

Metal-organic Framework-Modified Carbon Paste Electrode for Determining Lead in Aqueous Solutions

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In this work, a novel carbon paste electrode was modified with metal-organic framework (MOF) 235 for detecting lead ions in aqueous solutions using anodic redissolution voltammetry as analytical technique. Experimental parameters such as, amount of MOF-235, type of supporting electrolyte, potential and time deposition were evaluated to optimize the detection approach. The Pb²⁺ detection response of this MOF-modified electrode allowed to achieve a detection limit of about 18 µg L⁻¹ with a correlation coefficient (R²) of about 0.9962, extending in a linear concentration range from 50 to 300 µg L⁻¹. Drinking water samples (as-received or spiked with well-known lead concentration) were analyzed to determine the concentration of lead ions. Data were also confirmed by Atomic Absorption Spectroscopy (AAS). Furthermore, the electrochemical determination when compared with the AAS, has shown that the electroanalytical approach represents a fast and quite reliable alternative for monitoring heavy metals.

Keywords: “MOF – 235”; “carbon paste electrode”; “lead”; “modified electrode”

1. INTRODUCTION

Lead is known as an extremely toxic metal element, which can be accumulated in the skin, bones and bloodstream. It can be also accumulated in the brain, in the form of organic compounds, which are soluble in fat. A concentration of 10 ppb causes in children a significant decrease in intelligence and a delay in the development of neurological functions [1, 2]. Nevertheless, this heavy metal is industrially used in the manufacture of paints, batteries and metal alloys, reaching 40% of the

solder composition used in electronic components among other applications [3, 4]. For these reasons, lead must be monitored, identified and quantified in various medium and it is of utmost importance.

For this purpose, analytical chemistry has potent and precise instrumental techniques (flame atomic absorption spectrometry (FAAS), atomic absorption spectrometry with graphite furnace (GFAAS), inductively coupled plasma optical emission spectrometry (ICP OES) and inductively coupled plasma mass spectrometry (ICP-MS)) that allow the detection of lower concentrations of different chemical species. However, these methodologies have a high cost for analytical development, maintenance of equipment and need of a specialized labor to be handled, then, the applicability is limited by several parameters [5]. Conversely, electroanalysis (EA) can be considered as an advantageous alternative to other instrumental techniques for detecting, quantifying and monitoring the concentration of different organic and inorganic species due to the fact that these electrochemical methods offer high sensitivity and selectivity [6]

Among the electroanalytical methods, voltammetric approaches are the most used techniques due to their sensitivity, reproducibility and limits of detection. However, the role of the electrode material is of vital importance to enhance the detection response of the pollutant-target in study.

Carbon paste electrodes (CPE) are a special type of heterogeneous materials which consist of a mixture of carbonaceous powder and a water immiscible liquid as a binder. The applicability of this kind of materials was to replace the dipping mercury electrode. However, based-mercury materials continued to be more sensitive and precise for detecting different species. In this frame, the concept of “modifying agents” emerges as an alternative to improve the sensitivity and stability by using substances electrochemically active as modifiers of the surface electrodes. These materials were transformed in electrochemical sensors with important properties such as low background current, easy surface renovation and easy manufacturing.

In recent years, an efficient strategy was developed by mixing carbonaceous conductive materials (graphite, carbon, ink, diamond, nanocarbons, etc.) with electroactive compounds, such polymers, membranes, phenolic compounds, enzymes, metals and so on, to produce modified-electrodes. In this way, metal organic framework (MOF) materials appear as an innovative alternative to modify carbon paste electrodes. MOF components consist of metallic centers connected by organic binders, producing structures in microporous or mesoporous scale, having in their structure high surface area and malleability in their pores, allowing the use of MOF in several areas such as catalysis, adsorption, gas storage, and separation [7]. The special MOF features offer the opportunity to improve the sensitivity of the CPE because the MOF can act as Lewis acid in the catalysis as well as a mediator in the transfer of charge [7].

