



Effect of natural phosphate to remove silver interference in the detection of mercury(II) in aquatic algae and seawater samples



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ABSTRACT

A silver particles impregnated onto natural phosphate (Ag/NP) was synthesized using reaction in solid state. The obtained powder was characterized by X-ray diffraction (XRD) analysis and scanning electron microscopy (SEM). The (Ag/NP) was used as modifier of carbon paste electrode (CPE) to determine mercury by square wave voltammetry. The calibration graph obtained is linear from $1.0 \times 10^{-8} \text{ mol} \cdot \text{L}^{-1}$ to $1.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ at preconcentration time of 5 min, percentage loading of 7%, with correlation coefficient of 0.993. The limits of detection (DL, 3σ) and quantification (QL, 10σ) were $5.8 \times 10^{-9} \text{ mol} \cdot \text{L}^{-1}$ and $19.56 \times 10^{-9} \text{ mol} \cdot \text{L}^{-1}$ respectively. The repeatability of the method expressed as relative standard deviation (R.S.D.) is 2.1% ($n = 8$). The proposed method was successfully applied to determine mercury(II) in aquatic algae and seawater samples.

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1. Introduction

The analytical monitoring of mercury in environmental, industrial and food samples is extremely important because of the high toxicity of this metal both in its inorganic and organic compounds (e.g., methyl mercury). The ability of living organisms to convert inorganic mercury to organic mercury compounds, which are more toxic and accumulate to a greater extent in living organisms, additionally increases the danger of mercury exposure even at trace levels [1]. Numerous highly sensitive and selective spectroscopic methods for the determination of mercury compounds at low concentrations have been developed, the majority of them employ expensive and large instrumentation (e.g., neutron activation analysis [2], atomic fluorescence spectrometry [3], atomic absorption spectrometry [4] and inductively coupled plasma atomic emission spectrometry [5]). The electrochemical methods [6,7] provide an alternative platform for the detection of mercury at trace level due to the ease of miniaturization, low cost, timesaving, high sensitivity, and in situ determination [8]. Several solid electrodes, such as gold electrodes [9–13], platinum electrodes [14], graphite electrodes [15] and glassy carbon electrode (GCE) [13,16], have been employed. Gold electrodes are recently gaining confidence the detection for mercury [17].

The later have reported the methodology for the anodic stripping voltammetric determination of methyl mercury and inorganic mercury. Recently graphene-based materials have been highly concerned for constructing electrochemical sensors. Gong et al. [18] described a method for the preparation of a sensor with a monodispersed gold nanoparticles assembled on graphene nanosheet matrix for Hg(II) determination. Moreover, the recent trend to replacement of conventional electrodes by screen-printed electrodes (SPEs) is making possible to explore other options in this field [19]. The great versatility presented by the SPEs is based on the wide range of ways in which the electrodes may be modified (directly modifying the composition of printing ink or just depositing the substances on the surface) as demonstrated in recent published papers for Hg(II) determination [20–23]. Few papers concerning the use of silver nanoparticles-modified glassy carbon electrodes in electrochemical analysis of ion and molecule charge positive (lead, cadmium, lamotrigine) were published [24–26] and described the development of a procedure for the determination of molecules at a homemade silver nanoparticle electrode focusing in the study of the instrumental variables involved and the applicability for this molecules detection in pharmaceutical samples. Hg(II) and Au(III) ions represent the most critical element in the frame work of interference studies within the electro-chemistry of Ag(I) ions [27]. However, the most common problem in applying the bare-type silver electrode is the formation of undesirable silver amalgam, which may destroy the surface feature of

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the electrode. In addition, silver-based electrodes often suffer from the interference effect for several metal ions such as mercury, copper and bismuth. An effective way to overcome these barriers is protection of surface of silver particles to inhibit the formation of amalgam mercury(II).

The main objective of this work was to study the effect of natural phosphate as a support of silver particles for the determination of Hg(II) at carbon paste electrodes without interference of silver particles.

