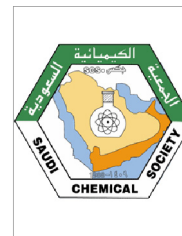




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ORIGINAL ARTICLE

Evaluation of a platinum electrode modified with hydroxyapatite in the lead(II) determination in a square wave voltammetric procedure

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Abstract The behavior of a modified carbon platinum electrode (Pt) for lead(II) determination by square wave voltammetry (SWV) was studied. The modified electrode is obtained by electrodeposition of hydroxyapatite (HAP) on the surface of a bare platinum electrode. The new electrode (HAP/Pt) revealed interesting electroanalytical detection of lead(II) based on the adsorption of this metal onto hydroxyapatite under open circuit conditions. After optimization of the experimental and voltammetric conditions, the best voltammetric responses-current intensity and voltammetric profile were obtained in $0.2 \text{ mol L}^{-1} \text{ KNO}_3$ with: 30 min accumulation time, 5 mV pulse amplitude and 1 mV s^{-1} scan rate. The observed detection (DL, 3σ) and quantification (DL, 10σ) limits in pure water were 2.01×10^{-8} and $6.7 \times 10^{-7} \text{ mol L}^{-1}$, respectively. The reproducibility of the proposed method was determined from five different measurements in a solution containing $2.2 \times 10^{-6} \text{ mol L}^{-1}$ lead(II) with a coefficients of variation of 2.08%.

The electrochemical of hydroxyapatite at platinum surfaces was characterized, after calcinations 900°C , by X-ray diffraction, infrared spectroscopy, chemical and electrochemical analysis.

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1. Introduction

The nondegradability of inorganic pollutants like heavy metals creates a hazard when they are discharged into a water body. Heavy metals are major contributors to the environmental pollution because of their involvement in many natural and industrial processes. The main sources of heavy metal pollution are mining, milling and surface fishing industries, which discharge a variety of toxic metals into the environment (Figueira et al., 2000). During recent decades, there has been a growing interest

in the development of analytical devices for the detection, quantification, and monitoring of these compounds (Dzyadevych et al., 2003; Zenki et al., 2005; Potedniok and Buhl, 2003; Harrington, 2000; Bonfil et al., 2000; Cankur et al., 2005; Demirci Cekic et al., 2004; Imran and Aboul-Enein, 2006). Flame atomic absorption spectroscopy (FAAS) is the most widely used technique for such determinations because of its simplicity and low initial and running cost. However, this technique suffers from the lack of sensitivity towards the ultra-trace metal concentrations usually encountered in environmental samples. Therefore, sample preconcentration is becoming an essential treatment step before flame atomic absorption determination. For this purpose, there are many methods which have been developed, including liquid–liquid extraction (Malvankar and Shinde, 1991; Shukla and Rao, 2002), coprecipitation (Santelli et al., 1989; Elçi et al., 1998; Kagaya et al., 2000), ion-exchange (Carrero and Tyson, 1997; Anezaki et al., 1998), chelating resins (Chang et al., 1992, 2001; Guo et al., 2004; Bao et al., 2002; Imran et al., 2008; Imran, 2009) and solid-phase extraction (Saracoğlu et al., 2002).

Electrochemical method is one of the most favorable techniques for the determination of heavy metal ions because of its low cost, high sensitivity, easy operation and the ability of analyzing element speciation.

Various materials have been used as working electrodes for detection of heavy metals, the most popular being mercury-based electrodes. The use of mercury electrodes for the determination of metal ions is due to their ability to form amalgams, allowing for preconcentration of the metal ions prior to their determination by voltammetric stripping methods. Another advantage of using mercury in working electrodes is associated with the high reproducibility and sensitivity (Economou and Fielden, 2003). The potential danger associated with mercury has led to the development of other strategies that avoid the use of a mercury solution.

Bismuth-film electrodes (BiFEs), consisting of a thin bismuth-film deposited on a suitable substrate, have been shown to offer comparable performance to mercury-film electrodes MFES in anodic stripping voltammetry ASV heavy metals determination (Wang et al., 2000). The remarkable stripping performance of BiFE can be due to the binary and multi-component “fusing” alloys formation of bismuth with metals such as lead and cadmium (Wang et al., 2001). Besides the attractive characteristics of BiFE, the low toxicity of bismuth makes it an alternative material to mercury in terms of trace-metal determination. However, the determination of copper using bismuth-film electrodes has been relatively ignored due to the similar stripping potentials of copper and bismuth with only a few reports in the open literature (Walcarius, 1999; Dias Filho et al., 2006).

