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Tunable Electrochemical Sensors Based on Carbon Nanocomposite Materials towards Enhanced Determination of Cadmium, Lead and Copper in Water †

Laia. L. Fernández [1,2], Julio Bastos-Arrieta [3], Cristina Palet [1] and Mireia Baeza [2,*]

[1] Grup de Tècniques de Separació en química (GTS), Departament de Química, Universitat Autònoma de Barcelona, Carrer dels Til·lers, 08193, Bellaterra, Catalunya, Spain; Laia.Lopez@uab.cat (L.L.F.); cristina.paletarrobauab.cat (C.P.)

[2] Group of biological treatment and of liquid and gaseous Effluents, Nutrient removal, and Odors and Volatile Organic Compounds (GENOCOV), Departament Química. Universitat Autònoma de Barcelona, Carrer dels Til·lers, 08193, Bellaterra, Catalunya, Spain.

[3] Grup de Biotecnologia Molecular i Industrial, Department d'Enginyeria Química, Universitat Politècnica de Catalunya, Rambla Sant Nebridi, 22, 08222 Terrassa, Spain; julio.bastos@upc.edu

* Correspondence: mariadelmar.baeza@uab.cat

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Abstract: Many carbon materials are well-known conductive material, widely used in the fabrication of composite electrodes. In this work, diverse allotropic forms of carbon as graphite, MWCNTs and rGO were tested. Furthermore, these materials allow the construction of cheaper, smaller, portable, reliable, and easy to use devices, which can be easily modified. The above-mentioned composites electrodes were developed for metal analysis in water, such as, Cu, Cd and Pb that at high concentration can have consequences on human health. SWASV is the selected technique. It would be ideal to exploit the potential properties of mercury for metal detection by tuning electrode's surface. Due to mercury's hazardous properties and to reduce the amount used in polarography, the use of nanoparticles is a good option due to their properties. Mercury nanoparticles were here used to modify the surface of the composite electrodes to improve electroanalytical sensor response. For this reason, using this modified composite electrodes lower detection limits and wider linear range can be achieved for Cd (0.05–1 mg·L^{-1}) and Pb (0.045–1 mg·L^{-1}) but for Cu (0.114–1.14 mg·L^{-1}) meaningful variations was not observed compare to the bare electrode.

Keywords: electrochemistry; Hg nanoparticles; graphite; composite electrodes; metal analysis; SWASV

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1. Introduction

Water is fundamental for all the Earth's living forms, and a key issue for social and economic development. Nowadays, water analysis is a concerning topic, for that reason monitoring some parameters is important to prevent some health problems. One of the parameters that has become important is determinate the concentration of heavy metals in water. To do this analysis several techniques are used, such as Atomic Absorption Spectroscopy (AAS) [1], Inductively Coupled Plasma (ICP) [2], High Performance Liquid Chromatography (HPLC) [3], etc. Some of the metals that can be found in water are: Cu, Cd and Pb and at high concentration can have consequences on human health [4–6].

In this work, voltametric techniques are the chosen ones, concretely Square-Wave Anodic Stripping Voltammetry (SWASV) [7,8]. SWASV consists in two steps. First, applying a potential to preconcentrate the analyte on the surface of the electrode and second the measurement is performed applying staircase potential and the current generated is recorded.

To use this technique, composite electrodes were construct using different carbon materials and a non-conductor epoxy. The behavior of graphite, reduce graphene oxide (rGO) and carbon nanotubes (CNTs) were tested in the detection of Cd, Pb, and Cu. However, we can work with the bare electrode and the modification of their surface with mercury nanoparticles (Hg-NPs) was also tested [9]. Mercury was used, long time ago, in polarography, and it is well-known for its ability to form amalgams with some metals reducing the potential where they appear [10,11]. Hence, taking advantage of these properties the aim of this work is to reduce the amount of mercury used in polarography for the Cd, Pb, and Cu determination.

