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Article

Epoxy/Graphite Composite Electrode Modified with Recycled Silver Nanoparticles: An Eco-Friendly Strategy to Improve Lead Detection

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In this work, silver nanoparticles (AgNPs) obtained from photographic waste were synthesized and electrodeposited via cyclic voltammetry using epoxy-graphite composite as an electrochemical substrate. Both electrodes, unmodified (Epoxy/C) and modified (Epoxy/C/AgNPs), were characterized electrochemically by electrochemical impedance spectroscopy (EIS), charge transfer constant (K^0), and electroactive area. The modified electrode provided lower charge transfer resistance (275 Ω), more kinetically favored electron transfer ($K^0 = 1.15 \times 10^{-3}$ cm s^{-1}), and a 1.7-fold increase in the active area compared to the unmodified electrode. Additional characterizations by scanning electron microscopy (SEM) and Raman spectroscopy confirmed the presence of AgNPs structures on the carbonaceous surface. As a proof of concept, Pb^{2+} was used as a model analyte, and a square wave anodic stripping voltammetry (SWASV) method was developed to evaluate the analytical performance of both electrodes. A wider linear range (4.0 to 40.0 µg L^{-1}), the appropriate limit of detection (1.2 µg L^{-1}), and a 6-fold increase in sensitivity were found using the modified electrode, suggesting that the AgNPs significantly contributed to the performance of the electrode. The proposed method was applied to three real water samples, where the Pb^{2+} levels varied from 11.3 to 19.5 µg L^{-1}. The proposed protocol (reuse of silver waste) has proven to be a powerful tool for improving the detection of Pb^{2+}, which can be helpful for other electrochemical sensing applications in locations with minimal infrastructure.

Keywords: large-scale production, electrochemistry, conductive materials, recycling, metals

Introduction

Composite electrodes are defined as the combination of two or more materials that gives rise to a hybrid material with physicochemical and mechanical characteristics of both substances or new characteristics resulting from the mixture between them.[1] Generally, a composite electrode is prepared from a mixture of conductive and insulating phases. The most commonly used conductive phase is graphite, while the insulating phases can be oils, waxes, polymers, and resins, which are responsible for agglomerating the graphite powder and giving the electrode stability and mechanical properties.[2-4] The properties of this material depend on the nature, quantity, and distribution of each component. These electrodes can be used in several electrochemical applications and present advantages of the low cost, simplicity, and versatility of preparation, mechanical resistance, durability, surface regeneration through simple procedures, good conductivity, and the possibility of surface modification.[5-8]

Many strategies to produce composite electrodes are found in the literature.[9] The ease of preparation of these materials allows the construction of sensors of different shapes and sizes, besides the possibility of incorporating modifiers, bringing infinite possibilities and applications. Some of the most common examples of these electrodes

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are graphite composites with epoxy resin,[10] paraffin,[11] polyurethane,[12] and polypyrrole,[13] among others. Such electrodes have been used to determine different analytes (organic and inorganic species) in various matrices, demonstrating their versatility.[14-16]

Surface modification of composite electrodes has been an approach used in many studies due to providing improved sensitivity and selectivity. Currently, several nanostructured materials are used temporarily or permanently for this purpose through electrodeposition and/or adsorption by covalent and/or ionic interactions. Among the various nanomaterials available for surface modification, silver nanoparticles (AgNPs) can be highlighted.[17,18] Some advantages associated with these particles are improved conductivity and signal-to-noise ratio of measurements, more favorable mass and charge transport, increased electroactive area, and control at the electrode/solution interface.[19] Moreover, in some cases, it avoids the formation of fouling on the electrode surface by adsorption and/or polymerization of reaction intermediates.[20] Although digital image processing has become popular in the last two decades, some sectors still employ chemical image processing on paper, especially photographic studios, generating a large amount of silver waste, which is an environmental concern. The process of recycling this silver for electrode surface modification is an environmentally feasible strategy following green chemistry protocols.[21]

Thus, in this work, we developed a composite electrode composed of epoxy resin and graphite, and its surface was modified with silver nanoparticles, obtained by recycling photographic waste. The produced electrochemical sensor (namely Epoxy/C/AgNPs) was characterized electrochemically, morphologically, and structurally. Subsequently, the sensor was applied to determine lead in environmental samples by square wave anodic stripping voltammetry (SWASV) as a proof of concept.