Hydroxyapatite-modified electrodes have attracted considerable attention during the past few years (Zejli et al., 2006; El Mhammedi et al., 2007, 2009). Hydroxyapatite attracts considerable interests in many areas because of acid–base properties, ion-exchange ability, and adsorption capacity (Mori et al., 2002). The great variety of cationic and anionic substitutions is justified by the “open structure” of apatite.

In the work discussed in this paper, we investigate the electroanalytical detection of lead(II) at a formed HAP-layer-modified platinum electrode (HAP/Pt) in potassium nitrate. The HAP-modified platinum electrode was prepared with the electrochemical deposition of hydroxyapatite onto

platinum surfaces without using binders such as silane; the increase of binder inserted for the electrode preparation leads to the decrease of a sensibility of electrode. With this method, the film layer of HAP formed on the surfaces of platinum was more dense, uniform and not disintegrated or detached from the surface when immersed in the electrolytic solution. The deposit of hydroxyapatite powder at platinum surfaces was characterized by scanning microscopy, X-ray diffraction; Fourier transformed infrared spectroscopy (FTIR) and chemical analysis.

2. Experimental

2.1. Reagents

A 1.0×10^{-3} mol L⁻¹ stock solution of lead was prepared by dissolving Pb(NO₃)₂ (Aldrich 98%) in water, without any additional purification step. All the other reagents used were of analytical reagent grade. All of the solutions were prepared from doubly distilled water. Carbon paste was purchased from (Carbone, Lorraine, ref. 9900, France).

2.2. Apparatus

Electrochemical experiments were performed with a potentiostat (model PGSTAT 100, Eco Chemie B.V., The Netherlands), equipped with a three-electrode system mounted on cell. A Ag/AgCl/3 M KCl reference electrode was used as reference electrode, and a platinum plate was the auxiliary electrode. The working electrode was platinum modified with hydroxyapatite.

The pH-meter (Radiometer Copenhagen, PHM210, Tacussel, French) was used for adjusting pH values.

XRD measurements were performed using a Philips PW 1710 power X-ray diffractometer with a Cu K α X-ray source. The 2θ range was scanned from 10° to 70° with a step size of 0.02° s⁻¹ 2θ . The phases were identified through the Power Diffraction File (PDF) database (JCPDS, International Centre for Diffraction Data) *09-0432* for hydroxyapatite. Scanning electron microscopy (SEM) was carried out on a Jeol JSM-5500 scanning electron microscope. Infrared transmittance spectra were measured at room temperature in KBr disc using the FTIR spectra of crystals recorded on Perkin–Elmer Fourier transform spectrometer 1700 in the frequency range 400–4000 cm⁻¹. In order to evaluate the Ca/P ratio of the powder, an inductively coupled plasma-atomic emission spectrometry (ICP-AES) analysis was performed.

2.3. Preparation of hydroxyapatite

A solution containing appropriate amounts of ammonium hydrogen phosphate (NH₄)₂HPO₄ was prepared and boiled. A second solution with correct amounts of Ca(NO₃)₂·4H₂O was added into this boiling solution with a roughly constant pouring speed. After the addition of the second solution, a concentrated ammonia solution was added occasionally so that pH was maintained at around 10. After the aging process the precipitate was filtered and washed thoroughly with BDW. The precipitate was maintained in contact with the reaction solution for 5 h at 90 °C under stirring, and repeatedly washed

with distilled water. The precipitate was then removed and dried overnight in an oven at 100 °C. Once the drying was finished, the precipitate powder was calcined at 900 °C for 3 h.

