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Electrochemical micro-extraction of lead (II) at a hydroxylapatite modified platinum electrode

Hanane Zejli [a,b,*], Khalid R. Temsamani [a], José Luis Hidalgo-Hidalgo de Cisneros [c], Ignacio Naranjo-Rodriguez [c], Patrick Sharrock [b]

[a] *Departement de Chimie, Faculte de Sciences de Tetouan, Université Abdelmalek Esaadi, Morocco*
[b] *Medical Bioinorganic Chemistry Laboratory, Paul Sabatier University, Toulouse, France*
[c] *Department of Analytical Chemistry, Faculty of Sciences, University of Cádiz, Apdo. 40, 11510 Puerto Real, Cadiz, Spain*

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Abstract

A simple approach for increasing the sensitivity and selectivity for the detection of lead (II) species in water is presented. The technique is based on two steps: (1) micro-extraction (uptake step) of lead (II) by simply incubating HAP modified platinum electrode, at open-circuit potential conditions, into a solution containing the heavy metal for 30 min; (2) the electrode is transferred from the analyte solution to an electrochemical cell (release step) for successive voltammetric determinations. Surprisingly, cyclic voltammetric measurements showed an anodic peak characteristic of oxidation of metallic lead to form lead (II) at -0.075 V. The reversed scan, showed a cathodic peak at -0.35 V, differential pulse measurements performed on the HAP electrode showed that the anodic peak exhibit a good linear concentration dependence in the range 7×10^{-7}–5.6×10^{-6} M. The detection limit was estimated to be 5×10^{-7} M. The analytical performances of the extraction method has been explored by studying the incubating time, and effect of interferences due to other ions. On the other hand, EDAX and Electrochemical Impedance Spectroscopy (EIS) measurements performed on HAP films confirmed the adsorption of the heavy metal on the polymeric film due to the extraction process.

Keywords: Modified electrode; Hydroxyapatite; Lead (II) determination

1. Introduction

Heavy metals present in agricultural, industrial or drinking water are a serious environmental problem. It is now well recognised that heavy metals cause many disorders in the plant and animal kingdoms, and tend to accumulate in the food chain. Public health concerns have led to the establishment of severe standards concerning the emissions of metal ions, but contaminated waters still exist, and the pollution may arise simply from the flow of water through old lead pipes. Simple, efficient and cost effective ways of removing heavy metal ions are of continuing interest [1–3]. For trace element concentrations, adsorption is the most common method used and research has focussed on natural adsorbents, either organic or mineral [4,5]. Hydroxylapatite (HAP) is a naturally occurring mineral mined for phosphoric acid production. It has been tested for remediation of soil pollution by heavy metals. We have produced synthetic apatites with controlled particle sizes and porosities. Here we present results showing this material can be used for water purification and for the analysis of heavy metal ions.

In natural or industrial waters containing significantly high concentration of natural/anthropogenic organic matter or inorganic colloids, the anodic stripping voltammetric

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[*] Corresponding author. Address: Medical Bioinorganic Chemistry Laboratory, Paul Sabatier University, Toulouse, France.
E-mail address: zejlih@yahoo.fr (H. Zejli).

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(ASV) analytical signals of trace metals at conventional mercury electrodes are often altered or even suppressed due to the adsorption of this surface active compounds onto the electrode [6,7]. Fouling of the electrode surface can occur also for electrodes other than mercury (id glassy carbon (GC) and graphite) in other complex media such as biological samples where proteins are usually present and thus they become a problem. The most promising procedure to minimize the electrode fouling by surfactants is to prevent the diffusion of the interfering species by coating the electrode surface with a thin layer of a semi-permeable material. The purpose is to preclude the income of the interfering species towards the electrode surface, for solve this problem it is necessary several different approaches: covering the electrode with ion exchange polymer [8] poly(ester sulfonic acid) [9] poly(ethyl 3-thiophenacetate) [10].

In this paper, we present news results on a very simple two step procedure for lead: detection and quantification based on an open-circuit potential preconcentration step at a HAP modified steal electrode followed by an electrochemical controlled release of lead in the blank solution. This method features fast experimentation time, good suitability for field trace lead analysis and long electrode lifetime. Analytical performances of the method and the HAP/Pb interaction were investigated using, cyclic voltammetry (CV), differential pulse voltammetry (DPV), Energy dispersive analysis of X-ray (EDAX) and electrochemical impedance spectroscopy (EIS). The effect of the incubating time and the effect of interferences from other ions are also discussed.