2. Composite Electrodes Construction, Characterization, and Modification

2.1. Composite Electrode Construction

Composites were constructed using three different carbon materials: graphite, CNTs and rGO. The first step is to weld a copper sheet to a commercial connector; after that, it is placed in a PVC tube. A mixture of one of the carbon materials and Epotek H77 is prepared, and the PVC tube (2.1 cm, ⌀ 6 mm) is filled with this mixture. Then, it is cured for 2 days at 80 °C and the surface must be polish.

The percentage tested of carbon materials are shown in **Table 1**. These percentages were optimized previously, and it's related which improved electroanalytical properties of developed sensors as detection limit and sensitivity [12].

Table 1. Percentages used in the construction of each electrode.

Material	% Carbon material	% Epotek H77
Graphite	15	85
	20	80
CNTs	10	90
rGO	15	85

2.2. Composite Electrode Chacaterization

Electrodes were characterized using Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS) using a computer-controlled Multi AUTOLAB M101 (Eco Chemie, Utrecht, The Netherlands) with a three-electrode cell: a platinum-based electrode 53–671 (Crison Instruments, Alella, Barcelona, Spain) as a counter electrode, an Ag/AgCl handmade electrode as a reference electrode, and the constructed composite electrodes were used as a working electrode. The characterization was performed in solution composed by: 0.01M $K_4Fe(CN_6)$, 0.01M $K_3Fe(CN_6)$ and 0.1 M KCl. For CV the scan rate was 10 $mV \cdot s^{-1}$ and the rate of frequencies used in EIS was 0.01 to 10^4 Hz.

The behavior of 15% rGO electrode was unusual, possibly related to the orientation of the layers in the Epotek H77 matrix, and its characterization using CV and EIS was not successful. In *Error! Reference source not found.* the characterization of the rest of the carbon electrodes, with graphite or CNTs, can be observed. The most notable difference is showed in EIS, where the 20% graphite presents the lower charge transference resistance. Thus, a highly conductive surface is then available for the preconcentration of cationic metals.

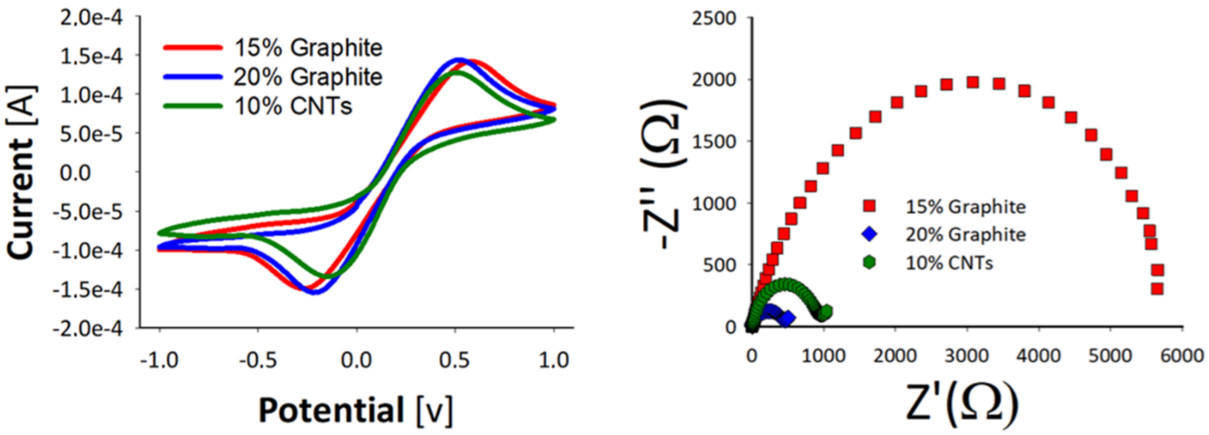

Figure 1. CV (a) and EIS (b) characterization of the different electrodes.

2.3. Composite Electrode Modification with Hg-Nps

After the electrode characterization, the surface of the electrode is modified with mercury nanoparticles (Hg-NPs) following the synthesis from [9]. In the synthesis, 78 mg $Hg_2(NO_3)_2 \cdot 2 H_2O$ are used, 1 mL 1N HNO_3 is added and then 0.5 mL of a solution of 3.5 g of PVA (Polyvinyl Alcohol) in 16 mL of Milli-Q water. All the steps of the synthesis were performed at 25 ºC and under stir.