Experimental

Reagents

All reagents were of analytical grade and used without any prior purification steps. Deionized water with a resistivity of 18.2 MΩ cm obtained by a pro system (Sartorius Arium®, Göttingen, Germany) was used to prepare the solutions. The Pb^{2+}, Cu^{2+}, Cd^{2+}, and Zn^{2+} standard solutions were purchased from Qhemis High Purity (São Paulo, Brazil). Graphite powder (particle diameter < 20 µm) was purchased from Sigma-Aldrich, (St. Louis, USA) and epoxy resin was purchased from Avipol (Santo André, Brazil). Potassium chloride and potassium ferricyanide were obtained from Vetec (Rio de Janeiro, Brazil). Ammonium sulfide from Dinâmica (Indaiatuba, Brazil), perchloric acid from Hexis (São Paulo, Brazil), nitric acid from Vetec (Rio de Janeiro, Brazil) and sulfuric acid from Nuclear (São Paulo, Brazil). Potassium thiocyanate and ammoniacal ferric sulfate were purchased from Synth (Diadema, Brazil) and used as titrants and indicators in the volumetric titration of silver extracted from photographic waste, respectively.

Instrumentation

A 797 VA Computrace potentiostat (Metrohm, Utrecht, Netherlands) controlled by software version 1.3.1 was used for all electrochemical measurements. Epoxy/C/AgNPs, $Ag|AgCl|KCl_{(sat.)}$, and stainless-steel wire electrodes were used as working, reference, and auxiliary electrodes, respectively. The scanning electron microscopy (SEM) images were obtained with a Vega 3 microscope (Tescan, Brno-Kohoutovice, Czech Republic) located in the Multipurpose Laboratory of the Institute of Chemistry, Federal University of Uberlândia (LMIQ-UFU). The instrument was operated at 5 kV using a secondary electron detector. Energy dispersive X-ray spectra were obtained from images acquired from the SEM using the INCA X-Act detector (Oxford Instruments, Abingdon, UK) coupled to the microscope. The equipment used to obtain the Raman spectra was the LabRAM HR Evolution microscope (HORIBA, Kyoto, Japan), located in the Laboratory of New Insulating and Semiconductor Materials (LNMIS) of the Physics Institute of the Federal University of Uberlândia. The incidence power was 50%, and the laser wavelength was 785 nm.

Production of the epoxy resin/graphite electrode

The composite electrodes were produced according to studies previously reported in the literature.[22,23] Briefly, the electrode was prepared by mixing graphite powder with epoxy resin (65:35 m/m, respectively), already containing an appropriate amount of the catalyst agent. The homogenized carbon paste obtained was added to a polyethylene syringe (internal volume of 1.0 mL, diameter of 4 mm) containing a copper wire (to make electrical contact with the potentiostat) and then kept under pressure for 24 h. For this purpose, a bench lathe was used, where both extremities of the syringe were pressed to compact the composite material. After this period, the electrode surface was polished on sandpaper of different sizes (600 to 1500 grit), followed by paper to obtain a homogeneous surface.

Extraction of silver from photographic industry effluent

After the last stage of traditional photo processing, the residual silver is solubilized in sodium thiosulfate. The residue used here was supplied by the Institute of Art and Communication photographic laboratory of at the Fluminense Federal University. The collection was performed using plastic bottles, and the material was subsequently stored at room temperature. The procedure adopted in this work was to extract silver from the complex formed with thiosulfate[24] through its precipitation with sulfide and the subsequent elimination in the acid medium under heating at 70 °C for 4 h. Initially, 100 mL of ammonium sulfide (3.0 mol L^{-1}) were added to 200 mL of the solution from photo processing. This solution was filtered, and the solid dissolved in 80 mL of HNO_3 (8.0 mol L^{-1}), and the resulting solution was heated on a hotplate using a closed system.[25] The quantification of silver in this solution was performed by volumetry, and a concentration of 0.0067 ± 0.0003 mol L^{-1} was found. This solution was stored at room temperature.

