

Chelating and Construction Effects on a Self-Assembled Blend for Electrochemical Lead (II) Detection

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This work presents a study of self-assembled platforms of polyelectrolytes constructed by drop casting on screen-printed electrodes for lead (II) sensing. Infrared characterization by attenuated total reflection (ATR) and electrochemical impedance spectroscopy (EIS) were carried out to evaluate the modification of the surface, its stability against treatment and the changes induced by the adsorption of lead cations. An equivalent circuit of the type R1 [R2 CPE1] CPE2 that explained

the results for the actual surface modification was obtained. Linear correlations with lead concentration in the range of 0.5–2.5 mM were found by differential pulse voltammetry (DPV) and EIS techniques for solutions at pH 3. There was a particular concentration in which the presence of citrate increased the DPV reduction signal of lead while ethylenediaminetetraacetic acid (EDTA) diminished it.

Introduction

Industries such as mining, metal coating (electroplating) and electronics, among others, generate a wide range of waste products, including heavy metal ions. They can affect natural environments and lead to serious human health effects.^[1] Therefore, it is necessary to obtain information of the concentration of heavy metal ions in several natural matrices and especially industrial aqueous solutions to improve the processes to reduce environmental impact. Furthermore, because of their economic value, the development of interfaces that can retain heavy metal ions for their reincorporation into the production process, as well as to prevent them from reaching natural environments, is of great importance.

New sensitive surfaces also play an important role in the development of sensors. Regarding the quantification of the heavy metal ions in industrial effluents, the challenging point is the development of an interface that can work despite the complexity of these aqueous matrices. In this kind of samples, the speciation of the analyte and its affinity to form coordination compounds determine the success of the design. A wide variety of organic compounds often used as additives, as well as humic and fulvic compounds,^[2,3] tend to act as chelating agents in industrial and natural samples. Consequently, it is relevant to assess their impact on sensor performance. In this sense, the different physicochemical properties of the samples like temperature, pH, ionic strength, additives concentration and a variety of pollutants that form stable coordination complexes in solution, make heavy metals analysis and recovery

a very difficult task.^[4] Among the industrial recycling processes involved in the recovery of heavy metals, the most important ones are the recycling of electronic waste and lead batteries. More than 99% of lead-acid batteries in Europe are collected and treated to reinsert lead into the production circuit avoiding its impact on the environment and health.^[1,5,6]

Lead (II) is a well-known pollutant that has been associated with health problems such as cancer, skin lesions, cardiovascular disease, and neurological disorders.^[7] Young children are particularly vulnerable to the toxic effects of lead, and can suffer permanent adverse health effects, especially affecting the development of the brain and nervous system.^[8] In fact, the maximum allowable content of lead (II) in water drinking recommended by EPA and WHO are 15 ppb and 10 ppb, respectively.^[9,10] This fact makes the determination of lead an interesting model system and has been the subject of numerous investigations within the quantification of heavy metals.^[11–18]

Frequently used techniques for heavy metal ions detection are inductively coupled plasma mass spectrometry and absorption spectrometry.^[4,19] De Almeida Pereira et al.^[14] determined aluminum, cadmium, chromium and lead in drinking water by atomic absorption spectrometry with a particular addition of a permanent modifier for each analyte. He et al.^[16] quantified organic and inorganic mercury species analysis using inductively coupled mass spectrometry in farmland water, soil and rice. They used complex pretreatments of the sample such as micro extraction and high performance liquid chromatography that were absolutely important for the success of the determination.^[16] These methods generally provide high selectivity and sensitivity, however, they involve expensive equipment and usually result impractical to be performed in the field or routine industrial processes.^[20] Their complicated operation, the requirement of highly qualified personnel and the sample processing time also limit the number of measurements.^[20] Electrochemistry provides several alternative detection methods that have been incorporated in sensors for heavy metal analysis.^[20] Its advantages include being non-expensive, highly

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sensitive, easy to use, portable, and applicable for field monitoring of environmental samples.^[20]

For the development of electrochemical methods in different conditions, it is particularly important the construction of working electrodes with novel properties. Many combinations of materials have been used to modify surfaces to improve the analytical performance. Graphene/graphite, biofilms, metallic nanoparticles (NPs), organic films and polyelectrolytes are the most typical materials used for electrochemical sensors for heavy metals ions.^[21,22] Raril et al.^[15] developed an electrochemical sensor modified with polyglycine and graphene for lead sensing in groundwater and blood. They performed cyclic voltammetry in 0.1 M phosphate buffer solution (pH 4.5) and they did not incubate in solution with the metal cation but measured directly. Baghayeri et al.^[13] described a glutathione coated magnetic nanoparticles sensor for lead and cadmium detection using anodic stripping voltammetry. Chen et al.^[11] described a polyamide-modified sensor for lead detection in blood samples through a multiple complex step modification including nanoparticles synthesis. In our case, compared to Raril et al.,^[15] the volume of the sample needed was much smaller since the electrodes are incubated with only 5 μL of solution. In this way, the measurement takes place in a Pb^{2+} -free solution, so that the signal obtained by DPV is unaffected by potential interferences present in the sample solution. In contrast to Baghayeri et al.,^[13] in this work an anodic current was unnecessary in the preconcentration stage, but rather preconcentration was performed at open circuit potential. In addition, the proposed modification in this work is simpler than the modified NPs proposed by them. Finally, considering an industrial application, in our work, we have chosen screen-printed electrodes (SPE) considering its ease for handling larger number of samples and suitable for chemical functionalization.

