

Article

A Sensitive Impedimetric Sensor Based on Biosourced Polyphosphine Films for the Detection of Lead Ions

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Abstract: In this work, impedimetric sensors were developed for the detection of the four WFD heavy metals Pb^{2+} , Cd^{2+} , Hg^{2+} and Ni^{2+} , by the modification of a gold electrode with four partially biosourced polyphosphine polymers. These polymers were obtained with satisfactory yields by polycondensation of the bis(4-fluorophenyl)(4-methylphenyl)phosphine sulfide and the bis(4-fluorophenyl)(4-methylphenyl)phosphine oxide using isosorbide or bisphenol A. The chemical structures and number-average molecular weights of the resulting polymers were determined by NMR spectroscopy (¹H, ¹⁹F, and ³¹P) and by size exclusion chromatography. Glass transition temperatures varied between 184 and 202 °C depending on the composition of polymers. The bio-based poly(etherphosphine) oxide modified sensor showed better analytical performance than petrochemical based oxide for the detection of Pb²⁺. A detection limit of 10^{-10} g/L or 0.5 pM, which is 10^4 times lower than that of the anodic stripping voltammetric and the potentiometric sensors. A reversibility is obtained through rinsing of the impedimetric sensor with an EDTA solution.

Keywords: biobased polyphosphine films; gold electrodes; electrochemical impedance spectroscopy; lead ions

1. Introduction

Heavy metals occur in the environment coming from industry effluents and emissions, fertilizers, mining and household wastes [1–3]. These micropollutants do not decompose and have a tendency to accumulate in the human body when ingested, causing various diseases and disorders to the nervous, immune, liver, skin, reproductive and gastrointestinal systems [4–7]. The Water Framework Directive (WFD) that governs European water policy cites four metals: lead, cadmium, nickel and mercury. The WFD has been placed as the main European regulation for the protection of the water resources [8]. One of its principal objectives is to achieve good chemical and ecological status and to restore and to preserve water bodies at a "good status". Chemical status refers to specific pollutants (e.g., priority substances or priority hazardous substances) and environmental quality standards (EQS) are defined for them. Environmental Quality Standards (EQS) for Cd, Ni, Pb, and Hg are, respectively, 0.7–2.2, 341, 35, and 0.25 nM. As the WFD implementation gradually comes into effect in European countries,



the environmental metrology market is bound to increase over the coming years. Consequently, faced with this metrological challenge and the urgency of the situation, a paradigm shift is required in order to imagine a new approach to the problem of water monitoring.

Atomic absorption spectroscopy (AAS) [9], X-ray fluorescence spectrometry (XRF) [10], inductively coupled plasma mass spectroscopy (ICP-MS) [11], neutron activation analysis (NAA) [12] and inductively coupled plasma-optical emission spectrometry (ICP-OES) [13], are the main techniques reported for the sensitive detection of heavy metals. However, these laboratory methods need expensive equipment, multi-step sample preparation and are not easy to use and require trained professionals. Electrochemical sensors based on a low cost and portative instrumentation are good candidates for the on-field detection of heavy metal ions. The flagship technique is the anodic stripping voltammetry, using alternative materials to mercury, such as boron-doped diamond [14,15]. This technique allows the simultaneous detection of WFD metallic ions and their detection limits are in the range of nM, quite compatible with the WFD requirements. The main problems related to this technique is the reusability of the electrode because the reduced deposited metal should be removed with aggressive solutions, not compatible with their on-field use. For the development of selective and sensitive chemical sensors, the design of selective metals-interacting assembled units is required in order to constitute the recognition layers at the surface of the electrochemical devices. Oxygen, sulfur, phosphorus and nitrogen heteroatoms allow the complexation of the metal cations according to their hardness or softness on the HSAB scale. These specific complexing groups being attached to the electrode through low or high molecular weight organic molecules, the surface complexation of the metal ions is detected through potentiometry [16] or voltammetry [17] or impedancemetry [18]. Molecules wearing phosphine groups were used particularly as ionophores for the detection of metals. Trioctylphosphine oxide was used for the impedimetric detection of chromium [19]. Phosphorylated hexahomotrioxacalix [3] arene was used for the potentiometric detection of lead [20]. In both cases, the molecules were inserted in a polymeric matrix such as polysiloxane or polyvinylchloride, then limiting the shelf lifetime of the sensor, due to the leakage of the ionophore molecule. Electrochemical sensors generally give detection limits in the range of nM or less, which is quite compatible with the requirements of the WFD. The main drawback is the reusability of these sensors. In this work, we propose phosphorus polymer-modified gold electrodes for the impedimetric detection of the WFD metallic ions. The phosphine groups are known to have affinity for metals and in the polymer chain, these groups will be numerous, stable and easily accessible. The sensor structure will then be robust for a long shelf lifetime.