2. Experimental

$Cr(NO_3)_3$, $Cd(NO_3)_2$, $CuSO_4$, $ZnCl_2$, $FeCl_3$, $AgNO_3$, $Ni(NO_3)_2$, $Pb(NO_3)_2$, $Hg(NO_3)_2$ and $K_2Cr_2O_7$ were all purchased from Riedel de Haen (Germany). Supporting electrolyte KNO_3 was from Panreac (Barcelona, Spain). Alumina powder 0.5 μm was from Labosi (Paris, France). All other chemicals used were of reagent grade. All reagents were used directly without further purification. Solutions were prepared using deionized doubly distilled water with a measured resistance of less than 15 $\mu S\ cm^{-1}$. Prepure nitrogen (98%) category–R, used to purge electrochemical reaction media, was obtained from Air Liquid (Toulouse, France). Cyclic voltammetry (CV), Anodic stripping voltammetry (ASV) and Differential pulse voltammetry experiments were performed with an Autolab PGSTAT20 (Ecochemie, Utrecht, The Netherlands). A conventional three-electrode 20 ml cell was used. A platinum electrode (BAS MF2014, 1 cm diameter) was used as the working electrode and its surface was polished with 0.5 μm alumina powder then cleaned by ultrasonication prior to the polymer electropolymerization. A Pt electrode and a Hg/Hg_2Cl_2 (Urdorf, Switzerland) were used as counter and reference electrodes, respectively. Nitrogen was bubbled for 20 min in solutions where O_2 was not desired.

2.1. Hydroxylapatite modified electrode preparation

Hydroxylapatite was synthesized by an aqueous solution route involving mixing calcium nitrate and ammonium phosphate [11] followed by precipitation with potassium hydroxide. The white precipitate was collected and washed several times with water before oven drying. A first calcination step to 750 °C was carried out prior to grinding (ball mill) and sieving. A second calcination at 1000 °C yielded sintered particles which were used in this work. Glycidoxypropyltrimethoxysilane and [3-(2-aminoethylamino)propyl]trimethoxysilane were mixed in equimolar ratios and diluted by 2 in 75% ethanol to make a sol–gel paste to bind Hydroxylapatite particles. The paste was spread on Platinum electrode for electrochemical studies. A special silane-hydroxylapatite suspension was prepared by mixing the fine HAP powder with the silane solution with a solid/liquid ratio of 1.5. Deposits were air dried during 4 h then oven dried at 50 °C for 72 h. An Autolab PGSTAT20 (Ecochemie, Utrecht, The Netherlands) apparatus was used for cyclic voltammetry and differential pulsed voltammetry (DPV).

2.2. Differential pulsed voltammetry experiments

Preconcentration of lead species in the HAP film under open circuit potential was usually performed by dipping carefully the HAP film electrode into the lead nitrate solution for 30 min. The obtained film was rinsed thoroughly with deionized water and electrochemical determination of the lead content was carried out in a lead-free fresh supporting electrolyte. Usually Voltammetric measurements were conducted at a scan rate of 100 mV/s, equilibration time of 0 s, deposition time of 0 s, modulation time of 0.06 s, initial potential of −0.5 V, and end potential of 0.2 V. The electrode was regenerated (to reach a free lead film) by continuous cycling between −1 and 1 V in lead free solution until a stable background was obtained.

2.3. EIS measurements

The EIS measurements were performed with a Voltalab® 10 type PGZ 100 from Radiometer. The impedance spectra were recorded using the same three electrode-cell setup described before. The initial frequency used was 100 kHz and the final one was 10 mHz with an 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 adsorbed lead. EIS spectra have also been recorded at other interesting potentials. All other conditions were as described in the Voltammetric part.

2.4. EDAX measurements

Energy dispersive analysis of X-ray measurements were performed at the University of Toulouse (France). The microscope, a JEOL, JSM 5400 type was coupled to the analyzer, a LINK type with a Si/Li detector and a ultra thin window. The HAP film was first washed then dried, and peeled off. The film was then introduced into the EDAX instrument under high vacuum.