Modification of the epoxy resin/graphite composite electrode with AgNPs

The procedure for electrodeposition of the AgNPs (0.0067 mol L^{-1}) film onto the composite electrode surface was properly optimized using scan rates between 50 to 200 mV s^{-1}, scan numbers from 1 to 6, with range potential of –0.9 to 0.6 V, step potential of 10 mV and HNO_3 remaining from the extraction process of silver as supporting electrolyte. The selected conditions were 50 mV s^{-1} and 4 scans, which provided a better electrochemical response for Pb^{2+}.

Electrochemical measurements

Electrochemical impedance spectroscopy (EIS) analyses were performed using 1.0 mmol L^{-1} $[Fe(CN)_6]^{3-/4-}$ in 0.1 mol L^{-1} KCl solution. For this, a frequency range of 50 kHz to 0.1 Hz with an amplitude of 10 mV and 10 data points *per* decade of frequency and a half-wave potential of +0.24 V were used. The equivalent Randles circuit was applied to determine the charge transfer resistance (Rct) related to the $[Fe(CN)_6]^{3-/4-}$ redox probe. The determinations of Pb^{2+} were conducted by SWASV, whose instrumental parameters were properly optimized.

Sample collection and preparation

Natural water samples were collected from three lagoons, Araruama, Saquarema, and Rio Vargem in Itaboraí, all located in the state of Rio de Janeiro, Brazil. Sampling was performed by a surface collection of approximately 1.5 L in plastic bottles previously decontaminated in HNO_3 (10% v/v) for 24 h. All samples were acidified using HNO_3 (5% v/v) and filtered in a membrane filter (pore size 0.2 µm) to eliminate suspended particles. After filtration, 5 mL of samples were diluted in 20 mL of supporting electrolyte and immediately analyzed by SWASV.

Analysis by graphite furnace atomic absorption spectrometry

All samples were also analyzed by graphite furnace atomic absorption spectrometry (GF AAS) using a spectrometer model SOLAAR Series M5, (Thermo Scientific, Waltham, USA) equipped with a hollow lead cathode lamp (Photron Lamps, Narre Warren, Australian) operating at a maximum current of 4 mA and equipped with a background corrector (deuterium lamp) and pyrolytically coated graphite tubes. The equipment was used with the following instrumental analysis conditions: wavelength 217 nm, bandpass 0.5 nm, and manual injection mode with 25 µL of solution. An analytical curve was constructed from 5 to 30 µg L^{-1}, and the water samples were also filtered and diluted 2-fold in HNO_3 solution (2% v/v). The heating program used for GF AAS analysis followed the recommendations provided by the equipment software and are shown in Table 1.

Table 1. Heating program used for Pb^{2+} analysis by GF AAS

Step	Temperature / °C	time / s	Heating ramp / (°C s^{-1})	Air flow / (L min^{-1})
Drying	100	30	10	0.2
Pyrolysis	800	20	150	0.2
Atomization	1200	3	0	off
Cleaning	2500	3	0	0.2

Results and Discussion

Characterization of the electrode surfaces

Firstly, EIS measurements were performed to investigate the Rct of both Epoxy/C and Epoxy/C/AgNPs electrodes. From the Nyquist plots (Figure 1), it was possible to estimate Rct values of 350 and 275 Ω for unmodified and modified electrodes, respectively, indicating faster electron transfer after the modification process. Subsequently, the electroactive areas of the three independent electrodes were also estimated by Randles-Sevcik's theory.[26] The values were estimated as 0.141 ± 0.002 and 0.249 ± 0.011 cm^2 for the bare and modified electrode, respectively, suggesting that AgNPs structures caused a 1.7-fold increase in the area. Such a result corroborates those obtained by EIS, with the favoring of charge transfer. A relative standard deviation (RSD) of 4.4% indicates adequate manufacturing reproducibility even after surface modification with AgNPs. Moreover, values of the heterogeneous electron transfer constant (K^0) achieved were higher for the modified electrode (1.15×10^{-3} cm s^{-1}) when compared to the unmodified electrode (9.23×10^{-4} cm s^{-1}). This demonstrated that in fact, the modification of the electrode surface was responsible for favoring the redox reactions kinetically.