Phosphorous polymers can be used as fire retardants, flame proofers, surface adhesion reagents, catalysts and tooth preservers [21–25]. To the best of our knowledge, no attempts have been made to use phosphorus polymers as films for electrode modification, for sensor application. In this aim, two phosphorus containing polymers, poly(arylene ether phosphine oxide)s and poly(arylene ether phosphine sulfide)s were synthesized in order to be used as films for the modification of gold electrode for the sensitive detection of heavy metals in water. The synthetic pathways adopted to produce the phosphorus containing polymers is the nucleophilic aromatic substitution of the two prepared difluor aromatics, phosphine sulfide and phosphine oxide monomers, with a petrochemical based aromatic monomer or a bio-derived cyclic monomer. The petro-based chosen monomer is the bisphenol-A (BPA), the key diol monomer for improving the mechanical and thermal properties of engineering plastics due to its heavy, rigid and distorted molecular structure [26–29]. For the bio-based monomer, we used the 1,4:3,6-dianhydro-D-glucitol, known as isosorbide (ISB) and particularly the unique bicyclic dianhydroalditol, commercially available to date. It was extensively used as monomer for the synthesis of numerous polymers [30–34]. It is an important bio-based diol monomer rigid suitable for the elaboration of heat-stable polymeric block and is one of the alternative candidates for replacing BPA [35–38]. ISB cannot only improve the mechanical properties of the incorporated polymer, but also possesses good optical and UV-resistive properties due to its unique molecular structure [36–38]. Moreover, the non-toxicity of ISB has been proven and it has been widely used in pharmaceuticals and cosmetics [39,40]. The use of isosorbide as raw material for plastics can address environmental

issues like reduction in CO_2 derived from petroleum-based plastics [38–41]. The hydrophilic ISB content can increase the degree of hydrophilicity compared to BPA-based polymers which should increase the affinity towards the polar micropollutants in aqueous solutions. The main aim of this work is to design phosphoryl derivatives polymers as film for the modification of the gold electrodes. The synthesized polymers were fully characterized using NMR spectroscopy, GPC, DSC and ATG and then the analytical performance of the modified electrodes for the detection of Cd, Pb, Ni and Hg was determined using electrochemical impedance spectroscopy.

2. Materials and Methods

2.1. Reagents and Standards

The reagents used in the synthesis of monomers, aluminum chloride anhydrous (AlCl₃), Fluorobenzene (99%), thiophosphoryl chloride (PSCl₃, 98%), toluene (99%) anhydrous potassium carbonate and N,N-dimethylacetamide (DMAc, 99%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). The reagents used for the polymerization, 2,2-bis(4-hydroxyphenyl)propane (bisphenol A) was recrystallized from toluene and isosorbide was recrystallized from acetone and dried under vacuum. Other solvents were of reagent-grade quality and were used without further purification.

Solutions of metallic ions were prepared from standard solutions for AAS in nitric acid (Sigma-Aldrich). Potassium citrate tribasic monohydrate (98%) and ethylenediaminetetraacetic acid (EDTA, \geq 99%) were purchased from Sigma-Aldrich.

2.2. Monomer Synthesis

The monomers useful for the polycondensation reactions were obtained in three steps as described afterwards and presented in Figure 1.



Figure 1. Different steps for the synthesis of the monomers.