2. Experimental

2.1. Reagents

All chemicals used were of analytical grade or of the highest purity available. Sodium sulfate and sodium hydroxide, silver nitrate and chloridric acid were obtained from Merck, Fluka, and Riedel de Haen Chemical Companies and were used as received. A natural phosphate (NP) used in this work was obtained from Khouribga region (Morocco) [28]. The material was treated previously by techniques involving attrition, sifting, calcination at 900 °C, washing and recalcination. Stock solution of mercury(II) were prepared by dissolving appropriate amounts of $\text{Hg}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in water. A chloridric acid at pH = 1.36 served as a supporting electrolyte solution. Graphite carbon was supplied from (Carbone, Lorraine, ref. 9900, France). All other reagents used were of analytical grade. Distilled water was used throughout the preparation of the solutions. Electrodes were thoroughly conditioned for trace analysis soaked in hot nitric acid at 10% for 48 h, rinsed with distilled water.

2.2. Synthesis of modifier

(Ag/NP) was synthesized by mixing the reagents Silver nitrate powder and natural phosphate in an agate mortar. A series of stages in the following steps: heating of the samples at 100 °C for (2 h) and 200 °C for (14 h) in the oven, in order to improve the homogeneity of the mixture and increase the kinetics of the solid state reaction. The resulting powder were reground and calcined at different temperatures from 600 °C to 1000 °C for 14 h in the kiln.

2.3. Preparation of the (Ag/NP)-CPE

The modified carbon electrodes were obtained by a mixture of carbon powder and silver particles impregnated natural phosphate (Ag/NP). The mixture was then incorporated into the electrode cavity (laboratory made, 0.1256 cm² geometric surface area) and was polished by smooth paper. Electrical contact was established by a bar of carbon. The resulting electrode is hereby denoted as Ag/NP-CPE. The carbon electrodes modified with compound contains natural phosphate, silver and silver/phosphate were prepared in a similar way.

2.4. Instrument

Cyclic and square wave voltammetry were carried out with a voltalab potentiostat (model PGZ 100, Radiometer Analytical Inc) driven by the general purpose electrochemical systems data processing software (voltalab master 4 software). The electrochemical cell was configured to work with three electrodes, using (Ag/NP) modified carbon as the working, platinum plate for counter and a system Ag/AgCl (3.00 mol·L⁻¹ AgCl) as reference electrodes. The pH-meter (Radiometer, SENSION™, PH3, Spain) was used for adjusting pH values.

X-ray diffraction studies of prepared powder Ag/NP were carried out using a diffractometer (XRD: Cu K α radiation, XPERT-PRO), ($k_{\text{Cu}} = 1.5406$ nm) produced at 30 kV and 25 mA scanned the diffraction angles (2 θ) between 10° and 80° with a step size of 0.02° 2 θ per second. The surface area was determined by the BET method (Autosorb iQ of Quantachrome instruments). Scanning electron microscopy (SEM)

measurements were performed on an FEI Nova SEM (Philips) instrument with an AMETEK energy dispersive X-ray (EDX) system (Nova 200) operated at an accelerating voltage of 30 kV. Imaging of solids deposited on the 3 mm GC electrodes was performed with the aid of a custom built electrode holder. Prior to SEM imaging, samples were thoroughly rinsed with acetone and Milli-Q water and dried under a flow of nitrogen.

2.5. Procedure

Standard solution of mercury was added into the electrochemical cell contained 40 mL of supporting electrolyte (0.1 mol·L⁻¹ HCl). A preconcentration step was first performed by immersing the electrode into mercury(II) solution under open circuit condition. The initial working procedure consisted of measuring the electrochemical response of mercury(II) at (Ag/NP)-CPE. An experiment control was also performed under the same conditions. The square wave voltammetry was recorded in the range from -0.3 V to 0.3 V, for which the scan rate is 1 mVs⁻¹, pulse 50 mV, amplitude 1 mV and duration 1 s. Optimum conditions were established by measuring the peak currents in dependence for all parameters. The suitability, of the electroanalytical method in determination of mercury in aquatic algae and seawater samples, was tested under the optimized condition. The aquatic algae samples, previously dried at 50 °C and finely ground in Agate mortar plants, have been dissolved by acid attacks. The resulting product was fortified by adding an appropriate amount of mercury(II). The electroanalytical curves were obtained by using square wave voltammetry in the range from 1.0×10^{-7} mol·L⁻¹ to 1.0×10^{-5} mol·L⁻¹ of mercury. All experiments were carried out under ambient temperature and performed in triplicate.