Polymeric materials are very attractive for electrode modification due to their low cost, their ability to stick to other materials, their conductivity, electrical and adsorption properties. Additionally, the blend of two polymers allows the adaptability of the sensing film with the proper selection of substituents of the main chain.^[17,23,24] Constructions with polymers are commonly based on ion imprinting, layer-by-layer assemblies, self-assembled systems or drop casting techniques on the electrode surface. In this sense, accordingly to the group experience, screen printed sensors are easy to modify, user-friendly, and disposable. The easy adaptation of the design to use lower sample volumes makes these sensors a suitable choice for sensing purposes.^[25]

Electrodes used in this work were specially designed by our research group. In our experience, drop casting is a simple technique to apply on these electrodes and is easily scalable.^[26,27] The interaction of the modified surface of the electrode with the analyte generates a signal that can be obtained by means of some electrochemical technique. Stripping voltammetry is the commonly used technique for metal ions analysis.^[12,18,28] It involves an anodic pre-concentration step that forces the cations to concentrate in the electrode regardless of the functional groups present. In contrast, incubation of the electrodes at open circuit potential improves

the electrode sensitivity because of the modified surface can provide adsorption sites for heavy metal ions. The latter strategy was the one preferred for the design of our assembly.

In this work it is presented a study of polyelectrolyte assemblies constructed by drop casting on screen-printed electrodes for lead (II) sensing. It is focused on the effect of anthropogenic chelating agents usually present in natural and industrial samples like citrate, EDTA and ethylenediamine (EN). Preliminary studies with self-assembled monolayers of mercaptopropionic sulfonate reveal the affinity of lead (II) for sulfonate groups (data not presented) in agreement with other authors.^[12] Therefore, to create a thin film with sulfonate groups, we chose polystyrene sulfonate (PSS). Furthermore, to obtain a better adhesion and improve electrical conductivity of the film on gold, we chose poly (allylamine) hydrochloride (PAH) to combine with PSS. The polymer PAH is a positive polyelectrolyte at acidic conditions with which the group has experience. Carbon electrodes with gold electrodeposited were employed due to the adhesion properties of the polymeric blend used. The influence on cation adsorption, the electrochemical signal obtained by metal ion reduction in DPV and the effect of complexing agents were evaluated. Infrared characterization by ATR was carried out to evaluate the modification of the surface, its stability against treatment and the changes induced by the adsorption of lead cations. Additionally, EIS measurements were performed to further characterize the system.

Results and Discussion

Construction conditions

Different construction conditions were evaluated to optimize the electrode behavior. Concentration of electrolyte solutions, number of successive deposits, thermal and washing treatments were varied causing different amounts of functional groups present on the surface, as verified by IR spectroscopy. Preliminary results (data not shown) for ratios of polymer mixtures between (0.25:0.75 to 0.75:0.25) and incubation times between 15 min and 1 hour show the best construction conditions. The maximum cathodic current after the incubation in lead (II) was obtained performing three successive deposits of polyelectrolytes in a 1:1 ratio, 30 minutes incubation in the lead solution. Neither thermal nor washing treatment was employed. The thickness of each deposition step was around 1.7 μm determined by profilometry.

Affinity to lead (II)

The affinity of the functionalized surfaces to lead (II) ions was evaluated by DPV (see experimental section). Working electrodes were incubated in 5 μL of lead solutions, washed with ethanol and voltammetry in 0.1 M potassium chloride was performed. Figure 1 shows the results obtained for 1:1 polyelectrolyte mixture incubated at different lead ion concentrations. Each experiment was performed on an independent