Among MOF materials, MOF-235 or $[\text{Fe}_3\text{O}(\text{1,4-BDC})_3(\text{DMF})_3][\text{FeCl}_4](\text{DMF})_3$ is presented as an orange powder, with octahedral formation in which the crystals formed have the trivalent iron atoms connected by ditopic ligands (1,4-benzenedicarboxylate acid). Based on the existing literature, MOF-235 has been already used as adsorbent to remove different compounds from water, such as dyes [8], methane, hydrogen and carbon dioxide [9]. Additionally, MOF-235 has been employed as a catalyst in the synthesis of 1,5-benzodiazepine [10] and as a photocatalyst [11]. Therefore, the novelty of this work is based on the use of MOF-235 to modified CPE to determine Pb^{2+} in aqueous samples; and it should be highlighted that, to the best of our knowledge, no attempts have been published about

the exploration of the MOF-235 application as electrochemical sensor yet. In this way, CPE was used as support to be modified with MOF-235 (MOF-235/CPE), aiming to increase the sensitivity, stability, reproducibility, and low detection limit for determining lead in aqueous solutions by using anodic redissolution voltammetry.

2. METHODOLOGY

2.1. Reagents

A standard solution of 1000 ppm Pb^{2+} was prepared by dissolving 0.16 g of $\text{Pb}(\text{NO}_3)_2$ in 100 ml of 1% (v/v) HNO_3 solution. Additional Pb^{2+} solutions were prepared from the standard solution. Ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), terephthalic acid (H_2BDC), N, N-dimethylformamide (DMF), ethanol, powder graphite, and mineral oil used in this work were of analytical grade. The acetate buffer solution of 0.2 mol L^{-1} (pH = 4.6) was used as supporting electrolyte.

2.2. Instrumentation

The X-ray diffraction patterns (XRD) of the MOF-235 were obtained in the BRUKER diffractometer, model: D2 PHASER from 3° to 70° with angular pitch of 0.02° in order to characterize the material used to modify the CPE. Mean Fourier transform infrared (FTIR) spectra were also obtained for the MOF-235 in the BRUKER model FT-IR VERTEX 70 in the range of 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1} . Electrochemical measurements were performed by using a potentiostat/galvanostat Autolab PGSTAT 302N with an electrochemical cell with three electrodes, Ag/AgCl KCl 3M as reference electrode, platinum as counter electrode and the MOF-235-modified carbon paste electrode as working electrode. The lead concentration was also quantified by AAS, using a Shimadzu Absorption model 1035; for these measurements, a calibration method was employed.

2.3. Synthesis of MOF – 235

MOF-235 was synthesized by the solvothermal method with autogenous pressure as previously reported in [8]. A well-known amount of terephthalic acid (0.205 g, 1.23 mmol) was mixed with 60 mL of DMF. This mixture was stirred for 30 minutes until that H_2BDC was completely dissolved. The ferric chloride (0.200 g, 0.738 mmol) was mixed with 30 mL of ethanol and stirred until its complete dissolution. Then, 30 ml of the DMF/ H_2BDC solution was added to the solution of ferric chloride/ethanol mixture, stirring for 10 min. After that, the precursor solution was then inserted into a Teflon reactor and placed in an electric oven at 80°C during 24 h. An orange powder was collected by centrifugation and it was washed with ethanol/DMF mixture for 5 times. Subsequently, MOF-235 was dried for 12 h at 150°C to remove solvent excess.

2.4. Preparation of the modified carbon paste electrode with MOF-235

The working electrode was prepared by weighting different amounts of graphite powder (0.95, 0.93, 0.90, 0.88 and 0.86 g) with a proportional quantity of MOF-235 (0.05, 0.07, 0.1, 0.12 and 0.14 g) to obtain ratios, in terms of w/w, about of 5, 7, 10, 12 and 14%, respectively. This mixture was mechanically homogenized in a mortar and pistil made from borosilicate glass. After that, 0.3 ml of mineral oil was added and mixed until that a homogeneous paste was formed, which was packed in a glass tube (7 cm × 6.5 mm² internal area). A copper wire was also used (6 mm²) as electrical contact.

2.5. Experimental Procedure

To obtain a higher sensitivity, differential pulse voltammetry with anodic dissolution procedure was used as analytical technique. During the experimental procedure, 10 ml of 0.2 mol L⁻¹ acetate buffer solution (pH 4.6) was added in a suitable cell. The pre-concentration step was performed under constant agitation by applying -0.9 V for 300 s, and an equilibration time of 30 s. After the pre-concentration step, anodic stripping voltammetry was used in a potential range from -0.9 V to -0.1 V at 10 mV s⁻¹. The calibration curve was obtained by plotting the current peak as a function of the concentration of lead in ng L⁻¹.