3. Results and discussion

3.1. Characterization of powder Ag/NP

The thermal stability of the Ag/NP were studied by heating a small amount of the sample at 900 °C for 14 h and cooling in air to room temperature. The XRD patterns showed the presence of the three peaks at 2 θ : 38.18, 46.62 and 66.42 attributed to metallic silver (Fig. 1) [29]. Scanning electronic microscopy (SEM) shows the formation of silver particles impregnated in the natural phosphate which are deposited in aggregated form (Fig. 1). The surface area of both Ag/NP, with 9.09% of silver, and of NP calcined at 900 °C was determined by the BET method, and was found to be respectively 11.75 m²/g, 11.45 m²/g. BET analysis shows that silver particles plays a major role for the mercury(II) detection than the accumulation effect. The small difference between BET values obtained for the natural phosphate and natural phosphate doped with silver, shows that mercury(II) is highly detected because of the dispersion of silver on the natural phosphate.

3.2. Electrochemical response of mercury(II)

The detection of mercury(II) at Ag/NP-CPE sensor was investigated using square wave voltammetry. No obvious peak is observed at low concentration of mercury in case of NP-CPE phosphate modified carbon electrode. In contrast, a much high stripping peak at 10 mV for mercury(II) is observed when using Ag/NP-CPE. The result indicates that the silver impregnated in the natural phosphate can greatly promote the detection of mercury(II) and significantly increase the sensitivity of the determination of mercury (Fig. 2). Natural phosphate is an effective reagent to avoid of the oxidation of the silver particles, of which is capable to protect the electrode surface from these silver interferences.

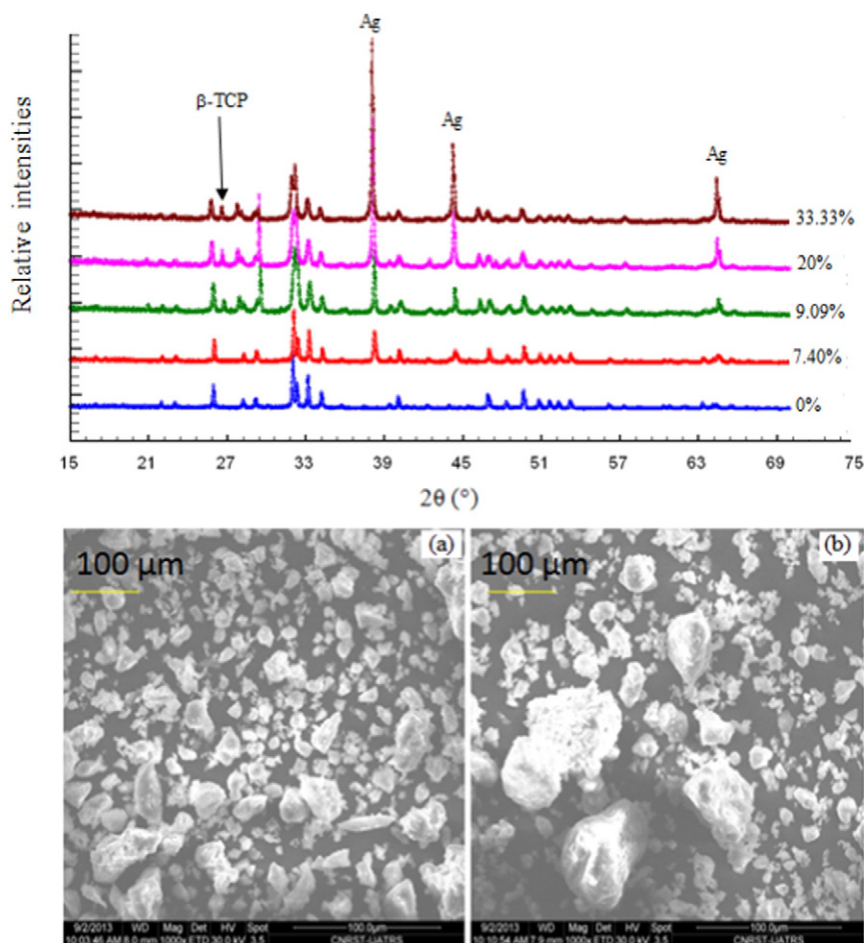


Fig. 1. XRD patterns of the Ag/NP calcined at 900 °C and scanning electron microscopy (SEM): (a) NP, (b) Ag/NP = 9.09%.