20 µL of the nanoparticle's solution are drop casted on the electrode surface and dried in the oven at 80 ˚C for 2h. The modified electrodes were characterized using Scanning Electron Microscopy (SEM) (MerlinFe-SEM, Carl Zeiss, Germany) and the Hg-NPs were characterized using Transmission Electron Microscopy (TEM) (JEM-2011 200 kV, Jeol, USA).

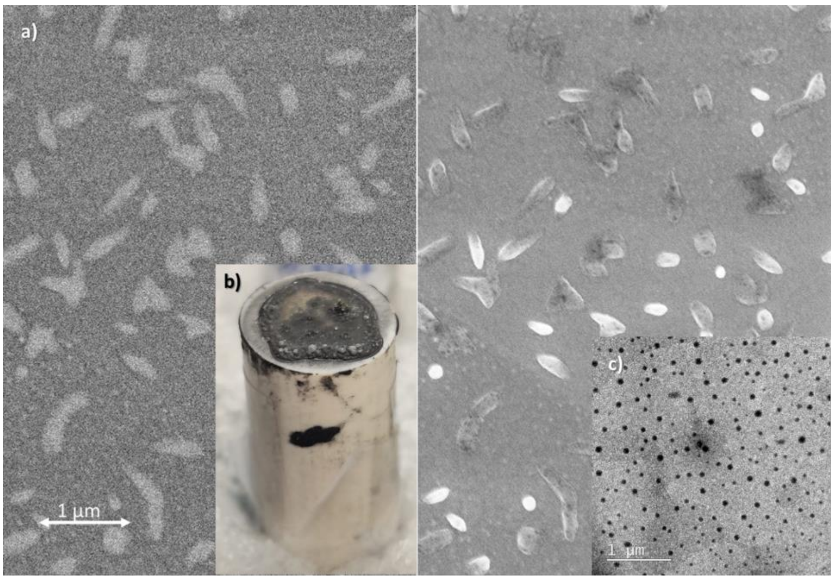

Figure 2. (a) Retrodispersive (left) and secondary electron (right) SEM images. (b) 20% graphite electrode drop casted with Hg-NPs image (c) TEM image of the Hg-NPs.

2.4. Metal Solution Preparation and Determination

The metal solutions were prepared using certified stock standards of 37 mg·L^{-1} $Pb(NO_3)_2$ (≥99%, supplied from Sigma-Aldrich), 11438 mg·L^{-1} $Cu(NO_3)_2$ (99.5 %, purchased from Merck) and 1000 mg·L^{-1} $Cd(NO_3)_2$ (99 %, obtained from Panreac). They were added to a 0.1 M Acetic acid (CH_3COOH, 99.9% acquired from J.T.Baker, HPLC reagent)

/ 0.1 M Ammonium acetate (NH_4CH_3COO, 97 % purchased from Panreac) buffer with Milli-Q water at pH 4.6 [13] .

2.5. Bare Composite Electrodes

For metal determination, the technique chosen was SWASV. It consists in applying a potential (-1.4 V) for 7 minutes that reduce the metal ions on the electrode surface, then and staircase potential is applied and the current generated is recorded. All this process is performed under N_2 bubbling. Moreover, a modification in the electrochemical cell is used, instead of using a handmade reference electrode, the one used for the measurements is Orion 900 electrode (Crison Instrument, Thermo Scientific, MA, USA).

Firstly, all the bare electrodes were used for the electrochemical detection of Cd, Pb and Cu. The results for all electrode studied are shown in Error! Reference source not found..