2.2.1. Bis(4-fluorophenyl)chlorophosphine sulfide (BFPCPS)

Into a 250 mL two round-bottom flask equipped with a magnetic stirrer, a condenser (the top of condenser was connected by a potassium hydroxide trap to recover the acid) and N₂ inlet, were added AlCI₃ (14 g, 0.105 mol), PSCl₃ (11.94 g, 0.07 mol), and excess of fluorobenzene (26.9 g, 0.28 mol), to serve both as reactant and solvent. The solution was stirred magnetically while being heated at 85 °C to reflux the fluorobenzene for a period of 3 h. Thereafter, 450 mL of ice water was added to cool the

solution. Ethyl acetate was added to help the phase separation. Afterwards, the organic phase was separated and subsequently washed three times with water. The organic layer was dried over Na_2SO_4 and after filtration, the solvent of the mixture was removed under reduced pressure. The BFPCPS was obtained as a white solid with a yield of 85%. The purification of the BFPCPC was carried out by washing twice with *n*-hexane. Its structure and its purity were checked through NMR spectra.

2.2.2. Bis(4-fluorophenyl)(4-methylphenyl)phosphine sulfide (1a)

Into a 250 mL two neck round-bottom flask equipped with a magnetic stirrer, a condenser (connected by a potassium hydroxide trap) and N₂ inlet, were added AlCI₃ (13.84 g, 0.104 mol), BFPCPS (10.00 g, 0.034 mol), and excess of toluene (12.75 g, 0.138 mol), to serve both as reactant and solvent. The solution was stirred magnetically while being heated at 110 °C for a period of 3 h. After cooling to room temperature, the reaction mixture was poured in 500 mL of ice water. Ethyl acetate was added to help the phase separation. The organic phase was dried over Na₂SO₄ and, after filtration, the solvent of the mixture was removed under reduced pressure. Then, the obtained solid was washed several times with petroleum ether and dried to give a brown solid with a yield of 65%. The monomer 1a was purified by recrystallization from cyclohexane.

2.2.3. Bis(4-fluorophenyl)(4-methylphenyl)phosphine oxide (2a)

To a three-neck round-bottom flask equipped with a condenser, (5.36 g, 0.155 mol) of (1a) and 17 mL of acetic acid were added under N₂. The temperature was then brought to 90 °C until the reagent (1a) was totally dissolved. Afterward, (1.67 g, 0.049 mol) of 35 % of H₂O₂ were added drop wise, over a period of 20 min then the mixture was stirred for 4 h. Thereafter, the reactor was allowed to cool to room temperature whereupon the sulfur containing by-product precipitated out. Next, the reaction mixture was filtered over a bed of celite in a Buchner funnel via gravity filtration and washed two times with acetic acid. Then, ethyl acetate was added to help in the phase separation. The aqueous phase was discarded and the organic phase was washed twice with saturated sodium carbonate solution. The organic layer was dried over Na₂SO₄ and after the filtration, the solvent was removed under reduced pressure. Finally, the obtained solid was washed several times with petroleum ether and dried to give a solid with a yield of 68%. The monomer 2a was purified by recrystallization from a mixture of ethyl acetate/cyclohexane with a ratio of 10/90 (vol/vol).

2.3. Synthesis of Polymers

The typical polymerization procedure for the synthesis of polymers P-P4 (chemical structures are given in Figure 2) was as follows. Isosorbide (1.6415 g, 5 mmol) (or BPA (1.1414 g, 5 mmol)), (2a) (1.6415 g, 5 mmol) (or (1a) (1.7218 g, 5 mmol)), and K_2CO_3 (3.040 g, 22 mmol) were added to 9.5 mL of DMAc (20% solid) and heated at 160 °C for 24 h, in a two-necked reactor equipped with a N₂ inlet and a mechanical stirrer. After cooling, the mixture was poured into water. The precipitated polymer was collected by filtration, washed with water and methanol, and dried under vacuum at 50 °C for 48 h.

2.4. Charaterization Methods

¹H, ¹⁹F, and ³¹P nuclear magnetic resonance (NMR) spectra were recorded on a Brucker Advance 300 spectrometer (Brucker, Palaiseau, France) operating at the following frequencies of 300 MHz for ¹H, 282 MHz for ¹⁹F, and 121 MHz for ³¹P. Tetramethylsilane (TMS), CFCl₃, and 85% H₃PO₄ were used as internal standards for ¹H, ¹⁹F and ³¹P, respectively.