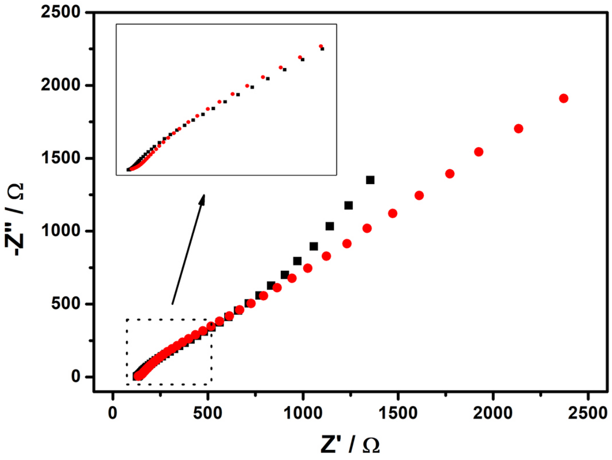

Figure 1. EIS spectra obtained on Epoxy/C (red ball) and Epoxy/C/AgNPs (black square) using 1.0 mmol L^{-1} $[Fe(CN)_6]^{3-/4-}$ as redox probe and 0.1 mol L^{-1} KCl as supporting electrolyte. The inserted graph represents the magnification of the EIS spectrum. Instrumental conditions: frequency range 0.1 Hz to 50 KHz and amplitude 10 mV.

SEM images were obtained under a magnification of 10,000 times for morphological analysis, as shown in Figure 2. On the unmodified surface (Figure 2a), it was noted compact sheets typical of graphite[27] with small deformations possibly generated during the manufacturing steps of the electrode. Already on the modified surface (Figure 2b), the contrast between the electrode surface and the electrodeposited silver nanoparticles can be observed, which have a spherical shape and particle size frequency of 121 ± 4 nm (see Figure 2c), indicating that the modification was successfully performed. Energy dispersive X-ray spectroscopy (EDS) spectra was also recorded for the unmodified and modified surfaces. As can be seen, on the Epoxy/C electrode (Figure 2d), there is a predominant peak referring to the carbon present in the graphitic material. In contrast, the Epoxy/C/AgNPs electrode (Figure 2e), besides this peak, there is also a peak related to silver. This result confirms the presence of AgNPs electrodeposited on the electrode surface. In the spectrum shown in Figure 2e, there is also a low-intensity peak related to oxygen that can be justified by the use of HNO_3 in the step of obtaining silver from the residue of the photo revelation process.[28] This oxidizing agent is capable of breaking part of the graphitic structure (sp^2 hybridized carbons) by the insertion of oxygenated functional groups forming structural defects, which may have occurred on the surface of the carbon material.

