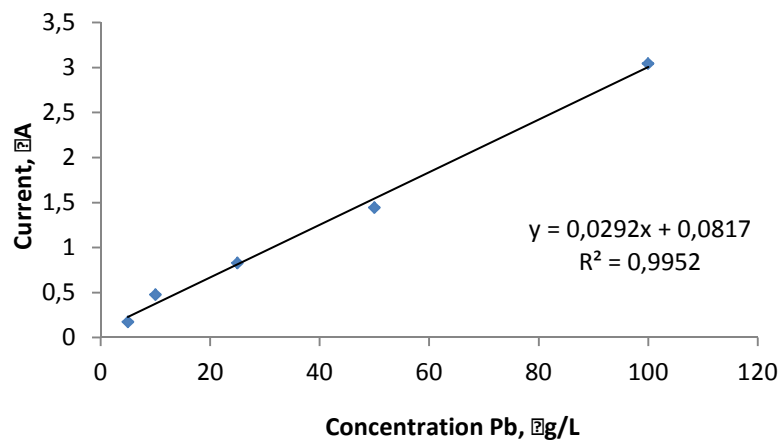
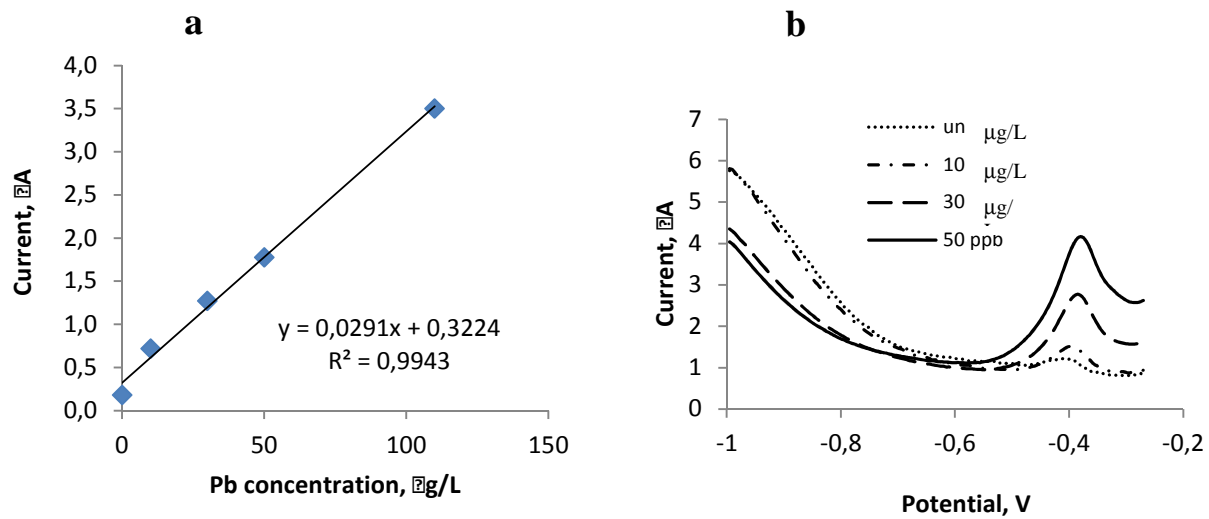**Fig.9.**

Table 1

Determination of Pb(II) on a CPE modified with MTZ-PMO-S-S in water samples

Sample [a]	Found (µg/L)	Spiked (µg/L)	Total found (µg/L)	Recovery (%)	RSD (n = 3)
Tap water 1	0.0	0.0	0.0		
	0.0	10.0	10.4	104	12
Tap water 2	0.0	0.0	0.0		
	0.0	10.0	9.5	95	10
Tap water 3	10.6	0.0	10.6		
	10.6	10.0	20.5	99	5
Tap water 4	0.0	0.0	0.0		
	0.0	10.0	9.9	99	6
Mineral water	0.0	0.0	0.0		
	0.0	10.0	10.4	104	12
Underground water	0.0	0.0	0.0		
	0.0	10.0	10.5	105	10

[a] Tap water 1 was collected in a house from Arroyomolinos city, Tap water 2 was collected in a house from Madrid city, Tap water 3 was collected in the laboratory from Mostoles city, Tap water 4 was collected in a house from Salamanca city

Table 2

Comparison of CPE modified with MTZ-PMO-S-S with others CPE modified with functionalized ordered mesoporous silicas

Analytes	Electrode modifier	Linear range [Pb(II), µg/L]	Detection limit (µg/L)	Preconcentration time (min)	Precision (RSD, %)	Reference
Pb(II), Hg(II)	SH-SAMMS	10 - 1,500	0.5	20	–	[26]
Cd(II), Cu(II), Pb(II)	Ac-Phos SAMMS	10 - 200	0.5	20	5	[27]
					12	
Pb(II), Cu(II), Hg(II)	Gly-UR SAMMS	2.5 - 50	1	2	–	[28]
Pb(II), Cu(II), Hg(II)	2-BTT-SBA-15	60 – 1,400	8	3	–	[29]
Pb(II), Cu(II), Cd(II)	MTTZ-HMS	1 - 100	0.3	5	5 - 10	[12]
Pb(II)	MTTZ-MPS1	1 - 30	0.8	5	3 - 9	[13]
	MTTZ-MPS2	1 - 100	0.3	5	3 - 10	[13]
	MTTZ-MPS3	1 - 15	0.5	5	6 - 12	[13]
	MTTZ-MPS4	5 - 100	2.6	5	3 - 13	[13]
Pb(II)	MTZ-PMO-S-S	2 - 100	0.5	5	7 - 14	This work

Abbreviations: SH-SAMMS: thiol terminated self-assembled monolayer on mesoporous silica (MCM-41); Ac-Phos SAMMS: acetamide phosphonic acid self-assembled monolayer on mesoporous silica (MCM-41); Gly-UR SAMMS: glycinylurea self-assembled monolayer on mesoporous silica (MCM-41); 2-BTT-SBA-15: 2-benzothiazolethiol-SBA-15; MTTZ-HMS: 5-mercapto-1-methyltetrazol-HMS; MTZ-PMO-S-S: mercaptothiazoline-disulfide-bridged PMO

 – Data not shown in the paper