3. Results and discussion

The voltammetric behavior of lead (II) has been followed after open-circuit preconcentration of a 6×10^{-5} M $Pb(NO_3)_2$ solution at a HAP modified platinum electrode for 30 min. The electrode was then subject to cyclic voltammetric measurements in a 0.2 M KNO_3 supporting electrolyte solution (the blank) at pH 5. The first cyclic voltammogram, Fig. 1b, shows a large anodic peak at −0.0753 V attributed to oxidation of metallic lead ($Pb \rightarrow Pb^{2+} + 2^{e}-$). The anodic peak current intensity was lead concentration dependant. A small cathodic peak was observed at −0.35 V. Fig. 1a shows the background voltammetric response of HAP film electrode in pure supporting electrolyte. Since no potential was applied during the preconcentration step, a chemical incorporation of lead (II) into the film is one logical explanation of this result.

3.1. Effect of preconcentration time

The time needed for the preconcentration of lead (II) in order to reach the optimal electrochemical results, has been simply determined by DPV measurements. A HAP modified electrode has been dipped in a 2.1×10^{-6} M solution of lead (II). Every 5 min the electrode was removed and transported to the measurement cell. Table 1 shows a rapid increase in the current in function of incubation time during the first 30 min. After this point, no significant variation in peak intensity was noticed. This result indicates that lead (II) can preconcentrate rapidly on the HAP film until a saturation of the host sites on HAP is reached. An incubation time of 30 min has been chosen then for optimal conditions.

Table 1
Kinetic studies of adsorption of lead (II) on HAP C (Pb^{2+}) = 2.1×10^{-6} M

Incubating time	I (A)
0	0
3	4.37×10^{-8}
5	8.75×10^{-8}
10	2.18×10^{-7}
15	3.75×10^{-7}
20	4.75×10^{-7}
25	5.31×10^{-7}
30	5.32×10^{-7}
35	5.32×10^{-7}

3.2. DPV measurements

In this experiment, the electrode was immersed at open-circuit into a solution of lead (II) during 30 min then rinsed with deionized water then put into an electrochemical cell which contains 0.2 M of KNO_3. The DPV mode was immediately applied.

The voltammogram (Fig. 2) clearly shows improved electrochemical kinetics and sharper oxidation peaks which are increasing with Pb(II) concentration from 7×10^{-7} to 5.6×10^{-6} M. The HAP electrode here could maintain its activity as a sensor for lead (II) during one month.

The calibration curve shows a linear response of the sensor toward lead (II) with the following characteristics: $R^2 = 0.9999$; slope = 0.2726 A L/mol and a limit of detection of 5×10^{-7} M.

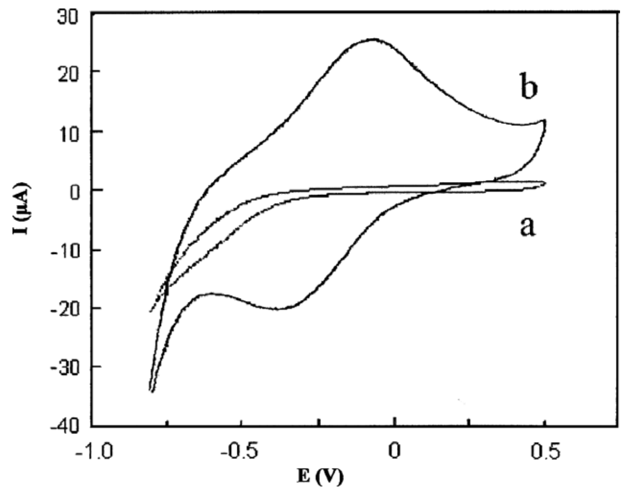

Fig. 1. Cyclic voltammogram of: (a) the response of the HAP electrode before any contact with lead. (b) HAP film electrode after incubation with lead (II) species during 30 min; supporting electrolyte is KNO_3 0.2 M, pH 5; the scan rate was 100 mV/s. C(Pb^{2+}) = 6×10^{-5} M.