Thermogravimetric analyses (TGA) were performed under nitrogen atmosphere, from room temperature to 500 °C, at a heating rate of 10 °C/min, using a TA Q50 Instrument (TA Instruments Division de Waters SAS, Guyancourt, France).



Figure 2. The synthetic routes of the poly(etherphosphine)s polymers P1–P4. (P1 = ISB and X = O/P2 = ISB and X = S/P3 = BPA and X = O/P4 = BPA and X = S).

Polymer glass transition temperatures (Tg) were determined by differential scanning calorimetric (DSC), with a Mettler-Toledo DSC822e equipment (Viroflay, France). Analyses were performed at a heating and cooling rate of 5 °C/min from 25 °C to 300 °C, in an argon atmosphere. The reported values were obtained from the second heat scan by the mid-point method.

Molecular weights were determined by size exclusion chromatography (SEC) and carried out on a system comprising a Shimadzu LC 20 AD pump (Shimadzu, Marne-la-Vallee, France), a Perkin Elmer Series 200 automatic injector (Perkin Elmer, Villebon sur Yvette, France), a Wyatt TREOS 3 angle light scattering detector (Wyatt Technology, Toulouse, France), a Shimadzu RID 10A refractometer and a PL gel 5 μ m Mixed C (300 × 7.5 mm, polystyrene/divinylbenzene) column. Chloroform was used as eluent. Reported values (number average molar masses (Mn), weight average molar masses (Mw) and chain disparities (PD) were determined from a polystyrene calibration curve.

2.5. Preparation of Polymer-Modified Gold Electrodes and Impedimetric Measurements

Gold substrates (300 nm of gold layer/30 nm of titanium layer/300 nm SiO₂/p-type Si/300 nm SiO₂) were provided by the French RENATECH network (LAAS, CNRS Toulouse). The gold electrodes were 1.2×1.2 cm square plates. The gold surface was rinsed with acetone for 15 min, rinsed with ultrapure water then dried under nitrogen flow. Then it was alternately immersed for 2 min in freshly prepared hot piranha solution, rinsed with ultrapure water, and dried under nitrogen flow. After the surface treatment, 5 µL of 1 w/w% chloroform solution of P1, P2, P3 or P4 polymer was dropped on the electrode surface and then dried under nitrogen flow. Drop-coating was chosen because spin-coating was not applicable, due to the volatility of chloroform.

Electrochemical measurements were performed in a 5 cm³ Pyrex glass electrochemical cell equipped with the polymer-modified gold electrode (0.07 cm² active area, defined by an O-ring seal), as a working electrode, a platinum counter-electrode and an Ag/AgCl reference electrode. All measurements were carried out at room temperature ($23 \pm 3 °C$). When the polymer-modified gold electrode was in contact with the 0.1 M potassium citrate solution (pH 4.0) containing the metallic ions, the measurements were performed after 10 min of equilibration. Electrochemical impedance spectroscopy (EIS) measurements were operated using a potentiostat-galvanostat Voltalab 80 (Hach, Düsseldorf, Germany). In these experiments, an amplitude of 10 mV, with a frequency range of 100 mHz to 100 kHz, was superimposed to a dc voltage. The value of the dc voltage was the free potential of the modified electrode in 0.1 M potassium citrate solution at pH 4.0. The real and imaginary impedances were computed and a Nyquist plot was drawn. The impedance values were fitted, using Zview software from Scribner Associates, to a standard Randles equivalent circuit consisting of a parallel combination of a constant phase element (CPE) and a Faradaic impedance Zf in

series with the solution resistance (Rs). The faradic impedance is a series combination of polarization resistance (Rp) and the Warburg impedance (W).

The surface topography of the polymer-modified gold electrode was characterized by AFM. The AFM measurements were carried out using an Agilent 5500 AFM (Agilent Technologies, Palo Alto, CA, USA). Silicon tips with a nominal spring constant of 20 N m⁻¹ were used in tapping mode at a frequency of ~300 kHz.