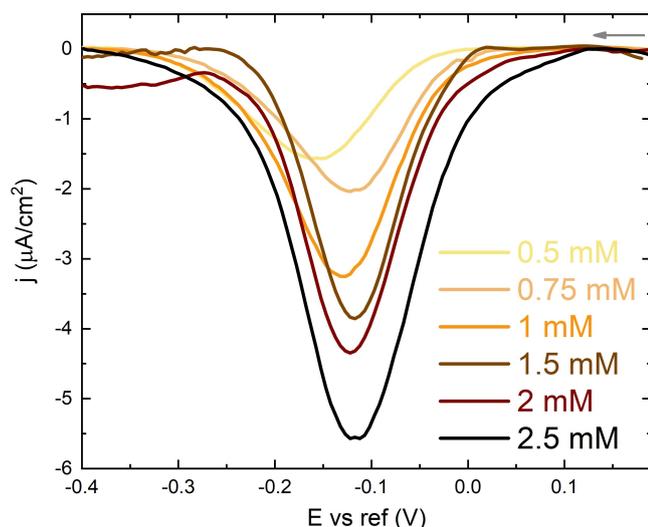


Figure 1. Voltammogram of gold electrodes modified with PAH:PSS incubated in lead solutions at pH 3. Measurements carried out in KCl 0.1 M, pH 7. Reference electrode: Ag/AgCl 3 M.

electrode. To evaluate the reproducibility, voltammograms after incubation in KNO_3 0.1 M were recorded for each electrode prior to incubation in the metal solution 0.5–2.5 mM and no significant peaks were detected in the applied potential window.

When performing incubations with samples containing lead, the voltammograms obtained showed a single reduction signal at around -0.135 V. The cathodic current density increased with the concentration of the lead (II) in the incubation solution due to increasing amounts of lead retained in the film. A good linear correlation between cathodic current density and lead concentration was observed and its linear regression is shown in Figure 2 (Analytical sensitivity: 3.8 mM, LOD: 0.6 mM and LOQ: 1.82 mM). This characteristic could be useful in the design of smart lead sensors.

Attenuated Total Reflection-IR

Electrodes were characterized by ATR-IR to evaluate the modification of the surface and the changes induced by the adsorption of lead cations. Figure 3 shows the spectra of the pure polyelectrolytes and the prepared films on the surface before and after immersion in lead solution. A representative intermediate concentration of lead was chosen to explain the trend. In the region between 1650 – 1512 cm^{-1} , signals mainly correspond to poly(allylamine) while the bands between 1250 – 650 cm^{-1} to polystyrene sulfonate.^[29] Green line in Figure 3 (line c), shows the spectrum of the film constructed by three successive deposits (dried in between them). Signals corresponding to the two polyelectrolytes are present, indicating that the surface modification was successful. No significant changes in the positions of the bands (respect to the spectra of the polymers alone) are observed, implying no specific interactions. After the interaction with lead ions, the signals do

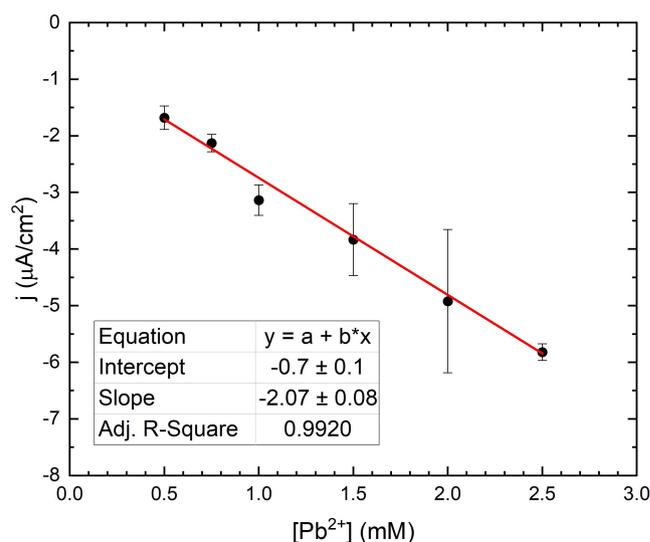


Figure 2. Peak current density for each incubation lead concentration and the corresponding linear regression ($Y = -(0.7 \pm 0.1) - (2.07 \pm 0.08) \cdot X$). Typically, three independent experiments were performed for each concentration.

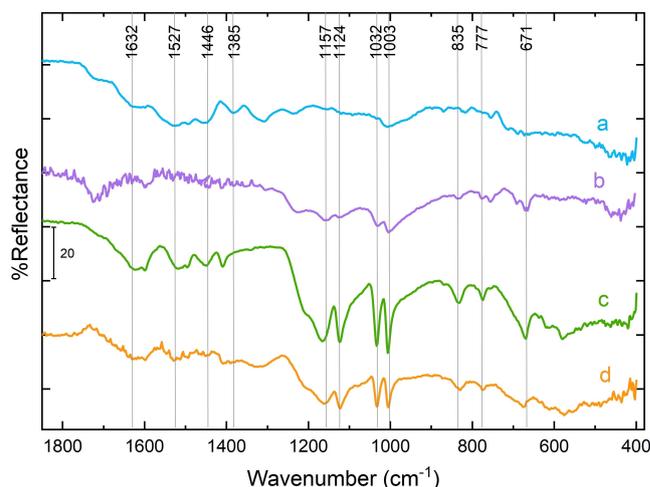


Figure 3. FTIR-ATR spectrum of functionalized gold electrodes with poly(allylamine) hydrochloride (PAH) (a), sodium polystyrene sulfonate (PSS) (b), both polyelectrolytes (PAH:PSS) (c) and the film after incubation in 1 mM lead solution at pH 3 (PAH:PSS Pb^{2+}) (d). Grey vertical lines correspond to the wavenumber values (in cm^{-1}) indicated on the top.