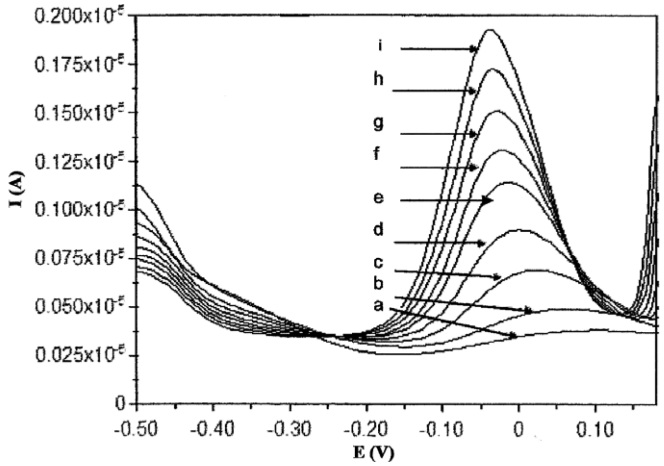

Fig. 2. DPV response of the HAP electrode incorporated with lead (II) after open circuit preconcentration during 30 min, the concentration of the lead solution varies as follow: (a) supporting electrolyte; (b) 7×10^{-7} M; (c) 1.4×10^{-6} M; (d) 2.1×10^{-6} M; (e) 2.8×10^{-6} M; (f) 3.5×10^{-6} M; (g) 4.2×10^{-6} M; (h) 4.9 10^{-6} M and (i) 5.6 10^{-6} M. Supporting electrolyte KNO_3 (0.2 M), pH 5.

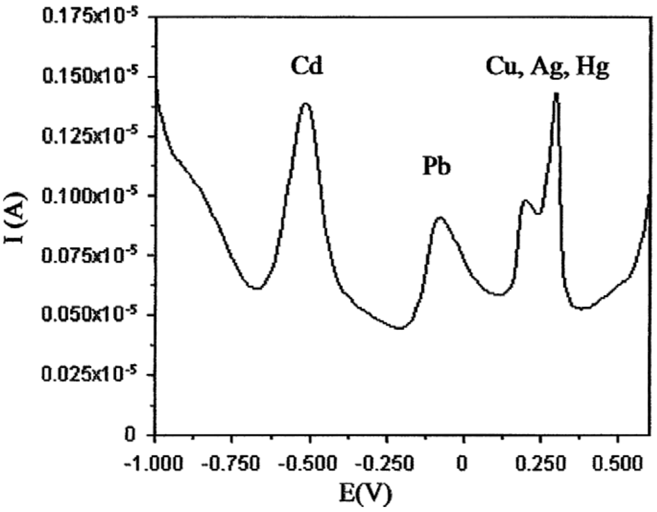

Fig. 3. Cyclic voltammogram after exposure to a solution containing Cd^{2+}, Ag^{+}, Fe^{3+},Cu^{2+}, Hg^{2+},Cr$_2$O$_7^{2-}$ and Cr^{3,} Pb^{2+} of concentration 2.1×10^{-6} M.

For seven measurements ($n = 7$) a relative standard deviation of 1.4% was obtained for a concentration of 2.1×10^{-6} M.

4. Study of interferences

Several common metal ions were subjected to DPV under the optimal conditions previously described. All the cations were submitted to the same open-circuit preconcentration procedure described above. The HAP modified platinum electrode was immersed in a mixture of Cr (III), Cd (II), Cu (II), Zn (II), Fe (III), Ag (I), Ni(II), Pb(II) and Hg (II) (2.1×10^{-6} M each one). The voltammogram of Fig. 3 shows one oxidation signal attributed to lead in position 0.04 V (as compared to pure lead (II) experiment) and another peak attributed to Cd (II), no interfering under our conditions. And other significant signal was observed at 0.19 V. This result, demonstrates that in spite of other metal interaction with the HAP film, its oxidation potential is far from that of lead (II). As a result of this, the lead toxic metal can be determined in water without any harmful interference from other common metal ions.

5. EDAX measurements

To verify and confirm the lead presence in our polymer films, EDAX measurements were performed on both the lead-free and lead-containing HAP films. Fig. 4a. shows the EDAX spectrum of the HAP film synthesized in 0.2 M KNO$_3$, pH 5. As can be seen, no lead is detected in the film under the equipment sensitivity range. As expected, we can notice in the EDAX spectra a significant amount of Calcium coming from the HAP. On the other hand, Fig. 4b clearly shows lead content in the spectra of the films HAP previously put in contact with lead (II). It seems that lead peak is probably due to the strong interaction between HAP and lead.