2.4. Electrode preparation

The cathode electrode was a platinum plate, with a dimension of $0.5 \times 0.5 \times 0.1 \text{ cm}^3$, abraded with SiC paper in successive grades from 400, 600 to 1200 grit (Leco Corporation, MI) and then ultrasonically cleaned in bi-distilled water and dried. The final polishing of the sample was performed with a cotton polishing cloth with 1 μm alumina suspension. The anode electrode was a platinum wire. The current was maintained by a galvanostat with a function generator. Then, the electrodes were immersed in electrolyte of hydroxyapatite gel contained glass chamber, and subjected to anodic oxidation by applying 14.5 V for 24 h. The separation distance between electrodes was 2 cm. Deposit powder was dried at 120 °C for 48 h and characterized by X-ray diffractometry (XRD), Fourier transform infrared spectroscopy and chemical analysis were performed to qualitatively identify the composition of the film.

2.5. Working procedure

For the accumulation step, the HAP-modified platinum electrode was first immersed in a preconcentration solution containing the target analyte at a given concentration and selected pH. The HAP/Pt electrode was then removed from the preconcentration cell, briefly rinsed with water and placed in the electrochemical cell containing only a supporting electrolyte (0.2 mol L⁻¹ KNO₃). Finally, cyclic and square wave voltammetric experiments were performed.

On the other hand, the electrodeposited powder was characterized at carbon paste electrode (CPE) in 1.0 mol L⁻¹ HClO₄ by cyclic voltammetry. The carbon paste was prepared by hand mixing graphite powder and ceramic film, in a weight ratio 1:1. The mixture was then compacted carefully in the electrode cavity.

Impedance measurements were obtained with the same three electrode-cell setup described before. The complete frequency spectrum from 100 kHz to 10 MHz can be measured with AC amplitude of 5–10 mV. In order to insure the inert effect of HAP electrode during the experiment, the potential of 0 mV was chosen in presence or in absence of accumulated lead(II).

For cyclic voltammetry the potential range was from -0.8 to -0.3 V versus Ag/AgCl/3 M KCl and scan rate was 50 mV s⁻¹. The parameters square wave voltammetry measurements were: a step potential of 25 mV; amplitude 5 mV and duration 5 s at scan rate 1 mV s⁻¹. All measurements were carried out at room temperature.

3. Results

3.1. Hydroxyapatite synthesis

The powder X-ray diffractogram of curve was consistent with the characteristic reflections of HAP phase (JCPDS 09-0432). It is indexed on the basis of the hexagonal system (space group $P6_3/m$). The crystallographic lattice parameters calculated using the AF-part program were $a = 9426 \text{ \AA}$, $c = 6887 \text{ \AA}$

and $V = 52,917 \text{ \AA}^3$. All the spectra in FT-IR spectrum shows absorption bands of PO_4^{3-} at 1092, 1039, 960, 602 and 566 cm⁻¹ and that of OH^- groups at 3571–3572 and at 631–632 cm⁻¹. The portion of calcium and phosphorus of the synthesized hydroxyapatite were: Ca (35.115%), P (16.171%).

3.2. Electrode synthesis

In order to evaluate the nature of HAP layer formed on the surface of platinum, the morphology of the coating was analyzed by SEM. The surface morphology of the electrodeposited HAP coating is shown in Fig. 1. In this figure, it can be observed that HAP particles covered the platinum plate. It was observed that the HAP film exhibited a porous microstructure with micropores, which were relatively well separated and homogeneously distributed over the surface. The microporous surface of HAP/Pt is beneficial to fix lead from preconcentration solution.

3.3. Phase components of HAP coatings

The ICP-AES analysis of apatite layer gives a Ca/P molar ratio of 1.67. FT-IR spectrum show two strong absorption bands at 3575.7 and 645 cm⁻¹, assigned to the stretching mode and bending mode of the OH^- group in the HAP structure (Mousavi et al., 2001). The phosphate modes at 475, 574, 609, 966 and 1020–1120 cm⁻¹ were also observed. The X-ray diffractograms present fine and intense lines indexed in the hexagonal system with space group $P6_3/m$ specific to the hydroxyapatite. These phases are well crystallized and do not contain any impurity.

3.4. Cyclic voltammetry

Fig. 2 shows the uptake of lead(II) by the HAP-modified platinum electrode (HAP/Pt) after open-circuit accumulation of $3 \times 10^{-4} \text{ mol L}^{-1} \text{ Pb}(\text{NO}_3)_2$ for 10 min at pH 5.6. The voltammograms were obtained in 0.2 mol L⁻¹ solution by using cyclic voltammetry (CV) at an effective scan rate of 70 mV s⁻¹. A well-defined oxidation peak is observed at -0.5 V attributed to oxidation of metallic lead. The Blanc curve, which shows no peak, was obtained at HAP/Pt before any contact with lead. The result shows that lead(II) was chemically fixed into/onto modifier.