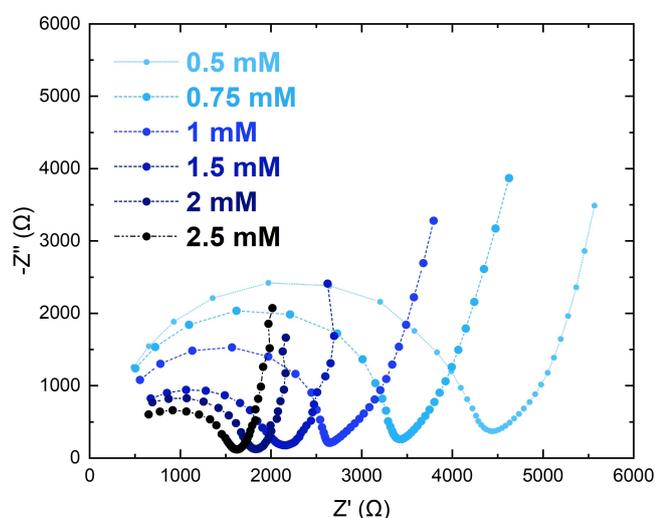
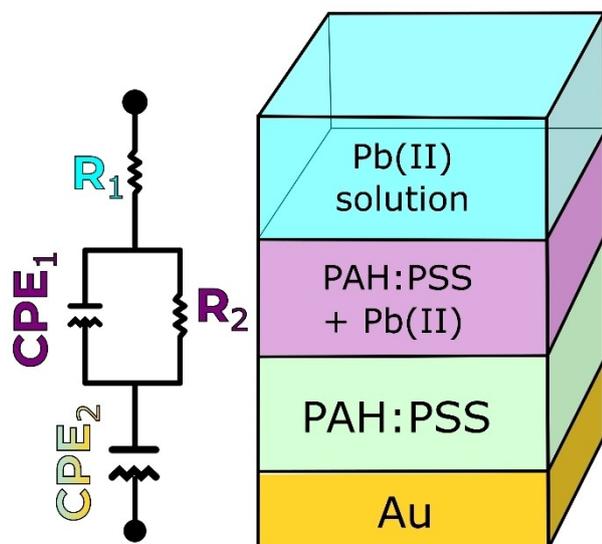
not change significantly. Again, no specific interaction can be deduced from the IR spectra (Table 1)

Electrochemical Impedance Spectroscopy

EIS is traditionally used in the study of corrosion and electro-deposition processes, in the evaluation of coatings and in the characterization of many types of sensors and semiconductors. In our experience, it is a very efficient tool to analyze the interaction of various compounds with functionalized surfaces.^[30,31]

Table 1. IR assignments of poly(allylamine) hydrochloride (PAH), sodium polystyrene sulfonate (PSS), both polyelectrolytes (PAH:PSS) and the film after incubation in 1 mM lead solution, pH 3 (PAH:PSS Pb²⁺).

Assignment	PAH	PSS	PAH:PSS	PAH:PSS Pb(II)
-NH ₃ ⁺ out-of-phase deformation	1614 cm ⁻¹	-	1605 cm ⁻¹	1603 cm ⁻¹
Amine	1525 cm ⁻¹	-	1518 cm ⁻¹	1529 cm ⁻¹
	1456 cm ⁻¹	-	1452 cm ⁻¹	-
	1385 cm ⁻¹	-	1410 cm ⁻¹	1408 cm ⁻¹
	1309 cm ⁻¹	-	-	-
	-	-	-	-
Sulfonate	-	1159 cm ⁻¹	1167 cm ⁻¹	1163 cm ⁻¹
	-	1124 cm ⁻¹	1122 cm ⁻¹	1124 cm ⁻¹
Sulfonate / Aromatic ring	-	1032 cm ⁻¹	1034 cm ⁻¹	1034 cm ⁻¹
	-	1003 cm ⁻¹	1005 cm ⁻¹	1005 cm ⁻¹
Aromatic ring	-	-	835 cm ⁻¹	829 cm ⁻¹
	669 cm ⁻¹	754 cm ⁻¹	775 cm ⁻¹	775 cm ⁻¹
	-	669 cm ⁻¹	673 cm ⁻¹	677 cm ⁻¹
	-	-	579 cm ⁻¹	577 cm ⁻¹
	-	-	-	-


Figure 4. EIS spectra 50 Hz–500 kHz, 10 mV, open circuit potential applied. Electrodes were incubated in lead solutions at pH 3. Measurements were carried out in KCl 0.1 M pH 7. Area of the electrode: 2 mm².