2.6. Real samples

Five samples of drinking water were collected at the Federal University of Rio Grande do Norte in different departments. The samples were preserved in glass reservoirs at 20°C. To analyze the samples by electrochemical procedure, 7 mL of each one of samples were putted in the electrochemical cell, and the pH was adjusted to 4.6 using the acetate buffer solution of 0.2 mol L⁻¹. After that, the standard solution of 1000 ppm Pb²⁺ was employed to spike each one of the samples to obtain a well-known concentration of 50 ppb. Anodic dissolution procedure was carried out to determine the concentration of lead as well as to establish the recovery, for each one of the samples. Values obtained were also confirmed by Atomic Absorption Spectroscopy (AAS).

3. RESULTS AND DISCUSSION

3.1. Characterization of MOF-235

Figure 1 shows the FTIR spectrum of MOF-235 with peaks at 1663, 1597, 1398, 1016 and 750 cm⁻¹ which are characteristic vibrations signals from carboxyl groups. Meanwhile, the peaks located at 597 and 1398 cm⁻¹ correspond to the symmetrical/asymmetric C=O vibrations by carboxyl groups, suggesting the presence of a dicarboxylate linker present in the sample. The peak at 750 cm⁻¹ is related to the C-H binding vibration present in the aromatic ring. These results confirm that the MOF-235 was obtained [12]. Figure 2 shows the X-ray diffraction (XRD) pattern indicating high crystallinity of the material obtained due to the well-defined peaks with 2 θ = 9.7, 10.8, 12.6, 19, 22 patterns. These signals have been previously reported in the literature [12]

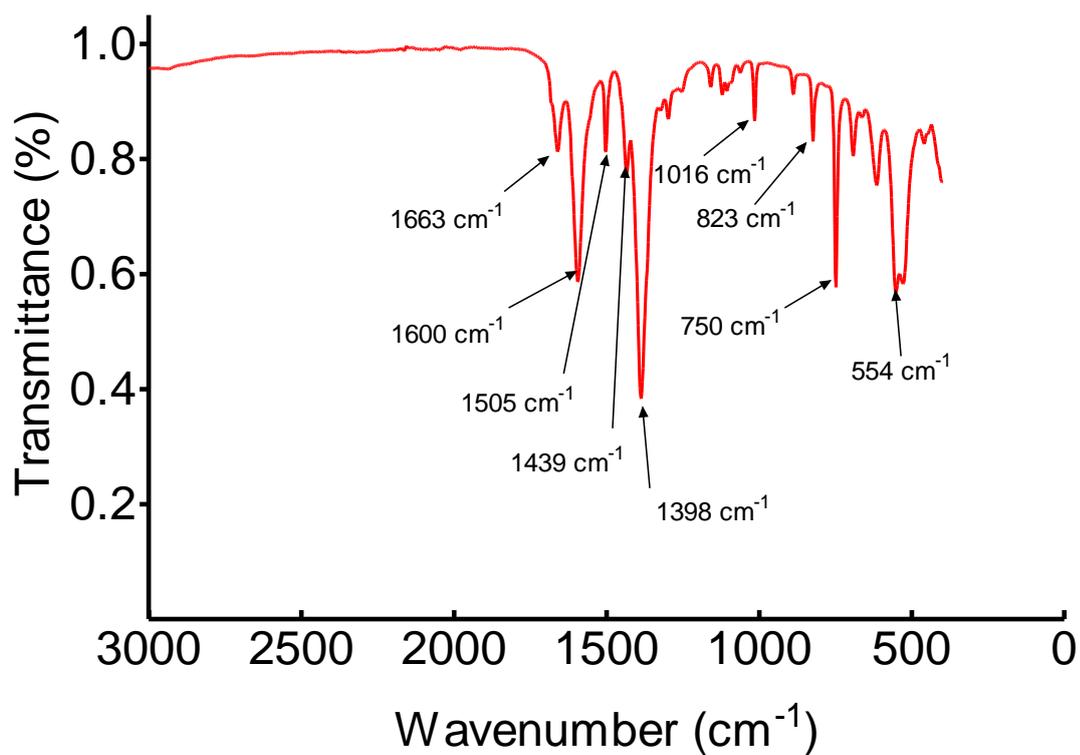


Figure 1. FTIR spectra of the synthesized MOF-235.