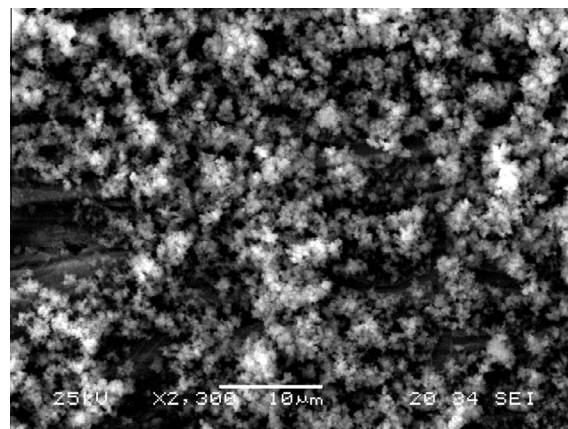


Figure 1 Scanning electron micrograph of apatite/platinum.

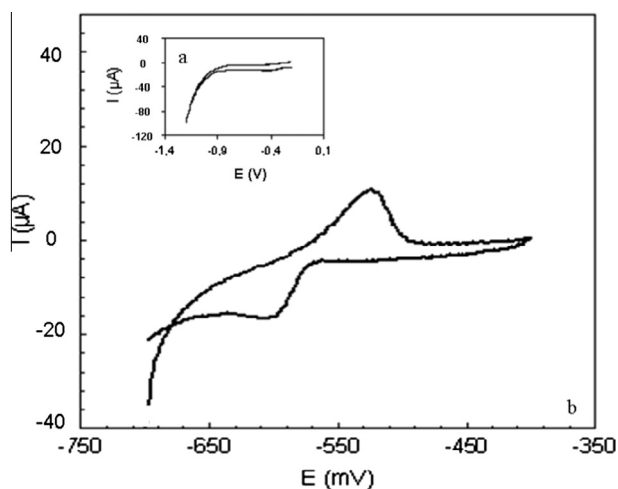


Figure 2 Cyclic voltammogram of: (a) HAP/Pt electrode before any contact with lead. (b) HAP/Pt electrode after incubation with lead(II) species during 30 min; supporting electrolyte is $0.2 \text{ mol L}^{-1} \text{ KNO}_3$, pH 5.6; the scan rate was 100 mV s^{-1} . $[\text{Pb(II)}] = 3 \times 10^{-4} \text{ mol L}^{-1}$.

3.5. EIS measurements

Fig. 3 shows the Nyquist plots for the electrochemical impedance spectroscopy (EIS) of HAP/Pt before and after a preconcentration step in lead(II) solution. The Nyquist plots are constituted of two regions: a depressed semicircle at high frequencies associated with charge transfer at the HAP/Pt-solution interface and a second region consisting of a straight line at 45° indicating a diffusionally-controlled process at the electrode. The calculated charge-transfer resistance (R_{ct}) and the double layer capacitance (C_{dl}) were $30 \text{ k}\Omega \text{ cm}^2$ and 212.1 pF/cm^2 for the starting electrode and $21.66 \text{ k}\Omega \text{ cm}^2$ and 261.4 pF/cm^2 for the lead exposed electrode, respectively, corresponding to the increased ionic contents.

3.6. Coatings analysis

The cyclic voltammograms of hydroxyapatite coatings before and after preconcentration in $2.2 \times 10^{-6} \text{ mol L}^{-1}$ lead(II) are

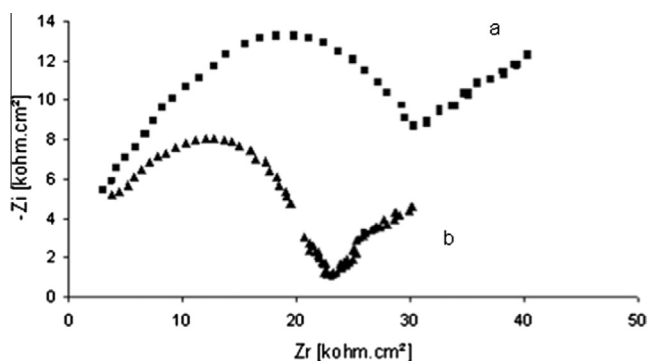


Figure 3 Impedance spectra at 0 V (a) HAP-modified platinum electrode and (b) Pb(II)-HAP/Pt. Conditions are as described in Fig. 2.