3.3. Optimization of experimental variables physical

The influence of the experimental variables (pulse, modulation amplitude and duration) which involved in the square wave voltammetric (SWV) determination of mercury(II) was investigated (Fig. 3). Measurements for $1.0 \times 10^{-6} \text{ mol}\cdot\text{L}^{-1}$ of mercury(II) standard solution, spiked in electrolytic solution, were performed for evaluating the heights and the shapes of the obtained signals. Pulse influence was investigated in the range from 1 to 50 mV. As expected, a significant increase of the signal intensity was observed until 50 mV. Modulation amplitude was studied in the range from 1 to 15 mV. From value of 1 mV, the mercury(II) signal was decrease until 5 mV and then increase. The maximum response was observed at 1 mV.

In agreement with the high peak current values, good shapes of the signal and better signal to noise ratio, the selected optimal values were 50 mV, 1 mV and 1 s for pulse, modulation amplitude and duration respectively.

Fig. 3 shows the effect of the temperature of calcination of (Ag/NP) on the square wave voltammetric response of $1.0 \times 10^{-6} \text{ mol}\cdot\text{L}^{-1}$ mercury(II). The current response increased from 600 °C to 900 °C and decreased. The maximum response was observed with (Ag/NP) calcined at 900 °C. Hence for all subsequent measurements, a mixture of the (Ag/NP) calcined at 900 °C was employed.

The effect of varying mass of the inserted silver on the current response for $1.0 \times 10^{-6} \text{ mol}\cdot\text{L}^{-1}$ of mercury is shown in Fig. 3. It has been observed that a poor response for mercury is obtained with an Ag/NP ratio higher than 20%. The XRD patterns of the heat-treated Ag/NP samples with different silver percentage are shown in Fig. 3. Three peaks were observed at 2θ : 38.18, 46.62 and 66.42 for all heat-

treated samples. However the increase of the silver mass leads to the increase of intensity of the peak [29]. The increase of silver percentage onto NP formed a silver film on the electrode surface. The poor response

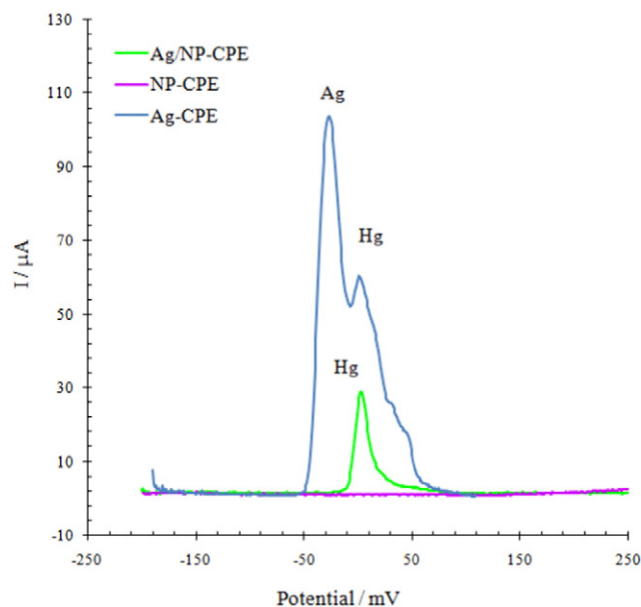


Fig. 2. Square wave voltammograms of $1.0 \times 10^{-6} \text{ mol}\cdot\text{L}^{-1}$ mercury in $0.1 \text{ mol}\cdot\text{L}^{-1}$ HCl at: (a) Ag/NP-CPE; (b) NP-CPE; (c) Ag-CPE; pH = 1.0, 5% of (Ag/NP)/CP, NP/CP, Ag/CP ratio.