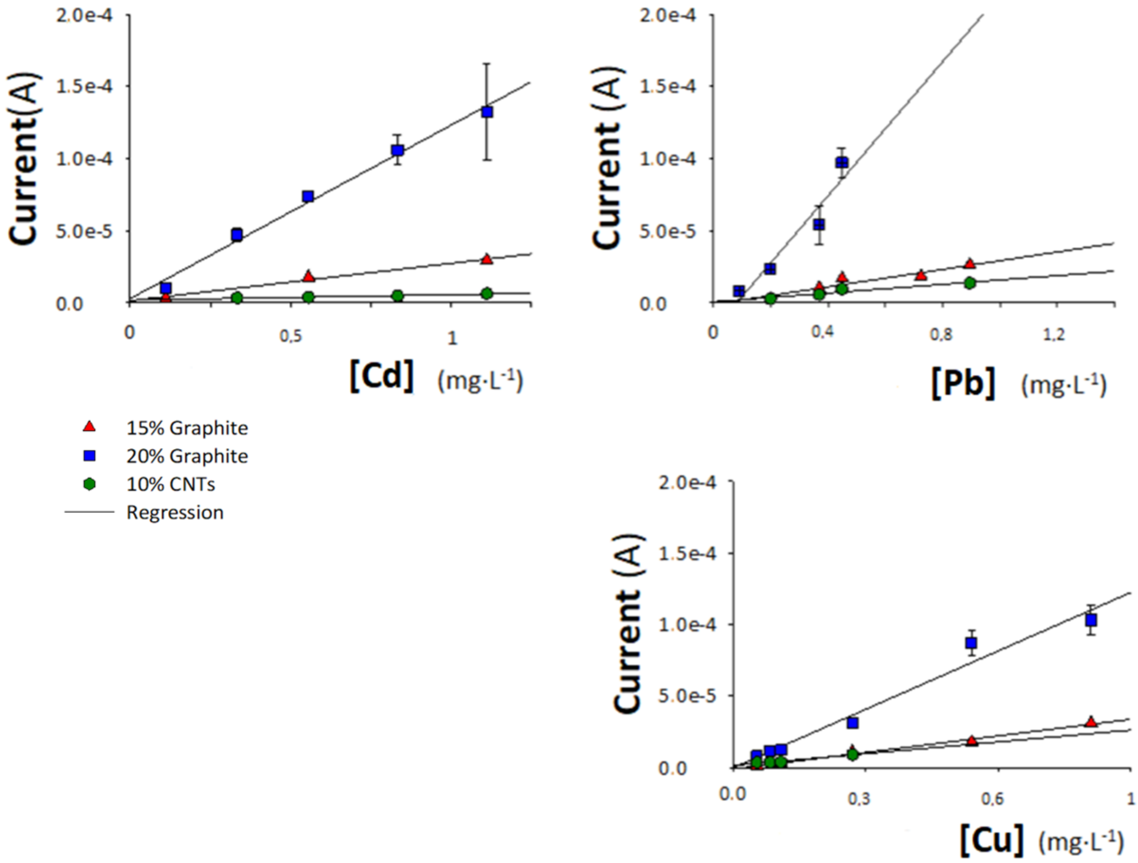

Figure 3. Calibration curves for Cd, Pb and Cu for each raw material.

As can be seen, 20% graphite electrodes showed the best response, as it has a better sensitivity compared with 15% graphite and 10% CNTs composite electrodes for three metal cations analyzed.

2.6. Hg-NPs drop casted electrodes

The next step is modifying the surface of the 20% graphite electrode with Hg-NPs, as mentioned above. Once the surface is modified, the electrode is tested for Cd, Pb and Cu determination using SWASV. The corresponding results are shown in **Error! Reference source not found.**.