enregistered at carbon paste electrode (CPE). As shown in Fig. 4, a pair of stable and well-defined redox peaks was observed for HAP/Pb(II). The anodic and cathodic peak currents were proportional to the scan rate in the range of $10\text{--}200 \text{ mV s}^{-1}$, demonstrating a reversible redox process and a surface-controlled process. This result confirms the presence of lead(II) into or/and onto apatite coating platinum electrode after preconcentration in lead solution. Our results suggest that the uptake of aqueous Pb(II) was associated with the surface complexation and/or hydroxyapatite dissolution and lead(II)-apatite precipitation.

3.7. Optimization of peak height

The aims of this optimization were to maximize the peak height. In this context we studied the effects of factors including pH and time of accumulation on the lead ion peak currents.

The dependence of the peak current on the accumulation time was investigated in $2.2 \times 10^{-6} \text{ mol L}^{-1}$ lead(II) solution. The peak current increases as the preconcentration time increases and starts a level of around 30 min. It can be expected that at a lower concentration of lead(II) it would take a longer accumulation time for the peak current to level off. Thus, to ensure sensitivity, a preconcentration time of 30 min was employed for the following low concentration investigation.

The pH effect on the square wave voltammograms peak current of HAP-modified platinum electrode was investigated in $2.2 \times 10^{-6} \text{ mol L}^{-1}$ lead(II) solution. The anodic peak current is strongly dependent to the pH solution. An optimum pH exists in pH 4.1–5.6, where a maximum peak current could be obtained. At higher pH, the low response of the electrode can be ascribed to the hydrolysis of lead(II), since it is not likely for the neutral lead(II)-hydroxide or the negatively charged lead(II)-hydroxide complexes to be taken up by the HAP coatings. At lower pH, the low response of the electrode can be ascribed to the competition of H^+ for the ion-exchange and the binding sites of $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$. On the other hand,

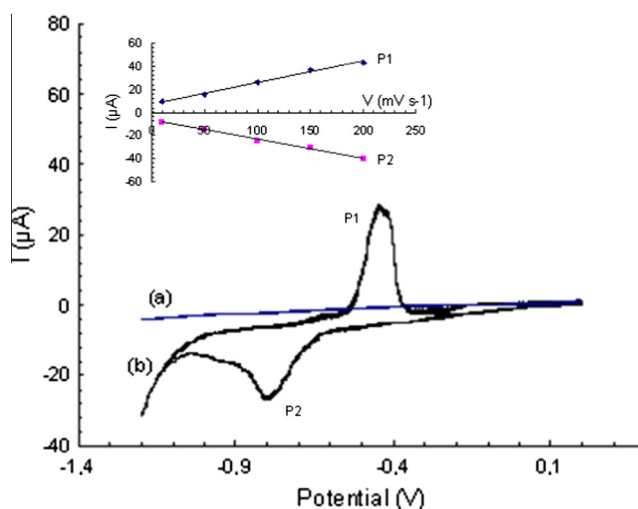


Figure 4 Cyclic voltammogram in HClO_4 (0.1 M) for HAP layer, at carbon paste electrode (CPE). (a) Before preconcentration step. (b) After preconcentration in $3 \times 10^{-4} \text{ mol L}^{-1}$ Pb(II), pH 5.6. $V_b = 100 \text{ mV s}^{-1}$, between 0.2 and -1.2 V .

the latter can slowly dissolve in acidic solution and lose its ability of immobilizing lead(II) ions. As reported by Chen et al. (1997), the formation of new solid phases via interaction of dissolved hydroxyapatite with aqueous Pb is dependent on the solution pH. When the pH value was acidic, protonation of surface complexes increases the positively-charged CaOH_2 and neutral POH^0 sites (Wu et al., 1991). As a result, the surface of the HAP is positively net charged. Increased net positive charge is less favorable in complexing Pb^{2+} on the HAP surface than the net negative charge that becomes dominant at higher pH.