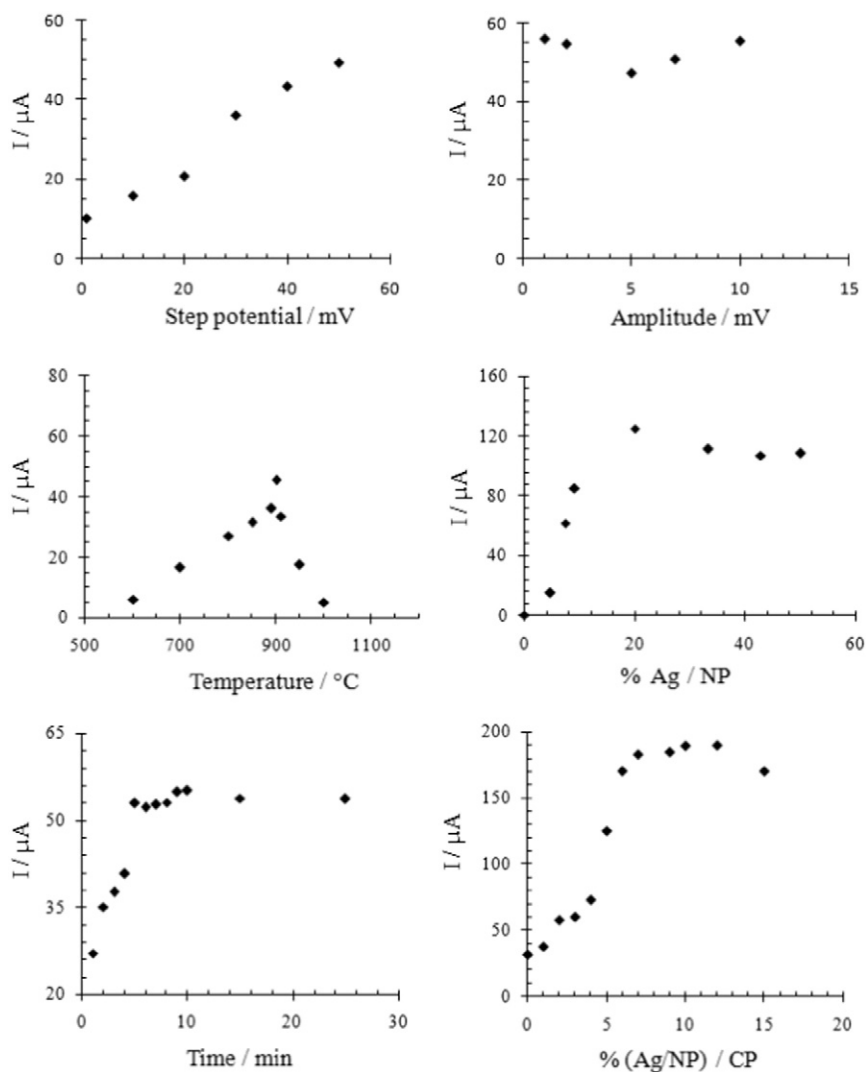


Fig. 3. Influence of the experimental variables (pulse, amplitude, calcination temperature of the Ag/NP, percentage of the silver) on differential pulse reduction peaks for $1.0 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$ of mercury in $0.1 \text{ mol} \cdot \text{L}^{-1}$ HCl at (Ag/NP)-CPE.

of the (Ag/NP)-CPE for mercury detection, observed with height amount of silver, can be explained by the formation of a partial film of silver on the CPE electrode [25]. The Ag/NP ratio was fixed at 20% for all further experiments. The XRD patterns of the Ag/NP heated samples with $\times < 9.09$ is found to be without any impurity phases. The presence of β -TCP phase was noticed for Ag/NP samples with $\times \geq 9.09$. The silver incorporated into natural phosphate inhibits apatite crystallization and destabilizes the structure of apatite and favors its conversion to β -tricalcium phosphate. However, the silver peak of 38.18 was observed for all the heat-treated samples.

The effect of preconcentration time on the mercury response was studied in the range 1–30 min. The anodic stripping peak current increased by increasing preconcentration time up to 5 min, above which it remained nearly constant. Therefore, a preconcentration time of 5 min was selected for further works. As far as the electrode conditions are concerned, the amount of (Ag/NP) is a control factor of great importance. As expected, an increase in amount of (Ag/NP) gives a higher peak current and the peak potential remains constant. The highest peak is obtained with electrode modified with 10% of (Ag/NP). When the amount of (Ag/NP) increases continuously, the peak current decreases. Presumably, more (Ag/NP) at the electrode surface reduces the amount of conductive area of the activated graphite particle [30].