3. Results and Discussion

3.1. Physicochemical Characterization of the Resulting Polymers P1–P4

The difluoro aromatic monomers, bis(4-fluorophenyl)(4-methylphenyl)phosphine sulfide (1a) and the bis(4-fluorophenyl)(4-methylphenyl)phosphine oxide (2a) were synthesized according the route described in Figure 2, with satisfactory yields. The bis(4-fluorophenyl)(4-methylphenyl)phosphine sulfide was synthesized via Friedel–Crafts chemistry. This synthesized approach consisted firstly in the preparation of bis(4-fluorophenyl)chlorophosphine sulfide (BFPCPS) and then the electrophilic substitution to the trisubstituted phosphine sulfide (2a). The bis(4-fluorophenyl)(4-methylphenyl)phosphine oxide (2a) was prepared via the oxidation of the prepared phosphine sulfide (1a) in acetic acid with aqueous hydrogen peroxide. Representative NMR data of protons related to the chemical structures of synthesized monomers and polymers are reported in Figure S1. All the synthesized monomers (Figure 1) used for the reactions of polycondensation and resulting polymers P1–P4 (Figure 2) were fully characterized by ¹H, ¹⁹F and ³¹P NMR, the results of their characterization positively confirms the proposed structure with high purity (Figure S1).

The obtained monomers were incorporated in poly(etherphosphine) structures by aromatic nucleophilic substitution (Figure 2). Typically, the polymerization was performed by condensation of the different monomers (Isosorbide, bisphenol A (1a) and (2a)) in a polar aprotic solvent (DMAc), in the presence of K_2CO_3 , at 160 °C. At the end of the polymerization reaction, the polymers were isolated by precipitation in water and dried in vacuum during 48 h at 50 °C.

As shown in Table 1, the yields of all the polymers were more than 78%. The number average molecular weight (Mn) of the synthesized polymers is between 1967 and 4252 Da and the dispersity index (PD) ranges from 2.02 to 2.86. These polycondensates possess polymerization degrees in the range of 5–10 therefore they can be considering as oligomers.

Ref. Polymer	Yield ^{a)} (%)	Tg ^{b)} (°C)	Td _{5%} ^{c)} (°C)	M _n ^{d)} (Da)	M _w ^{d)} (Da)	PD ^{d)}
P1	80	202	408	1967	3826	2.72
P2	82	196	403	4252	8575	2.02
P3	78	184	431	2856	8034	2.86
P4	89	185	431	3508	9798	2.79

Table 1. Yields, thermal behaviors and molecular weights of resulting polymers P1–P4.

^{a)} After precipitation into water and washing with methanol. ^{b)} Determined by DSC with a heating rate of 10 °C/min under an argon flow of (50 mL/min). ^{c)} Temperature at which 5% of weight loss was observed in the TGA traces recorded at 10 °C. ^{d)} Number and weight-averaged molecular weights and polydispersity (PD) determined by GPC in CHCl₃ (calibrated with polystyrene).

The chemical composition of the prepared poly(etherphosphine) was ascertained by NMR spectroscopy. A detailed description of the NMR data recorded from poly(etherphosphine) sulphides and oxides are given in Figure S1 and the ¹H and ³¹P NMR spectra of the bio-based poly(etherphosphine) oxide P1 are shown in Figure S2.

The spectrum exhibits the characteristic protons of isosorbide (H1-H6) and of the monomer 2a (H7-H11). Furthermore, spectral analyses show the presence of peaks with low intensity corresponding

to protons at the end groups of isosorbide (H4*, H2*, H1*, H6*) and of (2a) (H7* and H8*). For the phosphorus NMR analysis, the spectrum of P1 presents a single peak at 28 ppm, which is assigned to the phosphorus nucleus of phosphine oxide group (PO(R)3).

The thermal properties of the polymers were investigated by thermogravimetric analyses (TGA) and differential scanning calorimetric (DSC). The study of the thermal properties of polymers P1–P4 has, at least, double objectives: (i) this technique is one of the most important analytical techniques for the physico-chemical characterization of polymers whatever their molecular weights; (ii) these polymers can be used later as reversible adsorption phases for volatile pollutants in water with a possible combination with organo-mineral substrates for SPE, SPME or SBSE applications (work under progress).

The 5% weight-loss temperatures (Td_{5%}) of the petro-based poly(arylene etherphosphine oxide) (P3) was observed to be higher than 430 °C under nitrogen (Table 1 and Figure S2). This Td_{5%} is higher than that of the bio-based poly(arylene phosphine oxide) (P2, 408 °C). In addition, the petro-based poly(arylene ether phosphine sulfide) (P4) also has excellent stability compared to the bio-based polymers. Despite this, the Td_{5%} of P1 and P2 were higher than 400 °C in nitrogen, still demonstrating excellent thermal stability.