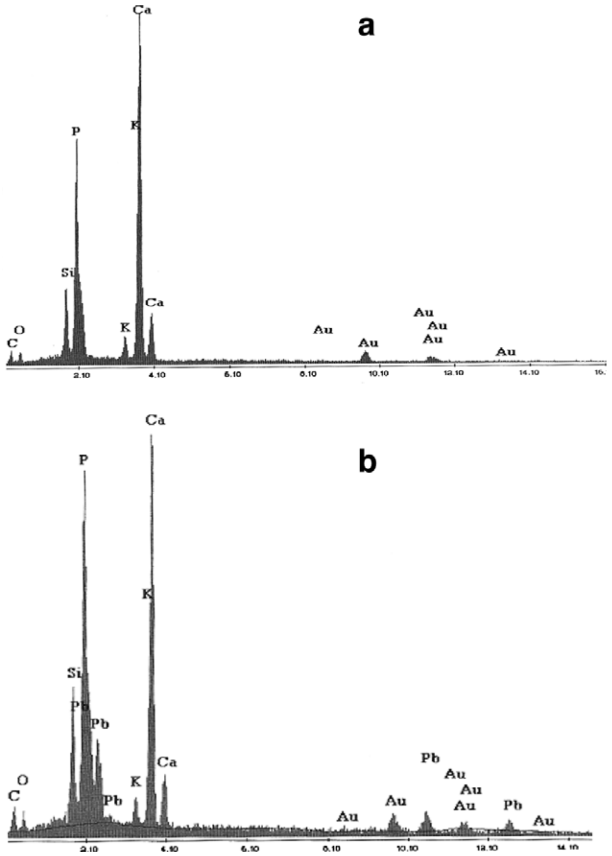

Fig. 4. EDAX spectra of (a) HAP film and (b) HAP film after being in contact with lead. Conditions are as described in Fig. 1.

5.1. EIS measurements

In order to confirm the mechanisms suggested in the voltammetric part of this work regarding the HAP/Pb(II)

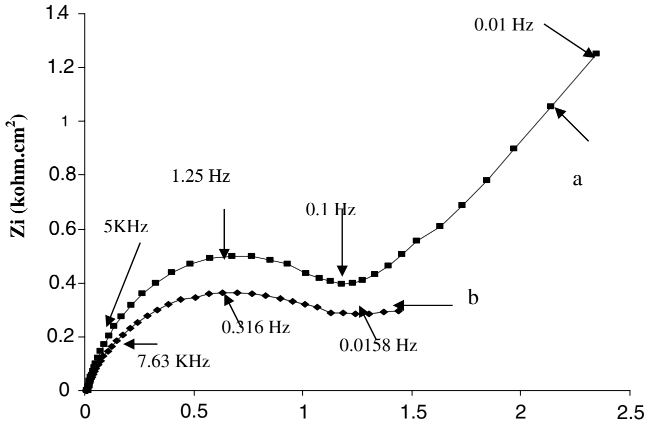

Fig. 5. Impedance spectra at 0 V (vs. SCE) (a) HAP modified platinum electrode and (b) HAP/Pb (II). Conditions are as described in Fig. 1.

interaction, we have performed some EIS measurements. The impedance spectra in Fig. 5 were collected at 1000 mV (vs. SCE) in a frequency range from 100 kHz to 10 mHZ with an AC amplitude of 5 mV. The potential of 0 V was chosen in order to insure the stability of the HAP/Pb (II) films during the measurements. Fig. 5a. shows the Nyquist plot for the HAP-modified electrode. The high frequency arc observed may be associated to charge transfer at the HAP /solution interface. If we admit the Randles equivalent circuit model, the calculated (Voltamaster® 4.0 software) charge transfer resistance R_{ct} and the double layer capacitance C_d are respectively: 1.385 kΩ cm^2 and 175.2 μF/cm^2. These data are typical of metal electrodes covered with polymeric films.

On the other hand, Fig. 5b also exhibits a arc like Nyquist plot for the HAP/Pb (II) system. The electrical parameters calculated were: $R_{ct} = 1.2$ kΩ cm^2 and $C_d = 725.7$ μF/cm^2. It appears clearly from these data that the capacitance at the interface increases when the HAP film is exposed to Pb(II). This observation is in agreement with Ref. [12] in the case of adsorption phenomenons at the electrode surface. Our result, give another evidence for Pb(II) adsorption on the HAP film. The observed decrease of the charge transfer resistance means also that the modified electrode becomes more conductive which can be explained by the presence of lead on the electrode surface.

6. Conclusion

In this work, we have prepared a new modified platinum electrode based on the incorporation of HAP for the detection of Pb(II) in aqueous solution. This method is very simple and offers a relative short analysis time, it is inexpensive and presents easy operability. It could be applicable for field use, the good sensitivity and the detection limit of 5×10^{-7} M makes it a promising tool for heavy metals detection in future.

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