3.4. Repeatability, linearity and detection limit

Calibration graphs were constructed under the optimum conditions described above using (Ag/NP) as modifier in the preparation of the electrode: pulse of 50 mV, the pulse amplitude of 1.0 mV, duration 1 s, time preconcentration of 5 min (Ag/NP)/CP loading of 10% with (Ag/NP) = 20%. Fig. 4 shows the net square wave voltammogram for different concentrations of mercury(II) obtained under the optimum conditions described above. The relationship between the peak current of mercury(II) and its concentration is linear in the dynamic range from 1.0×10^{-8} to $1.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$. The detection limit, defined as $DL = 3S_b/m$, where DL, S_b and m are the limit of detection, standard deviation in the blank and the slope of the calibration graph respectively. S_b was estimated by 10 times determination of blank signals. The repeatability of the electrode in the determination of mercury(II) was evaluated by performing seven determinations with the same standard solutions of mercury(II). The relative standard deviation (RSD) of the response of electrode towards a $5.0 \times 10^{-7} \text{ mol} \cdot \text{L}^{-1}$ of mercury(II) solution was 2.45%. The limit of detection is obviously obtained comparative than that of other electrodes reported in literatures (Table 1). Such a high sensitivity and low detection limit obtained is most likely ascribed to the ensemble behavior of the nanostructured platform. Our results

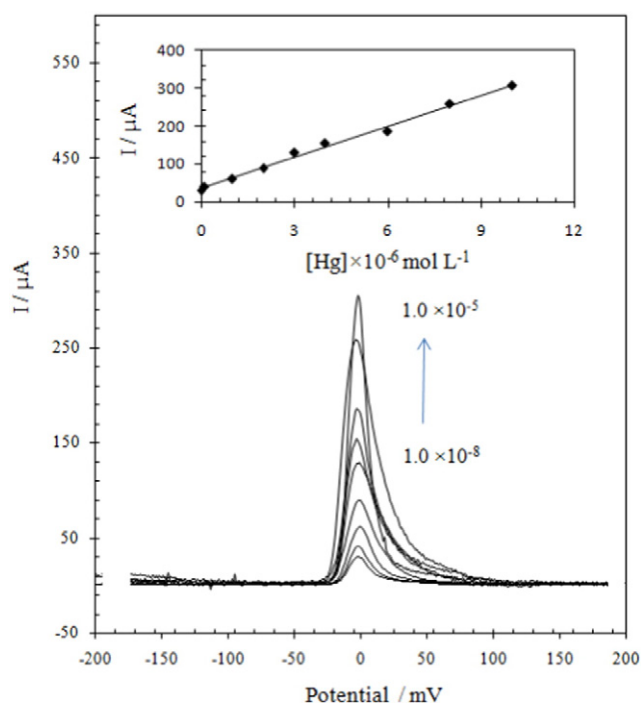


Fig. 4. Net square wave voltammograms of (Ag/NP)-CPE of mercury(II): 1.0×10^{-5} , 8.0×10^{-6} , 6.0×10^{-6} , 4.0×10^{-6} , 3.0×10^{-5} , 2.0×10^{-6} , 1.0×10^{-6} , 1.0×10^{-7} , 1.0×10^{-8} , $\text{mol} \cdot \text{L}^{-1}$. Conditions: pulse of 50 mV, the pulse amplitude of 1.0 mV, duration 1 s, time preconcentration of 5 min, (Ag/NP) loading of 10% with (Ag/NP) = 20%.

demonstrate that the proposed Ag/NP-CPE sensor is reliable for the detection of mercury(II).

The Ag/NP-CPE electrode here could maintain its activity as a sensor for mercury(II) during 4 months; the response was 98.25% of its initial value which shows long-term stability and very good sensitivity for the analysis of mercury(II). NP was an effective way to avoid the oxidation of the silver particles; thus, the properties of the electrode do not change. We can use the electrode three times, after the cleaning procedure [40].

3.5. Practical application in aquatic algae and seawater samples

3.5.1. Aquatic algae

The aquatic algae, especially brown algae, are widely used in the fabrication of pharmaceutical products. Unfortunately, they are often exposed to different kinds of pollution. The industrial waste discharged into the seawater can be a potential source of contamination of the aquatic algae. In order to determine the possibility of such contamination of aquatic algae samples with mercury(II), the standard addition

method was investigated, in three replicate ($n = 3$). The purpose of using this method is to compensate the matrix effect from aquatic algae samples that contain high concentrations of heavy metals ions and other foreign ions as high as over thousand times of mercury concentration.