From the results given in Figure S3, we can observe that polymers based on isosorbide (P1 and P2) showed higher Tg values, compared to those obtained from bisphenol A (P3 and P4). In a previous work, we have obtained similar behavior for poly(ether-sulfone) from isosorbide and bisphenol A [42]. Not a big difference on Tg values was observed between oxide or sulfide functions.

3.2. Detection of Pb^{2+} Ion by EIS Measurements

The morphology of the polymer-modified electrode was characterized by AFM. The AFM image for polymer P1, presented in Figure S4, shows that the dip-coated polymer film is quite homogeneous and rather smooth, a roughness of less than 3 nm is observed. The thickness of the polymers was determined by AFM, after a groove was created in the polymer film. The found thickness was $2 \pm 0.2 \mu m$ for the four polymers.

1. Comparative sensitivity of (P1–P4) polymers modified gold electrode

The impedance of the polymer-modified gold electrode/electrolyte interface decreased when the concentration of lead increased in the acetate solution. The response of the sensor was characterized by the value of the polarization resistance Rp that decreased when the lead concentration increased. In order to obtain the calibration curves, we have plotted the relative variation of the polarization resistance Δ Rp/R0 versus the co-logarithm concentration of Pb²⁺ (Figure 3). In the previous formula Δ Rp/R0, R0 is the polarization resistance in presence of the acetate solution and Δ Rp is the difference between Rp in the presence of different concentrations of lead ion and R0.

The linear range, the limits of detection and the sensitivities obtained for the different polymers are reported in Table 2. The sensitivities are the slopes of the calibration curves: Δ Rp/R0 = f(–log [Pb]. Both parameters being without units, these slopes are without unit. The comparison of the data reveals that the poly(etherphosphine) oxide based on isosorbide (P1) as modifier of the electrode gives the better results in comparison to P2, P3 and P4. The ratio of the sensitivities for the different polymers are the following ones: P1 is 2.4 times more sensitive than P2, 1.8 more sensitive than P3 and 2.5 times more sensitive than P4. This sensitivity of P1, obtained from isosorbide, can be related to the fact that it is the most hydrophilic polymer when compared to P3 due to the presence of oxygen atoms in the chemical structure of the biobased diol. A similar study was performed on partially bio-based polymers derived from isosorbide and petroleum-based polymers derived from bisphenol A, using the contact angle measurements [43]. We then demonstrated that more hydrophilic the polymer is, higher the affinity for the metallic ions is. In fact, the contact angle measurement shows that the presence of isosorbide in the chemical structure of polymers increase the surface hydrophilicity and in contrary polymers containing BPA is more hydrophobic. Likewise, the P = S groups in polymer chain can make the polymer more hydrophobic than polymers containing the P = O groups in the main chain,

thereby increasing the hydrophobicity of the polymers and thus decreasing the probability of stronger interaction with the lead ions.



Figure 3. Relative variation of the polarization resistance of the polymer-modified gold electrode interface as a function of $-\log$ concentration of Pb^{2+} ion (g/L).

Sensing Polymers Ref.	Sensitivity	LOD [g/L]	Linear Range [g/L]
P1	80.7 ± 2.0	10^{-10}	$[10^{-10} - 10^{-3}]$
P2	33.2±0.8	10^{-8}	$[10^{-8} - 10^{-5}]$
Р3	44.5 ± 1.1	10^{-8}	$[10^{-8} - 10^{-5}]$
P4	31.9 ± 0.8	10 ⁻⁸	$[10^{-8} - 10^{-5}]$

Table 2. Comparative study: responses of sensors based on P1–P4 polymers for the Pb²⁺ ion.

The detection limit obtained with P1 is 10^{-10} g/L or 0.5 pM. This detection limit is 10^4 times lower than that obtained by anodic stripping voltammetry on BDD, 5.5 nM [15] and that obtained by potentiometry, 4 nM [21]. The measurements were performed with three different electrodes and the RSD was 2.5%. The value of RSD corresponds to the size of the symbols used in Figure 3.