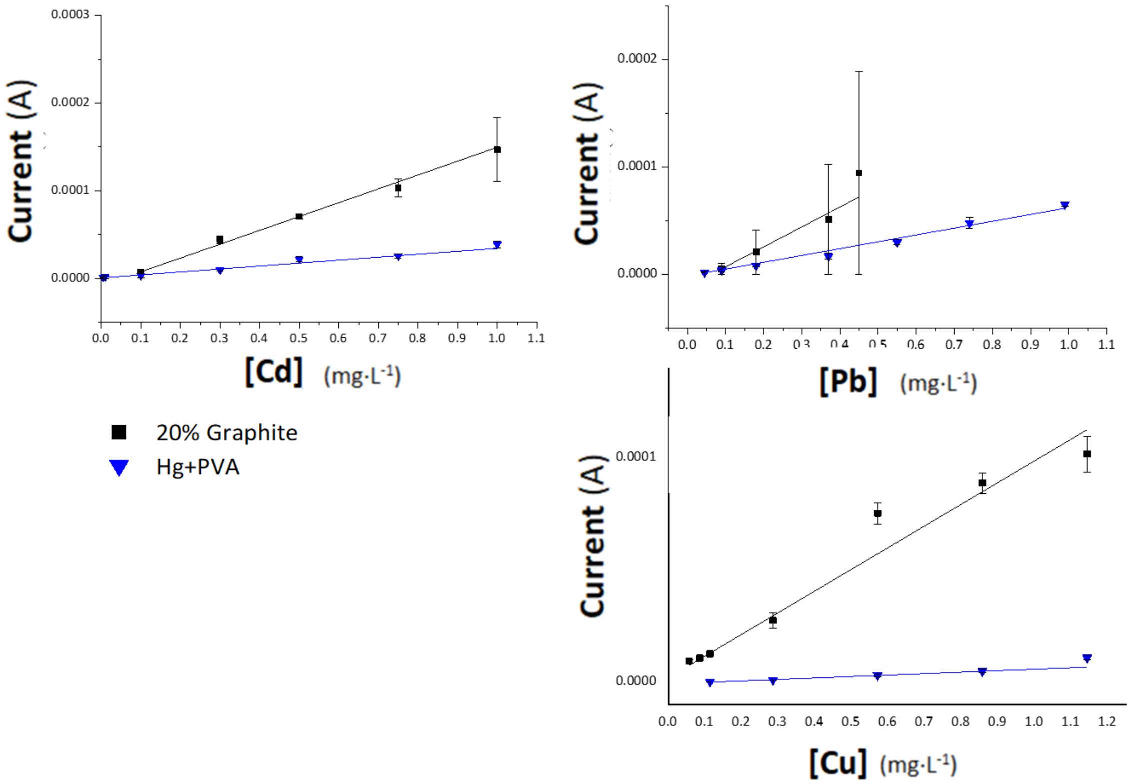

Figure 4. Calibration curves for Cd (a), Pb (b) and Cu (c) for 20% graphite (black) and 20% graphite plus Hg-NPs (blue).

With this modified 20% graphite electrode lower quantification limits can be achieved. In Error! Reference source not found. all the parameters of the calibration curves are summarized.

Table 2. Feature's parameters: sensitivity, r² and linear range of each cationic metal detected separately.

	[Cd^{2+}]		
Electrode (20% graphite)	**Sensitivity** [A·(mg·L^{-1})$^{-1}$]	**r^2 (n)**	**Linear Range** (mg·L^{-1})
Bare	(1.6±0.1) x10^{-4}	0.995 (n= 5)	0.1 – 1
plus Hg-NPs	(3.4±0.2) x10^{-5}	0.98 (n=6)	0.05 – 1
	[Pb^{2+}]		
Electrode (20% graphite)	**Sensitivity** [A·(mg·L^{-1})$^{-1}$]	**r^2 (n)**	**Linear Range** (mg·L^{-1})
Bare	(1.9±0.2) x10^{-4}	0.95 (n= 4)	0.09 – 0.45
plus Hg-NPs	(6.4±0.3) x10^{-5}	0.98 (n= 7)	0.045 – 1
	[Cu^{2+}]		
Electrode (20% graphite)	**Sensitivity** [A·(mg·L^{-1})$^{-1}$]	**r^2 (n)**	**Linear Range** (mg·L^{-1})
Bare	(9.7±0.9) x10^{-5}	0.95 (n= 7)	0.057 – 1.14
plus Hg-NPs	(7±1) x10^{-6}	0.90 (n= 5)	0.114 – 1.14