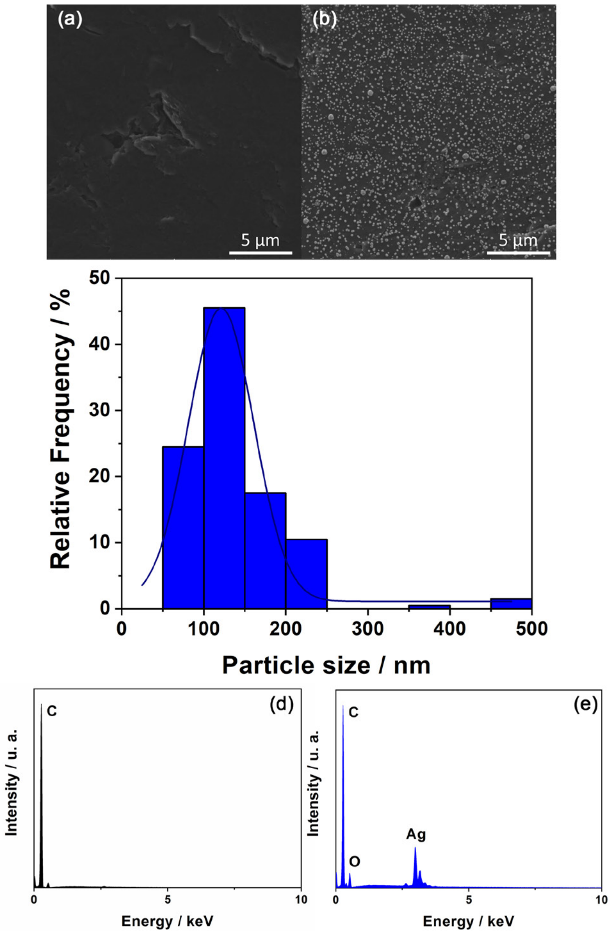

Figure 2. SEM images obtained from (a) Epoxy/C and (b) Epoxy/C/AgNPs electrodes, (c) relative frequency histograms of particle sizes Epoxy/C/AgNPs (n = 200), and EDS spectra recorded from (d) Epoxy/C and (e) Epoxy/C/AgNPs surfaces.

The Raman spectra were normalized as a function of the G-band (at around 1580 cm^{-1}) of the unmodified material due to the surface-enhanced Raman scattering (SERS) effect, which is a phenomenon occasioned by the presence of nanoparticles, which intensifies the light scattering, significantly increasing the acquired signal.[29] In fact, the presence of nanoparticles affects the structure of the material used as a substrate, which can be seen by the difference in intensity of the bands characteristic of graphitic materials (D and G) in both spectra (Figure 3).

The spectra of Epoxy/C/AgNPs (Figure 3, line blue) exhibit a vibrational band around 248 cm^{-1} related to the Ag–O bond present in the nanoparticle network.[30] The intensity of this band is directly associated with the morphology presented by these nanostructures.[31] When modifying the surface with AgNPs, a higher I_D/I_G ratio is observed than the unmodified electrode.[27] This factor is related to the electrode modification procedures since the insertion of nanoparticles breaks the network ordering of sp^2 carbon atoms.[32]

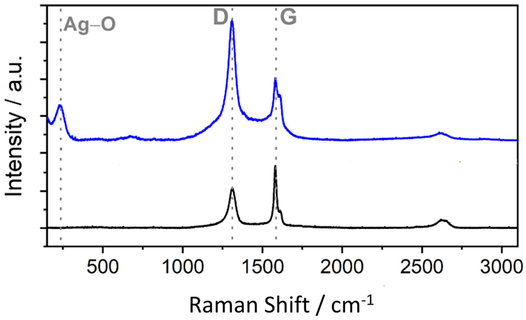

Figure 3. Raman spectra obtained from Epoxy/C (black line) and Epoxy/C/AgNPs (blue line) electrode surfaces.

Analytical performance of the proposed electrode for Pb^{2+} determination

The influence of SWASV parameters on the electrochemical profile of Pb^{2+} were appropriately studied. Special attention was devoted to the deposition potential and deposition time, which are directly associated with the accumulation of Pb^{2+} species on the electrode surface, and, consequently, the method's detectability. It was noted that at potentials more negative than –0.6 occurred a considerable decrease in analytical response probably due to the evolution of hydrogen gas (blocking the active sites) on the electrode surface. On the other hand, at deposition times greater than 150 s, there was no significant increase in current, owing to the saturation of the active sites. Therefore –0.6 V and 150 s were selected for the accumulation step. In experiments using SWASV, conditioning steps are usually used to clean the electrode surface between measurements, but under the proposed platform this additional step was not required, as no memory effects and/or surface fouling were observed between successive measurements. The other SWASV parameters were selected considering the compromise between peak resolution and current intensity (Table 2), and the supporting electrolyte was adapted from the previous work.[33]

Under the previously optimized instrumental parameters, electrochemical measurements were performed using the non-modified and modified electrodes with 40 µg L^{-1} Pb^{2+} (Figure 4a). An approximately 7-fold increase in the peak current of Pb^{2+} was achieved when the modified electrode (Figure 4a, red line) was used, indicating that the AgNPs caused an improvement in the Pb^{2+} response. Subsequently, calibration curves were prepared using both electrodes, Epoxy/C (Figure 4b) and Epoxy/C/AgNPs (Figure 4c), with Pb^{2+} concentrations ranging from 4.0 to 48.0 µg L^{-1} (n = 3). Linear ranges between 28.0 and 48.0 µg L^{-1} ($I_p = -1.04 + 0.08\ [Pb^{2+}]$ / µg L^{-1}, Pearson's correlation coefficient (r^2) = 0.982) and 4.0 and 40.0 µg L^{-1} ($I_p = 1.74 + 0.47\ [Pb^{2+}]$ / µg L^{-1}, r^2 = 0.996) were attained for the unmodified (Figure 4d, black line) and modified electrode (Figure 4d, red line), respectively. The limit of detection (LOD) and quantification (LOQ) values were calculated following the principles of the International Union of Pure and Applied Chemistry (IUPAC),[34] where LOD = 3sB/S and LOQ = 10sB/S (sB is the standard deviation of ten measurements with the lower concentration level of Pb^{2+} and S is the slope of the calibration curve). The analytical parameters, such as linear range, LOD, LOQ, and sensitivity are shown in Table 3.