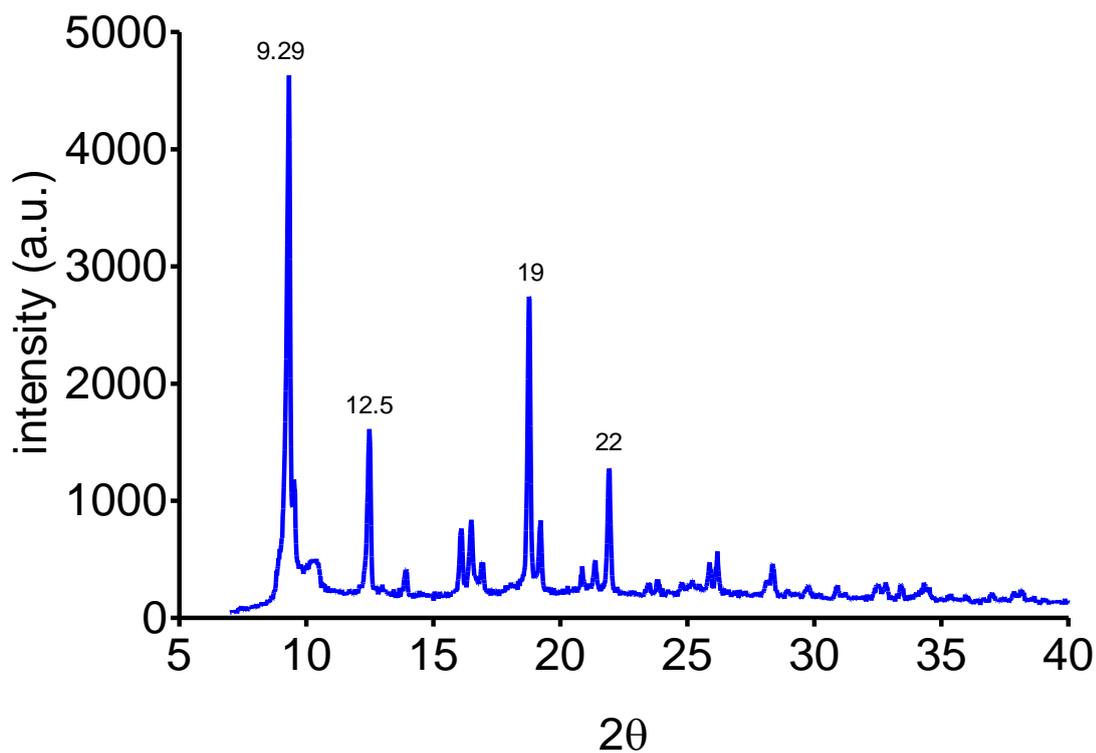


Figure 2. XRD pattern of MOF-235.

3.2. Electrochemical characterization of MOF-235/CPE

In order to determine the effect of MOF-235 concentration for determining Pb^{2+} , a set of experiments were performed by evaluating the peak intensity as a function of the percentage of MOF-235 that was used to modify CPE. As can be observed in Fig. 3, different MOF-235/CPE with 5%, 7%, 10%, 12% and 14% of MOF-235 were used for detecting Pb^{2+} ions in aqueous solutions by anodic redissolution voltammetry (potential ranging from -0.9V to -0.1V) with buffer acetate (0.2 mol L^{-1} , $\text{pH} = 4.6$) as supporting electrolyte. Depending on the MOF-235 percentage, the modified electrodes were identified as MOF-235(5%)/CPE, MOF-235(7%)/CPE, MOF-235(10%)/CPE, MOF-235(12%)/CPE and MOF-235(14%)/CPE. All modified electrodes were also compared with CPE. Pb^{2+} voltammetric signal appears between -0.55V and -0.58V, in all cases, as shown in Fig. 3. The results clearly showed that the unmodified CPE exhibited a different current peak respect to the voltammetric signals obtained with MOF-235/CPE varying the MOF-235 ratio. For MOF-235(5%)/CPE and MOF-235(7%)/CPE, lower current responses were registered when compared with CPE; while the modified MOF-235 electrodes in proportions of 10%, 12% and 14% presented higher voltammetric signals (see inset in Fig. 3). This behavior is due to the behavior of MOF-235 as Lewis acid when it was introduced in the CPE, and consequently, facilitating that the Pb^{2+} ions can be trapped into the MOF structure. Probably, the transfer of charge-resistance between the electrode material and the lead ions decreases during the pre-concentration step, allowing a better detection of Pb^{2+} when the MOF-235 ratio is increased in the CPE. As the MOF-235(10%)/CPE had an excellent performance, it was the sensor selected for the next experiments. It is not necessary to increase the MOF ratio until 12% to obtain a most significant current response.