3. Conclusions

Carbon composite electrodes are very versatile, robust, and reliable electrodes to work with for Cd, Pb and Cu detection. The well-known properties of mercury to form amalgam with other metals can be taking in advantage to modify the surface of the carbon composite electrode in order to decrease the limit detection of the bare electrode. To emulate the polarography, the use of Hg-NPs reduces the amount of mercury used without losing its properties. In this case, Cd, and Pb form amalgam with Hg, reducing the detection limit (Cd = 0.05 mg·L^{-1}; Pb = 0.045 mg·L^{-1}) in comparison with the bare electrode. Cu metallic cation doesn't have this behavior. Although the bare electrode has higher sensitivity because its electroactive area is not modified, when the electrode was modified with Hg-NPs its electroactive area decreases. We added a polymer (from the synthesis of the NPs) over the electrode's surface that is not as good conductor as graphite. On the other hand, we improved the detection limit due to the specific interaction of mercury with metals cations.

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Conflicts of Interest: the authors declare no conflict of interest.

Reference

1. Hashim R, Song TH, Muslim NZM, Yen TP. Determination of heavy metal levels in fishes from the lower reach of the kelantan river, Kelantan, Malaysia. Trop Life Sci Res. **2014**, *25*, 21–39.
2. Pérez-Ràfols C, Trechera P, Serrano N, Díaz-Cruz JM, Ariño C, Esteban M. Determination of Pd(II) using an antimony film coated on a screen-printed electrode by adsorptive stripping voltammetry. Talanta. **2017**, *167*, 1–7, doi:10.1016/j.talanta.2017.01.084
3. Okano G, Igarashi S, Yamamoto Y, et al. HPLC-spectrophotometric detection of trace heavy metals via 'cascade' separation and concentration. Int J Environ Anal Chem. **2015**, *95*, 135–144, doi:10.1080/03067319.2014.994619
4. Wani AL, Ara A, Usmani JA. Lead toxicity: A review. Interdiscip Toxicol. **2015**, *8*, 55–64, doi:10.1515/intox-2015-0009
5. Azaman F, Juahir H, Yunus K, et al. Heavy metal in fish: Analysis and human health-a review. J Teknol. **2015**, *77*, 61–69, doi:10.11113/jt.v77.4182
6. Godt J, Scheidig F, Grosse-Siestrup C, et al. The toxicity of cadmium and resulting hazards for human health. J Occup Med Toxicol. **2006**, *1*, 1–6, doi:10.1186/1745-6673-1-22
7. Nor YM, McNeal BL. Square wave anodic stripping voltammetry: Determination of trace metals in aqueous extracts of soil samples. Chem Speciat Bioavailab. **1993**, *5*, 135–140, doi:10.1080/09542299.1993.11083214
8. Scarponi G. Optimization of square wave anodic stripping voltammetry (SWASV) for the simultaneous determination of Cd, Pb, and Cu in seawater and comparison with differential pulse anodic stripping voltammetry (DPASV). 2002; (April). http://citeweb.info/20020474074.
9. Ramesh G V., Prasad MD, Radhakrishnan TP. Mercury nanodrops and nanocrystals. Chem Mater. **2011**, *23*, 5231–5236, doi:10.1021/cm2022533
10. Ross JW, Demars RD, Shain I. Analytical Applications of the Hanging Mercury Drop Electrode. Anal Chem. **1956**, *28*, 1768–1771, doi:10.1021/ac60119a039
11. Pujol L, Evrard D, Groenen-Serrano K, Freyssinier M, Ruffien-Cizsak A, Gros P. Electrochemical sensors and devices for heavy metals assay in water: the French groups' contribution. Front Chem. **2014**, *2*, 1–24, doi:10.3389/fchem.2014.00019
12. Muñoz J, Montes R, Baeza M. Trends in electrochemical impedance spectroscopy involving nanocomposite transducers: Characterization, architecture surface and bio-sensing. TrAC - Trends Anal Chem. **2017**, *97*, 201–215, doi:10.1016/j.trac.2017.08.012
13. Dropsens S.L. Serie:Prácticas de laboratorio Ref.: DRP-PL4, "Determinación de cobre en agua de grifo."