Figure 5. Schematic representation of the system and the equivalent circuit proposed: R1 [R2 CPE1] CPE2.

For further characterization, EIS was performed to evaluate the proposed system after the interaction with lead (II). Measurements were performed in KCl 0.1 M at pH 7 after incubation in lead (II) solutions at the open circuit potential (OCP). The experimental impedance spectra of modified electrodes, for each concentration of lead, are shown as Nyquist plot in Figure 4. The data was fitted to be evaluated as a function of electrical components.

Equivalent circuit proposed to interpret data, shown in Figure 5, consists of: A Resistance (R1) in series with a Constant Phase Element (CPE1) in parallel with a Resistance (R2) followed by a Constant Phase Element (CPE2) in series. R1 or also called R_s usually is related with the resistance of the solution and is affected by the setup construction, such as distance between electrodes, electroactive area, etc. An electrode-electrolyte double-layer interface is usually modelled as a capacitor but when the surface inhomogeneity of the electrode is important, a constant phase element may better describe the non-ideal behavior of the double-layer.

The expression for the impedance of a CPE is $Z = (j\omega)^{-n} / Y_0$, where j is an imaginary number ($j^2 = -1$), ω is the angular frequency ($\omega = 2\pi f$), and n is the CPE power ($0.5 < n < 1$). The closer the n value is to one, the more likely it is to exhibit the properties of an ideal capacitor. Graphically, the non-ideal behavior of the system studied is evidenced by a depressed semicircle in the Nyquist plot in Figure 4.^[32] Another important element in the circuit is R₂, which represents the Charge transfer resistance or R_{ct}. It represents the energy barrier to interchange electrons that redox species experience due to electrostatic repulsion and steric hindrance within the assembly. Furthermore, as Daniels et al.^[33] pointed out, in faradaic sensors, R_{ct} is one of the most used equivalent circuit elements to study the affinity of a redox compound at an interface.^[34] The fitted parameters values are listed in Table 2.

In our results, an electrical circuit with capacitive elements in series can be related to a system of homogeneous layers. Adjusting the data with the proposed circuit with two capacitive elements allows us to infer that there are two different areas in the assembly: an area where lead ions penetrate and another area where they do not. This behavior could be due diffuse effects or transport properties of the

Table 2. Fitted parameters values for the electrochemical impedance spectra shown in Figure 4A. Equivalent circuit proposed is: R1 [R2 CPE1] CPE2.

Pb [mM]	R2 [Ω]	CPE 1 n	Y_0 [$\cdot 10^{-10}$ S.s]	CPE 2 n	Y_0 [$\cdot 10^{-10}$ S.s]
0.50	4754 \pm 277	0.89 \pm 0.01	1.00 \pm 0.10	0.98 \pm 0.02	3.0 \pm 1.0
0.75	3422 \pm 166	0.88 \pm 0.01	1.09 \pm 0.03	0.99 \pm 0.02	2.5 \pm 0.9
1	2741 \pm 85	0.88 \pm 0.01	1.08 \pm 0.09	0.94 \pm 0.05	6.0 \pm 4.0
1.5	2034 \pm 165	0.77 \pm 0.06	4.00 \pm 2.00	0.94 \pm 0.05	7.0 \pm 4.0
2	1816 \pm 11	0.87 \pm 0.01	1.20 \pm 0.10	0.91 \pm 0.09	20 \pm 20
2.5	1603 \pm 38	0.84 \pm 0.02	2.50 \pm 0.60	0.90 \pm 0.07	14 \pm 9