3.8. Calibration data of HAP/Pt

Electrochemical detection of lead(II) was performed using SWV because of the excellent sensitivity of this technique. Using the optimized parameters, calibration curves were obtained for lead(II) in an electrolyte prepared with pure water. For this, aliquots from the stock lead(II) solution were consecutively added to the electrochemical cell. The SWV responses were recorded for a range of concentration from 2.0×10^{-7} to $1.1 \times 10^{-5} \text{ mol L}^{-1}$ in $0.20 \text{ mol L}^{-1} \text{ KNO}_3$. The SWV for different concentrations of Pb(II) were illustrated in Fig. 5. The resulting calibration plot is linear. The calibration curves and correlation coefficients are $y = 0.58 + 0.036x$, $r^2 = 0.991$. The value of standard deviation calculated has been used for the determination of the detection limit (DL) and quantification limit (QL). The limits of detection (DL, 3σ) and quantification (QL, 10σ) were 2.01×10^{-8} and $6.7 \times 10^{-7} \text{ mol L}^{-1}$, respectively.

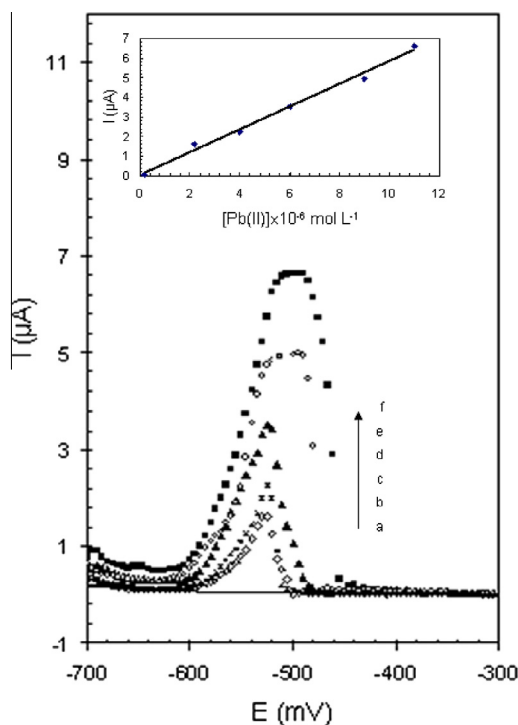


Figure 5 Square-wave voltammograms in $0.2 \text{ mol L}^{-1} \text{ KNO}_3$, pH 5.0, $t_p = 30 \text{ min}$, at HAP/Pt of lead(II); (a) 0.2×10^{-6} , (b) 2.2×10^{-6} , (c) 4×10^{-6} , (d) 6×10^{-6} , (e) 9×10^{-6} , (f) $11 \times 10^{-6} \text{ mol L}^{-1}$.

The DL and QL values obtained by the proposed procedure are similar to those previously obtained with chromatographic techniques (Laschi et al., 2006; Purves, 1985) indicating that the method could be employed to analyze lead(II) in natural water samples, where the recommended maximum residue stipulated is $25 \mu\text{g/kg}$ (Fowler, 1974).

The reproducibility of the proposed method was determined from five different measurements in a solution containing $2.2 \times 10^{-6} \text{ mol L}^{-1}$ lead(II) and realized on different days, with coefficients of variation of 2.08% being obtained. The repeatability of this method was also determined from measurements performed for seven different solutions of the same composition as stated above, and coefficients of variation of 2.11% were obtained.

3.9. Study of interferences

The selectivity of the chemically modified platinum electrode was evaluated by intentionally introducing concentrations of other metal ions as interferences into Pb(II) solutions during preconcentration. These ions were chosen because they might reasonably be expected to exhibit redox activity in roughly the same potential range as Pb(II)-HAP/Pt and exist in real samples.

The HAP-modified platinum electrode was immersed in a mixture of Cd(II), Cu(II), Ag(I), Pb(II) and Hg(II) ($6.3 \times 10^{-6} \text{ mol L}^{-1}$ each one). The voltammogram of Fig. 6 shows one oxidation signal attributed to lead in position -0.5 V . Under our conditions, no interference was observed. The clear separation of the potential peaks offers us the possibility of the determination of lead(II) without any harmful interference from other common heavy metals.