Table 2. SWASV conditions used for the determination of Pb^{2+}

Parameter	Studied range	Selected values
Deposition potential / V	–0.3 - –0.8	–0.6
Deposition time / s	30-180	150
Step potential / mV	5-30	5
Amplitude / mV	10-100	20
Frequency / Hz	10-100	50
Scan rate / (mV s^{-1})	50-500	250
Supporting electrolyte	–	0.1 mol L^{-1} $HClO_4$

It is observed that lower LOD (1.2 µg L^{-1}), and higher sensitivity (ca.6-fold increase) were attained using the Epoxy/C/AgNPs electrode. In addition, the surface modification process provided a wider linear working range for Pb^{2+} monitoring. These results agree with the electrochemical characterizations discussed earlier, which showed that after modification with AgNPs, there was an increase in charge transfer and active sites, allowing the detection of low levels of Pb^{2+}, which is mandatory when environmental samples are analyzed. It is important to highlight that solutions obtained from the silver residues of the photographic process were stable for 4 years for Epoxy/C surface modification. This stability was evaluated by monitoring the peak current intensity of 28 µmol L^{-1} Pb^{2+} solution (relative standard deviation (RSD) = 7.1%) after different surface modifications using the same silver residue solution.

The selectivity of the proposed method was evaluated in the presence of other metallic species, such as Cd^{2+}, Zn^{2+}, and Cu^{2+}, using two ratios (1:1 and 1:2) between Pb^{2+} and each interfering agent, respectively (Figure 5). These studies were performed using 20 µg L^{-1} Pb^{2+} and 20