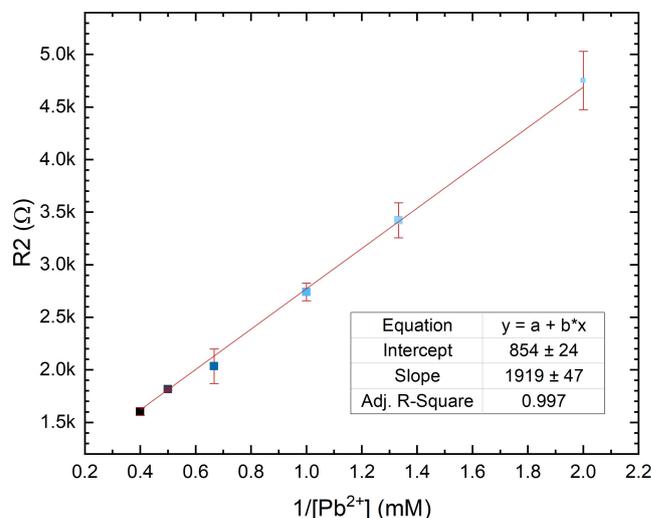
cation in the polymer mixture. The value of Y_0 of the CPE 2 is about four times greater than the Y_0 value of CPE 1. Furthermore, each of these values remained in the same order of magnitude when the lead concentration changed. Although these parameters do not provide an accurate value for capacitance, fitting the data with two CPE allows us to infer that there are two well defined areas due to the presence or absence of lead ions. The value of n of the CPE 2 is close to 1 for the lower concentrations and, as the concentration increases, it decreases to 0.9. When this value is close to the unity it describes an ideal behavior of the capacitor, so the presence of more lead ions may cause inhomogeneities that deviate from the ideal behavior. A more pronounced effect on this deviation is evidenced in the value of n of the CPE 1: it decreases from 0.89 to 0.84 as the lead concentration increases. This allows us to explain that CPE1 is related to the outermost polymer layer that is in contact with the solution and thus being the layer with which metal ions can interact.

Regarding the other components, the solution resistance (R1) has a large error, of the same order of magnitude as itself, because the measurement frequency range does not complete the semicircle and an extrapolation must be done to estimate these values. (See SI, Figure S3). Despite this fact, the value obtained is several orders of magnitude smaller than the estimated error for R2 not affecting the calculation of R2. The charge-transfer resistance (R2) decreases as the concentration of lead ions increases in the range 0.5–2.0 mM, revealing an increase in lead concentration. This does not modify the capacity of the functionalizing layer but affects the possibility of exchanging electrons with the working electrode. A very good linear correlation was found between this resistance and the inverse of the concentration, as seen in Figure 6 (LOD: 0.15 mM and LOQ: 0.45 mM). This characteristic could be useful in the design of smart lead sensors.^[35,36]

Effect of complexing agents

Chelating agents are usually present in industrial and natural samples. They are expected to compete with the functionalized surface for the cations. Therefore, we performed the analysis of the effect of chelating molecules to show the relevance in the development of sensors for complex samples.

The effect on the signals obtained by DPV and ATR of three complexing agents was studied. The modified electrodes with

**Figure 6.** Resistance of charge transfer vs. inverse of lead (II) concentration and the linear regression ($y = 1919 \pm 47 \cdot x + 854 \pm 24$).

PAH:PSS were incubated in lead solutions in presence of one of the following substances: Sodium citrate (with carboxylic acid groups), ethylenediamine (with amino groups) or ethylenediaminetetraacetic acid (EDTA, which has both functional groups in its structure) in concentrations ranging from 0.1 mM to 5.0 mM. After 30-minute-incubation, the electrodes were rinsed and DPV in potassium chloride was carried out.

Figure 7 shows the effect of each chelating agent (percentage of increase or decrease of the signal) observed by DPV. The cathodic current obtained in EDTA containing solutions was the only case in which the signal decreased. In the other two cases, the cathodic peak current increased by more than 20%. Probably due to its chelating effect, EDTA does not allow the lead ions to enter the film. In the case of the other complexing agents, because of their structure, they could be adsorbed on the surface of the film, acting as extra places for retaining lead ions on the surface. It was also observed that there was a certain concentration of citrate where the increase in the signal is maximum. At that concentration, the complexes on the surface would be maximized, while at greater concentrations, complexation of the lead ion in solution would be more favorable and the signal would thus decrease.

To explain the observed behavior by evaluating the presence of chelating agents on the modified surface, a spectroscopic characterization of the film was conducted with

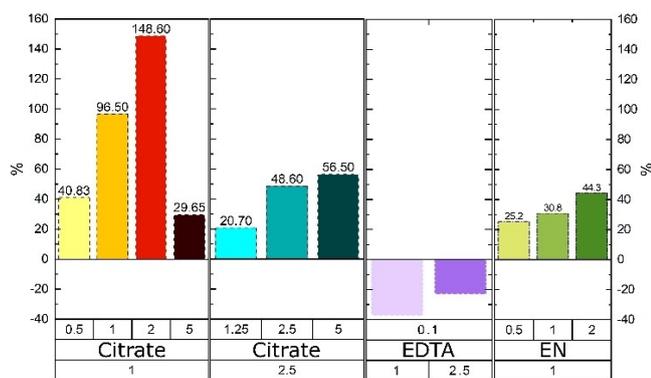


Figure 7. DPV Effect of complexing agents on the cathodic current, related to the reduction of lead(II) adsorbed in the modified electrode at pH 3. The bottom row indicates the concentration of lead (II). All concentrations are expressed in mM.