Fig. 5 shows that the intensity of peak currents versus mercury amount added into real sample increase linearly, and hence the proposed methodology is suitable for the determination of mercury in the aquatic algae. Interference is possible due to the complexity of the matrix. Recovery experiments were carried out in order to evaluate the interference of electrolytes effects of the aquatic algae samples on the detection of mercury(II) at (Ag/NP)-CPE. The recovery and relative standard deviation studies were realized by adding $6.0 \times 10^{-7} \text{ mol} \cdot \text{L}^{-1}$ of mercury(II) to electrochemical cell. The statistical calculations for the assay results showed suitable precision of the proposed method (Table 2). Results obtained for R.S.D. and recovery percentage were 3.25% and 96.5% respectively. These results were related to slight interference effects of the constituents of each sample. The comparative determination of mercury(II) in aquatic algae by the proposed method and inductively coupled plasma-atomic emission spectrometric (ICP-MS) method is shown in Table 2. The mean percentage recoveries of added mercury(II) were found to be 96.5% and 97.56% using the proposed method and ICP-MS, respectively. The excellent average recoveries in aquatic algae samples suggest that the electrode (Ag/NP)-CPE developed in this work has a practical significance and is able to determine mercury(II) in aquatic algae.

3.5.2. Seawater samples

Mercury, particularly in the organic form, is a toxic pollutant that can adversely affect the health of people, but in aquatic environment this metal is also present as complexes of the inorganic divalent cation [41]. Mercury concentrations in the surface ocean (upper 100 m) have increased fourfold over the past 500 years, with a two-fold increase over the last century concurrent with increasing industrialization and energy production [42]. Fish consumption is the main source of methylmercury exposure for people worldwide [43], and marine fish constitute 92% of the global fish harvest for human consumption [44]. Methylmercury concentrations in commonly consumed marine fish exceed the U.S. Environmental Protection Agency's human health criterion of 0.3 ppm (ppm) in most marine systems studied. Most of the mercury (about 90%) in fish consumed by humans occurs as methylmercury. This is the main reason why it is necessary to find a technology to analyze this compound, especially in the seawater.

The proposed methodology was tested to determine mercury(II) in seawater samples obtained from El Jadida region, Morocco. The support electrolytes were prepared by addition of $0.1 \text{ mol} \cdot \text{L}^{-1}$ of HCl to fresh seawater. When the method was applied to algae and seawater samples, the concentration of the mercury was found to be lower than the DL. The electroanalytical curves were obtained, using square wave

Table 1

Comparison with the proposed electrode and other voltammetric techniques for the determination of mercury(II).

Electrodes	Calibration range ($\text{mol} \cdot \text{L}^{-1}$)	Detection limit ($\text{mol} \cdot \text{L}^{-1}$)	References
Gold solid electrode	5.0×10^{-9} – 25.0×10^{-9}	2.0×10^{-9}	[31]
SAMMS-SH/CPE	1.0×10^{-7} – 8.0×10^{-6}	15.0×10^{-9}	[32]
Gold ultra-microelectrode arrays	–	16.0×10^{-9}	[33]
Metallothionein/gold electrode	1.50×10^{-7} – 3.0×10^{-7}	80.0×10^{-9}	[34]
Gold microelectrode array	1.0×10^{-8} – 1.0×10^{-7}	4.0×10^{-9}	[35]
Gold microwire electrode	to 2.35×10^{-7}	12.0×10^{-9}	[36]
Vibrating gold microwire electrode	–	3.5×10^{-9}	[7]
Screen-printed gold electrodes	2.5×10^{-8} – 15.0×10^{-8}	5.5×10^{-9}	[23]
On-chip integrated Au-Ag-Au three-electrode	5.0×10^{-8} – 5.0×10^{-6}	15.0×10^{-9}	[37]
Sb film electrode	5.0×10^{-8} – 5.0×10^{-7}	6.5×10^{-9}	[38]
Mercaptopropyl functionalized silica/Gold electrode	1.0×10^{-7} – 1.0×10^{-6}	100.0×10^{-9}	[39]
Electrode modified by gold nanoparticles	–	41.0×10^{-9}	[6]
Ag/NP-CPE	1.0×10^{-8} – 1.0×10^{-5}	$5.8 \times 10^{-9} \text{ mol} \cdot \text{L}^{-1}$	This work

SAMMS-SH/CPE: Thiol terminated self-assembled monolayer on mesoporous silica/carbon paste electrode.