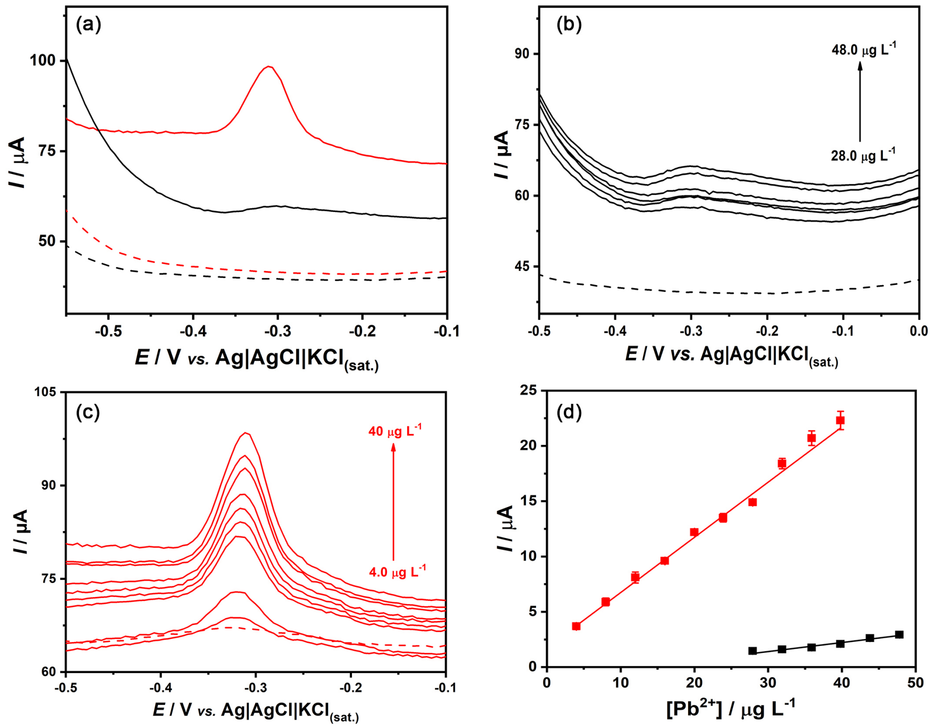

Figure 4. (a) SWASV recordings of 40 µg L^{-1} Pb^{2+} solution using the Epoxy/C (black line) and Epoxy/C/AgNPs (red line) electrodes. SWASV voltammograms achieved using Pb^{2+} concentration ranging from 4.0 to 48.0 µg L^{-1} on Epoxy/C (b) and Epoxy/C/AgNPs (c) surfaces and the respective calibration curves (d) using unmodified (black line) and modified (red line) electrodes. The dashed lines indicate the corresponding blanks. SWASV conditions: see Table 2.

Table 3. Analytical parameters obtained for the detection of Pb^{2+} using unmodified and modified electrodes

Analytical parameter	Electrode	
	Epoxy/C	Epoxy/C/AgNPs
Linear range / (µg L^{-1})	28.0-48.0	4.0-40.0
LOD / (µg L^{-1})	8.9	1.2
LOQ / (µg L^{-1})	29.6	4.0
Sensitivity / (µA L µg^{-1})	0.08	0.47

LOD: limit of detection; LOQ: limit of quantification.

and 40 µg L^{-1} of the other metals. Considering both ratios investigated, there were no variations greater than 10% on the electrochemical response of Pb^{2+}, indicating adequate selectivity in the presence of these metals.

Real water samples (collected from three lakes) were submitted for analysis to demonstrate the developed sensor's applicability. Only one sample presented Pb^{2+} levels lower than LOD (1.2 µg L^{-1}) and consequently in agreement with the maximum limit allowed (10.0 µg L^{-1}) by Brazilian regulatory agencies (CONAMA No. 347 of 2005),[35] which can be seen in Table 4. On the other hand, the other samples showed Pb^{2+} levels above the limit allowed by the same legislation. These results were statistically compared to those obtained by GF AAS at a 95% confidence level using the paired student *t*-test ($t_{calculated} < t_{critical}$), which confirmed the accuracy of the SWASV analysis.

The analytical performance of the proposed electrode was compared to other silver-modified electrodes for the sensing of Pb^{2+} in environmental water (Table 5). As can

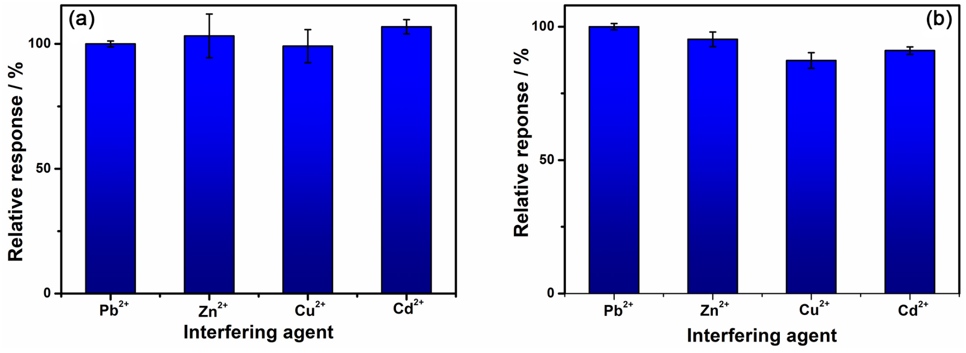

Figure 5. Influence of possible interfering species (Cd^{2+}, Zn^{2+}, and Cu^{2+}) on the electrochemical response of 20 µg L^{-1} Pb^{2+} using 1:1 (a) and 1:2 (b) ratios.