ATR. After the incubation in solutions containing 0–5 mM of citrate and 2.5 mM of lead, the electrodes were rinsed, dried and ATR spectra were taken. Figure 8 shows the ATR spectra of electrodes incubated at a lead concentration of 2.5 mM with different concentrations of citrate. Peaks between 1699 cm^{-1} and 1716 cm^{-1} are assigned to carboxylic acid of the citric acid. It can be observed that increasing concentration of citrate up to 1.25 mM caused an increase in the carboxylic acid peak intensity while for greater concentrations than that, the peak intensity decreased. This confirms that there would exist a concentration at which the adsorption of citrate to the surface is maximum. This trend was also observed in experiments conducted with other lead concentrations (0.5 mM, Figure S1).

In contrast to experiments conducted with citrate, IR Signals in PAH:PSS spectra after incubation in EDTA solutions did not change, indicating that it did not adsorb on the surface

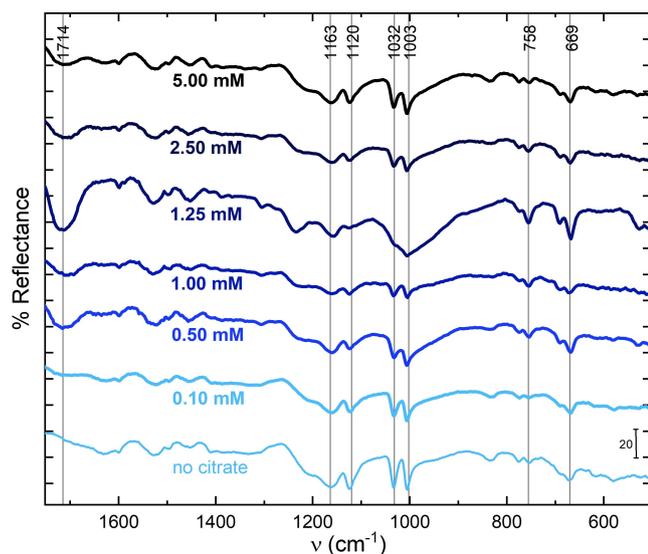


Figure 8. ATR spectra of disposable electrodes with Au modified with PAH:PSS and incubated in lead (II) 2.5 mM solutions (pH 3) with increasing concentration of sodium citrate to 5.00 mM. Grey vertical lines correspond to the wavenumber values indicated on the top.

appreciably. Spectra of ethylenediamine incubated samples showed no changes. This was expected and attributed to the similar characteristics of IR spectra of EN and PAH. (See SI, Figure 2)

Conclusion

We investigated a platform that could be used for sensing lead ions using a minimum sample volume. The construction was simple and could be adapted to massive production. The film construction from solutions of poly(allylamine) (PAH) and poly(4-styrene-sulfonate) (PSS) was studied by ATR resulting in a stable functionalization for the purposes of the experiments carried out.

We confirmed the affinity of the functional groups to lead ions by electrochemical techniques such as DPV and EIS. The first technique allowed the identification of the ion of interest through the reduction potential of the cation as adsorbed species correlating with the reduction current. The second one allowed us to analyze the interaction of the ion with the constructed interface, relating it to an equivalent circuit in which a resistive element resulted inversely proportional to the concentration of the analyte. We were able to obtain calibration curves with the DPV and EIS techniques for lead solutions at pH 3 in the range of 0.5–2.5 mM in both cases.

For the DPV measurements, the functionalized surfaces were exposed to the solutions of interest during an incubation period and then measured in solutions containing only supporting electrolyte. This guaranteed that the reduction current obtained was due solely to the adsorbed species. The maximum current peak was directly proportional to the concentration. EIS measurements, though the variation in the value of the elements of the equivalent circuit may be somewhat nonspecific, allowed us to analyze the interaction of the lead (II) cation in the film.

Lead (II) was chosen as a model system because of its environmental and toxicological relevance. Studying the effect of the presence of chelators and given the ubiquitous presence of this type of compound in natural environments, the importance of including them as a variable in these systems was demonstrated. It was expected that the presence of compounds that acted as complexing agents would affect the adsorption of cations on different interfaces. We have observed for lead that, in the entire range of concentrations studied, the cathodic current obtained by DPV in presence of EDTA decreased. In the other two cases, in presence of sodium citrate or ethylenediamine, it increased by more than 20%. This is related to the difference in the stability of complexes formed. The formation constants of EDTA complexes with lead were greater than those of with ethylenediamine and citrate.^[37,38]

At this point, the presence of the chelating agent on the surface would increase the number of coordination sites available for the analyte. We can observe by ATR that a concentration where maximum adsorption of citrate to the surface exists.

Overall, this platform seems promising for the construction of a sensor for lead quantification in acidic medium. The relevance of considering the presence and concentration of chelating agents and their interaction with the modified surfaces to be measured was established.