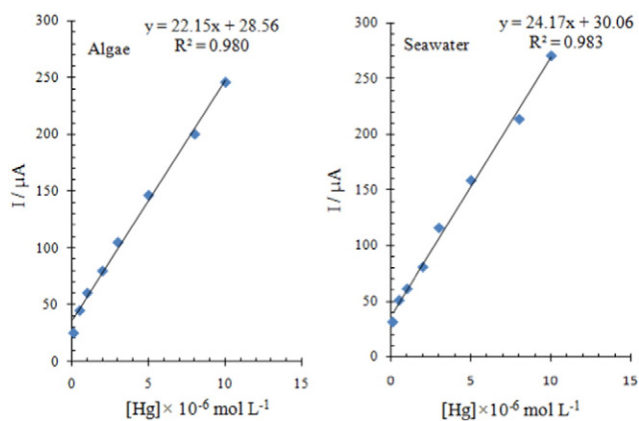


Fig. 5. Calibrations curves of mercury in algae and seawater samples.

voltammetry, by spiking the seawater samples with mercury(II) in the range from $1.0 \times 10^{-7} \text{ mol} \cdot \text{L}^{-1}$ to $1.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$. The electrical dependence, with mercury(II) concentration, was linear indicating the efficiency of the Ag/NP-CPE to determine mercury(II) in complex samples. The percentage of the extraction signal of mercury(II) was studied by divided the current of the peak in seawater by the current of the peak in pure water. The obtained recovery (98.5%) was satisfactory to extract mercury(II) from seawater samples. The same procedure was investigated but this time using inductively coupled plasma-atomic emission spectrometric method (ICP-MS). The mean percentage recovery of added mercury(II) was found to be 98.81%. There were no significant differences between the recovery, of mercury(II) extraction in seawater samples, obtained using Ag/NP-CPE and ICP-MS in confidence level of 95% and within an acceptable range of error $\alpha = 5\%$. These results demonstrate the applicability of the procedure for mercury(II) determination in seawater samples.

4. Conclusion

Thermals processing was found to be effective in synthesizing of Ag/NP particles at temperature of $900 \text{ }^\circ\text{C}$ with a ratio (Ag/NP) equal 20%. Electrochemical activity of Ag/NP samples was observed even with low content of silver, which also exhibited an excellent detection of mercury. Measurements of mercury in aqueous solution were carried out at (Ag/NP)-CPE under the optimal conditions. Analytical results show that, under the optimized working conditions, the proposed sensor was able to detect $5.8 \times 10^{-9} \text{ mol} \cdot \text{L}^{-1}$ of mercury with a good sensitivity.

The use of SWV, coupled to Ag/NP-CPE, is faster and sensitive with other conventional techniques (ICP-MS) in confidence interval of 95%. The applicability of (Ag/NP) in the preparation of modified carbon paste electrode showed to be an interesting alternative in the electroanalytical determination of mercury in the aquatic algae and the seawater.

Table 2

Statistical parameters obtained at Ag/NP-CPE for the determination of mercury(II) in seawater aquatic algae samples.

Parameters	Aquatic algae	Seawater
Calibration range	1.0×10^{-7} – 1.0×10^{-5}	$1.0 \times 10^{-7} \text{ mol} \cdot \text{L}^{-1}$ – 1.0×10^{-5}
Slope (A) $\text{mol}^{-1} \text{L}$	22.15	24.17
R ²	0.980	0.983
Detection of limit ($\text{mol} \cdot \text{L}^{-1}$)	1.28×10^{-8}	8.8×10^{-9}
Quantification of limit ($\text{mol} \cdot \text{L}^{-1}$)	4.28×10^{-8}	29.31×10^{-9}
RSD (%)	3.25	2.68
Recovery (SWV) (%)	96.5	98.5
Recovery (ICP) (%)	97.56	98.81

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