Table 4. Concentration values of Pb^{2+} found in the analyzed water samples

Sample	$[Pb^{2+}]$ / (µg L^{-1})	
	SWASV	GF AAS
A	19.5 ± 1.7	20.5 ± 0.9
B	11.3 ± 1.8	9.1 ± 0.5
C	< LOD[a]	< LOD[b]

Samples from the Araruama (A), Saquarema (B), and Itaborai (C) lagoons. All analyzes were performed in triplicate (n = 3); Student's *t*-test: $t_{calculated} = 0.37$ $t_{critical} = 12.71$, confidence level: 95%. [a]1.2 µg L^{-1}; [b]1.3 µg L^{-1}. SWASV: square wave anodic stripping voltammetry; GF AAS: graphite furnace atomic absorption spectrometry; LOD: limit of detection.

be seen, all works show better analytical performance in terms of LOD, linear range and deposition time when compared to the sensor developed here. Even using shorter deposition times, the other works achieved a lower LOD. Thus, probably the substrate and material used for surface modification, as well as other instrumental parameters, are also relevant in affecting the detectability of the method. However, it is worth noting that the estimated LOD is lower than that recommended by the Brazilian regulation agency, and therefore perfectly suited for the proposed application. On the other hand, it is important to note that such sensors use expensive materials as substrate (glassy carbon electrode), and the surface modification procedures are time-consuming. Opposite to this, we use an affordable epoxy/graphite composite as an electrochemical platform which is easily produced on a large scale in laboratories with minimal infrastructure. Moreover, we demonstrate a user-friendly approach following green chemistry principles by reusing residual silver from photo-developing processes. It is also worth mentioning that the modification step via electrodeposition is very fast (120 s); only four consecutive scans are required.

Conclusions

A new strategy to produce silver-modified electrodes was demonstrated based on the reuse of silver residue from photographic processes. The residual silver was properly extracted and electrodeposited using epoxy-graphite composite as substrate. Morphological (SEM images) and structural characterizations confirmed that the modification was carried out successfully. As a proof of concept, Pb^{2+} was selected as a model analyte and a SWASV method was developed. Better detectability and sensitivity were obtained on the modified surface, suggesting that recycled AgNPs are good candidates for improved Pb^{2+} detection. In fact, the modified electrode provided sufficient LOQ value (4.0 µg L^{-1}) to detect Pb^{2+} levels as required by regulatory agencies (10.0 µg L^{-1}). The approach proposed here is extremely feasible for low-income locations and can be extended to the sensing of other metallic species as well as organic analytes.

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Author Contributions

Taíssa S. Cabral was responsible for conceptualization, data curation, investigation, and validation; Suéllen F. L. do Nascimento for data curation, investigation, visualization, writing original draft, writing-review and editing; Lucas V. de Faria for data curation, investigation, validation, visualization, writing original draft, writing-review and editing; Thalles P. Lisboa validation, visualization, writing-review and editing; Pedro H. S. Borges for data curation, investigation, validation; Edson Nossol for investigation, visualization, writing-review and

Table 5. Comparison of the proposed electrode with other electrochemical sensors reported in the literature for Pb^{2+} determination

Electrode	Technique	Deposition time / s	LOD / (µg L^{-1})	Linear range / (µg L^{-1})	Reference
GCE/poly(1,8DAF)/AgNPs	SWASV	120	0.03	0.005-0.058	36
GCE/AgNPs	SWASV	50	0.010	0.010-0.062	37
GCE/Ibu-AgNPs	DPASV	n.m.	0.01	0.1-1500	38
Epoxy/C/AgNPs	SWASV	150	1.2	4.0-40.0	this work

GCE/poly(1,8DAF)/AgNPs: glassy carbon electrode modified with silver nanoparticles deposited on poly(1,8-diaminonaphthalene); GCE/AgNPs: glassy carbon electrode modified with silver nanoparticles; GCE/Ibu-AgNPs: glassy carbon electrode modified with ibuprofen and silver nanoparticles; Epoxy/C/AgNPs: epoxy-graphite composite modified with recycled silver nanoparticles; SWASV: square wave anodic stripping voltammetry; DPASV: differential pulse anodic stripping voltammetry; LOD: limit of detection; n.m: not mentioned.

editing; Felipe S. Semaan for visualization, writing original draft, writing-review and editing; Rafael M. Dornellas for formal analysis funding acquisition, project administration, resources, writing original draft, writing-review and editing; Wagner F. Pacheco for formal analysis funding acquisition, project administration, resources, writing original draft, writing-review and editing.

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