Experimental Section

Reagents

The lead (II) solutions were made from $\text{PbCO}_3 \cdot \text{Pb(OH)}_2$ (Mallinckrodt, CAS N° 598-63-0). Solutions of poly(allylamine) (PAH) 3 mg/mL pH 8 were made from poly(allylamine) 10% wt. in water ($M_w=65000$, Aldrich, CAS N° 30551-89-4) and solutions of poly(4-styrene-sulfonate) (PSS) 3 mg/mL pH 2 were made from poly(4-styrene-sulfonate) 18% wt. ($M_w=75000$, Aldrich, CAS N° 28210-41-5). Disodium ethylenediaminetetraacetate (EDTA) (Merck, CAS N° 6381-92-6), sodium citrate (JT Baker, CAS N° 6132-04-3), ethylenediamine (Merck, CAS N° 107-15-3), potassium chloride (Baker, CAS N° 7447-40-7), potassium nitrate (Carlo Erba, CAS N° 7757-79-1), nitric acid 65% (Merck, CAS N° 7697-37-2), hydrochloric acid (Carlo Erba, CAS N° 764-01-0), absolute ethanol (Sintorgan, CAS N° 64-17-5) and all other reagents used were of analytical grade and were used as received. All solutions were made with deionized water (resistivity $18 \text{ M}\Omega \text{ cm}$) from a Millipore(R) System.

Preparation of the electrodes

Disposable screen-printed electrodes from Donflex according to our own design (with working electrode and counter electrode of carbon ink and a pseudo reference of silver) were used. The area of the working electrode was 0.07 cm^2 or 0.02 cm^2 . The connection of the electrode to the potentiostat was through a USB connector (see Figure 9). Gold was electrodeposited on the carbon surface with an



Figure 9. Screen-printed electrodes purchased from Donflex. Counter and working electrodes of carbon and a pseudoreference of silver. The right electrode (2) has a central working electrode with electrodeposited gold.

external counter of gold, in presence of $\text{K[Au(CN)}_2]$ 15 mg/mL, free of additives, provided by Vilmet as reported in a previous work.^[26] Electroactive surface area of electrodes obtained: $0.069 \pm 0.005 \text{ cm}^2$ ($n=12$), roughness 3.5 ± 0.2 ($n=12$). Gold electroplating is stable for at least two months. But the functionalization of the electrode with the polymer mixture must be built within 48 hours of the measurement, but this is not an inconvenience due to the ease of construction.

Gold plated working electrodes were modified by drop casting with 5 to $1.1 \mu\text{L}$ of a 1:1 mixture of solutions of PAH 3 mg/mL pH 8 and PSS 3 mg/mL pH 2. This mixture was prepared the same day it was used and mixed in a vortex device (Decalab SRL). For successive depositions, to allow drying, we waited at least 30 minutes. In all cases, the electrodes were left to dry at room temperature in controlled humidity conditions (with saturated solution of calcium chloride).

Incubation in lead (II) solution

Each electrode was first incubated in KNO_3 0.1 M for 30 minutes to get the background. Then, only the working electrode was covered with $5 \mu\text{L}$ of lead (II) solution 0.5–2.5 mM, pH 3 at room temperature for 30 minutes in controlled humidity conditions (with saturated solution of potassium nitrate), rinsed with ethanol and dried with argon flow. For evaluating the effect of chelating agents, incubation solutions with lead (II) and sodium citrate, EDTA or ethylenediamine from 0.1 to 5 mM were prepared and pH was adjusted at 3 with nitric acid.

Electrochemical studies

Differential pulse voltammetry (DPV) was conducted in an $\mu\text{Autolab}$ type III system operated with Nova 2.4 software. Conditions: Start = 0.0 V, stop = -0.8 V, Step = -5 mV, Modulation amplitude = 10 mV, Modulation time = 0.05 s, Interval Time = 0.1 s. A solution of potassium chloride 0.1 M at pH 7 was used as a supporting electrolyte and a commercial Ag/AgCl (saturated KCl) was used as the reference electrode. All measurements were conducted under argon atmosphere and at room temperature.

EIS measurements were performed in an $\mu\text{Autolab}$ type III system operated with Nova 2.4 software. Frequencies from 1 Hz to 500 kHz, an amplitude of 10 mV vs OCP in lead (II) solution of different concentrations. "EIS Spectrum Analyser" (EISSA) software was used for data processing.

Attenuated Total Reflection-IR

A Thermo Nicolet 8700 with an ATR Smart orbit accessory with diamond prism and a DGTS detector was used and operated with Omnic® Software. Since it is a non-destructive technique, IR spectra were measured before and after the modification of each electrode and the electrochemical treatment. The spectra were recorded from 400 to 4000 cm^{-1} . Typically, resolution was set at 4 cm^{-1} and 64 scans were recorded.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: Electrochemical Impedance Spectroscopy · Electrochemistry · Heavy metals · Screen Printed Electrodes · Sensor

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