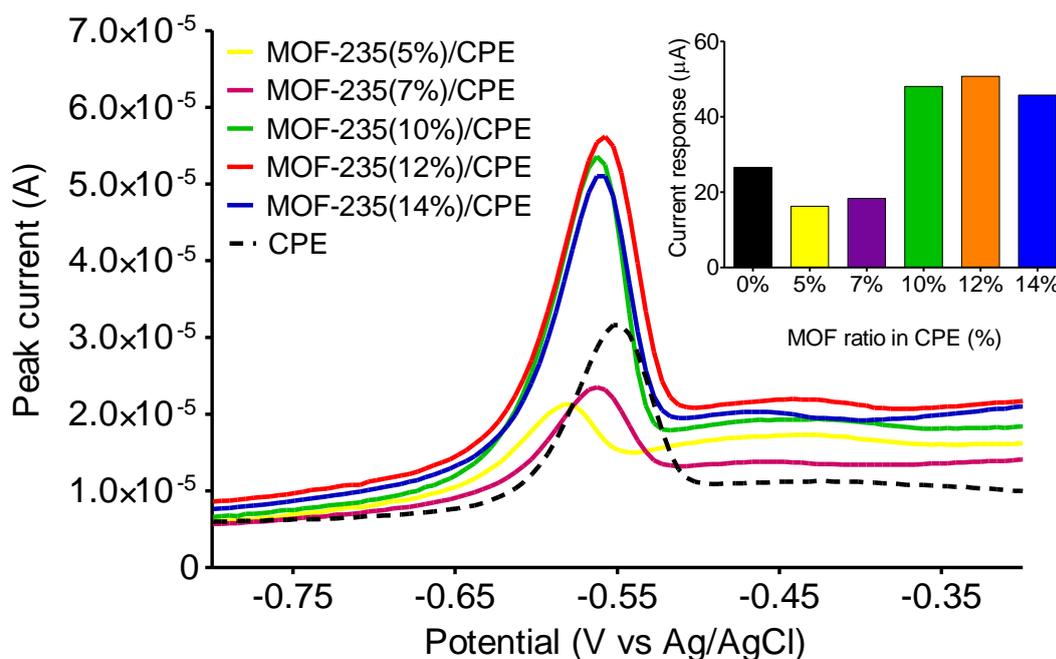


Figure 3. Effect of the MOF-235 ratio used to modify the CPE on the Pb^{2+} detection response. Experimental conditions: $[\text{Pb}^{2+}] = 150 \text{ ng L}^{-1}$, pre-concentration potential: -0.9 V, volume of solution: 10 mL.

Although the preliminary results about the voltammetric response, using acetate buffer solution as supporting electrolyte (the most used electrolyte according the literature [2, 5, 13–17], are very interesting; different supporting electrolyte solutions were also tested (such as sodium nitrate (0.2 mol L^{-1}), nitric acid (0.2 mol L^{-1}), sulfuric acid (0.2 mol L^{-1}) and phosphate buffer (0.2 mol L^{-1}) solutions) in order to enhance the current peak response during the detection of Pb^{2+} . Results clearly demonstrated that the acetate buffer solution (0.2 mol L^{-1}) was the most suitable electrolyte solution, which contributes to obtain a well-defined voltammetric signal, increasing the response respect to the other supporting electrolytes (see Fig.4).