2. Selectivity study of polymer (P1) modified gold electrode versus Pb²⁺ ion

In order to investigate the sensitivity of the chemical sensor based on polymer P1 different concentrations of the four metallic ions of the Water Framework Directive: Pb^{2+} , Ni^{2+} , Hg^{2+} and Cd^{2+} were added to the citrate solution. Each metal was separately studied. The calibration for each metallic ion is presented in Figure 4 The results obtained for lead ion are the same than those presented in Figure 3.

The linear range, the limits of detection and the sensitivities obtained for the different metallic ions are reported in Table 3.



Figure 4. Relative variation of the polarization resistance of the P1 polymer-modified gold electrode interface as a function of $-\log$ concentration [Ion] (Pb²⁺, Ni²⁺, Hg²⁺ and Cd²⁺ ions).

Table 3. Comparative study: responses of sensors based on polymer P1 for the different ions Pb^{2+} , Hg^{2+} , Ni^{2+} and Cd^{2+} .

Sensitivity	LOD [g/L]	Linear Range [g/L]
80.7 ± 2.0	10^{-10}	$[10^{-10} - 10^{-3}]$
16.3 ± 0.4	10^{-8}	$[10^{-10} - 10^{-5}]$
10.0 ± 0.2	10^{-8}	$[10^{-10} - 10^{-5}]$
35.9 ± 0.9	10^{-8}	$[10^{-10} - 10^{-5}]$
	Sensitivity 80.7 ± 2.0 16.3 ± 0.4 10.0 ± 0.2 35.9 ± 0.9	SensitivityLOD [g/L] 80.7 ± 2.0 10^{-10} 16.3 ± 0.4 10^{-8} 10.0 ± 0.2 10^{-8} 35.9 ± 0.9 10^{-8}

The measurements were performed with three different electrodes and the RSD was 2.5%. The value of RSD corresponds to the size of the symbols used in Figure 4.

As it can be concluded from the obtained results, a good response for the detection of the four metals is revealed, principally for Pb^{2+} . The ratio of the sensitivities for the different metallic ions are the following ones: the sensitivity for Pb^{2+} is 4.9 times higher than that of Hg^{2+} , 8 times higher than that of Ni^{2+} and 2.2 times higher than that of Cd^{2+} . Detection limit for Pb^{2+} is 100 times lower than that of the other metallic ions. This phenomenon can be explained by the relatively high electronegativity of Pb ion compared to mercury, cadmium and nickel.

3. Reusability and shelf lifetime of the P1 modified gold electrode

The original value of impedance is restored after washing with a 0.1 M EDTA solution, due to the desorption of Pb^{2+} . Then the adsorption of Pb^{2+} is studied and the same calibration was obtained. A variation of 5% in the sensitivity was observed after 10 adsorption-desorption cycles, every week, as presented in Figure S5. After one month of storage, a variation of less than 3% in the sensitivity was observed

4. Conclusions

In this work, impedimetric sensors were developed for the detection of the four WFD heavy metals Pb^{2+} , Cd^{2+} , Hg^{2+} and Ni^{2+} , by the modification of a gold electrode with four polyphosphine polymers. The bio-based poly(etherphosphine) oxide (P1) modified gold electrode showed better analytical performance than petrochemical-based oxide. A detection limit of 10^{-10} g/L or 0.5 pM which

is 10⁴ times lower than that of the anodic stripping voltammetric and the potentiometric sensors. A reversibility is obtained through its rinsing with an EDTA solution, allowing an effective reusability. This novel impedimetric sensor is a good candidate for on-line monitoring of Pb²⁺ during the treatment of wastewater generated by industrial activities.

Supplementary Materials: The following are available online at http://www.mdpi.com/2227-9040/8/2/34/s1, Figure S1: Representative NMR data of protons related to the chemical structures of synthesized monomers and polymers, Figure S2: TGA thermograms of resulting polymers P1–P4 under nitrogen, Figure S3: DSC heating curves of resulting polymers P1–P4 under nitrogen, Figure S4: AFM image of the P1-modified gold electrode, Figure S5: Relative variation of the Pb²⁺ signal after one adsorption-desorption cycle every week.

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