The sensitivity for Pb(II) is higher than that achieved for Cd(II). This can be explained by the capacity of adsorption of HAP that varies according to the scale of affinity decreasing: $\text{Pb} > \text{Cd}$. Because the cadmium(II) peak appears very close to the lead(II) peak and both peaks overlap when the two metals are present in the solution.

3.10. Analytical applications

Under the optimum conditions, the HAP-modified platinum electrode was applied to the determination of lead(II) in river water sample (Oum Er Rbia, Mechraâ Eddahk, Tadla-Azilal region, Morocco) without any pretreatment. It should be

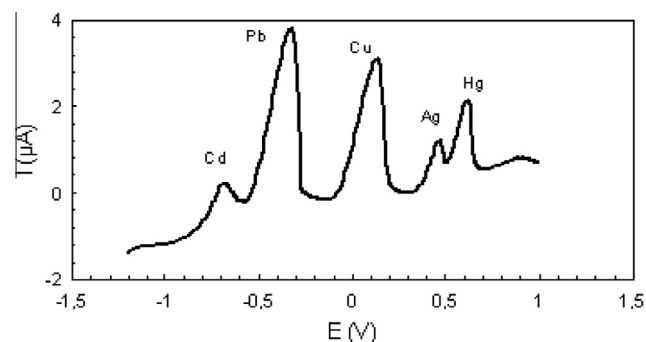


Figure 6 Cyclic voltammogram after exposure to a solution containing Cd(II), Ag(I), Cu(II), Hg(II), and Pb(II) of concentration $6.3 \times 10^{-6} \text{ mol L}^{-1}$.

Table 1 Physicochemical parameters of used natural water.

Parameters	MES	O ₂ (dissous)	NH ₄ ⁺	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	NO ₂ ⁻	NO ₃ ⁻	HCO ₃ ⁻	SO ₄ ²⁻	PO ₄ ³⁻	Azote total	DCO	DBO ₅
Values (mg L ⁻¹)	20.3	11.5	0.024	328.3	3.9	88.4	39.4	523.2	< 0.031	8.0	202.52	85.8	0.016	0.59	15.63	1.0

Table 2 Determination results in river water samples.

Sample	Pb(II) added ($\times 10^{-6}$ mol L ⁻¹)	Pb(II) found (HAP/Pt) ($\times 10^{-6}$ mol L ⁻¹)	Pb(II) found (ICP-MS) ($\times 10^{-6}$ mol L ⁻¹)	RSD (%)
River water	2.0	1.77	1.75	2.76

mentioned at this point that the reason for using the standard addition technique is to compensate the matrix effect from natural water samples that contain high concentrations of nitrate ions and other foreign ions (Table 1). The recovery and relative standard deviation studies were realized by adding an appropriate volume of lead(II) standard solution (2×10^{-6} mol L⁻¹) to electrochemical cell. The results obtained, in quadruplicates, were related to interference effects of the constituents of each sample. The comparative determination of lead(II) in river water sample by the proposed method and inductively coupled plasma-atomic emission spectrometric method is shown in Table 2. The mean percentage recoveries of added lead(II) were found to be 88.72% and 87.51% using the proposed method and ICP-MS, respectively. The excellent average recoveries of river water samples suggest that the HAP-modified platinum electrode developed in this work has practical significance and is able to determine Pb²⁺ in real water samples.

4. Conclusion

The above results clearly demonstrate the potential utility of the hydroxyapatite modified platinum electrode for square wave voltammetric determination of lead(II). The modification of the electrode increases the sensitivity significantly, compared with the unmodified platinum electrode. Additionally, the proposed procedure is fast, of high precision and accuracy and can be employed for quantification of lead(II) in natural water samples, where the results obtained showed a lower influence of the matrices on the procedure response. All the results obtained using the optimized experimental and voltammetric parameters confirmed the practicality and viability of the proposed procedure, providing an important tool for quantification of lead ions in natural water samples. The use of SWV is faster and more sensitive than other conventional techniques. Besides, the use of HAP/Pt enables direct analysis of water samples without preparation or cleaning of the sample.

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