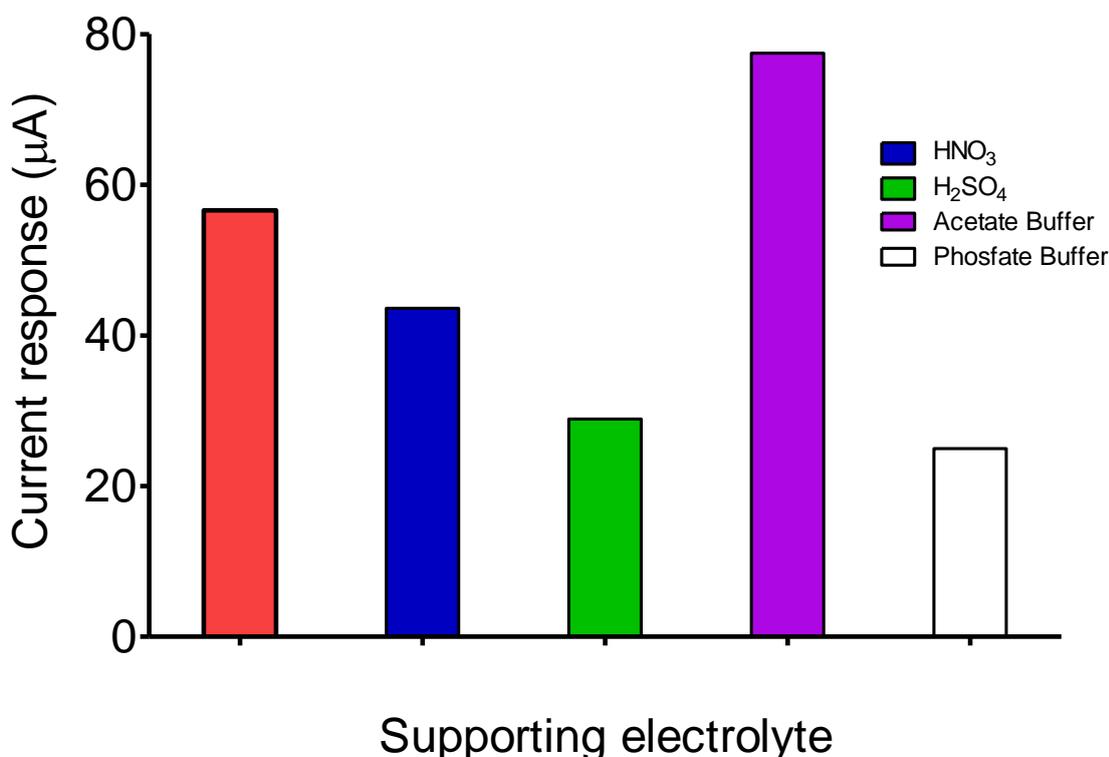


Figure 4. The influence of supporting electrolyte on the current response to detect Pb^{2+} ions with MOF-235(10%)/CPE. Experimental conditions: $[\text{Pb}^{2+}] = 150 \text{ ng L}^{-1}$, pre-concentration potential: -0.9 V , volume of solution: 10 mL .

The effect of pH conditions was also studied on the current sensibility-response by using acetate buffer solution. As can be observed in Figure 5, higher current response was achieved at pH 4.6. Meanwhile, an increase on the pH conditions avoids the determination of soluble Pb^{2+} ions by electroanalysis technique. This behavior is related to the formation of complexes between the Pb^{2+} and the OH^- ions. For this reason, the solution of buffer acetate was used as supporting electrolyte for further electrochemical measurements.

The appropriate potential and time of deposition can significantly improve the determination of traces of lead in water, making the pre-concentration stage one of the most important parameters. Therefore, the potential deposition and time were studied in order to understand the effect of these

experimental conditions on the detection of Pb^{2+} . This information is of extreme importance since the difference on the current response is significantly marked when a remarkable time range is used, from 30 to 300 s, as shown in Figure 6.

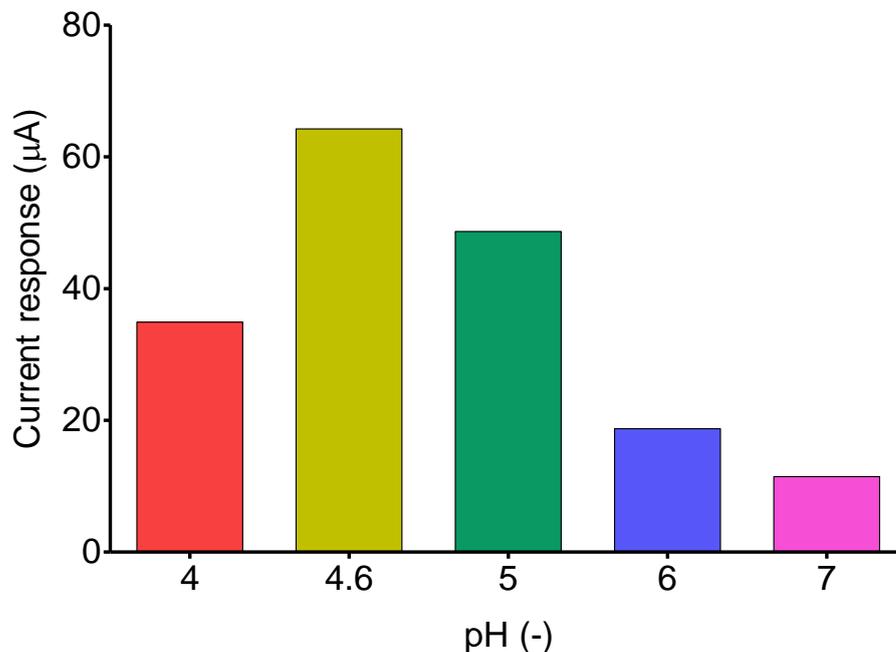


Figure 5. Effect of pH on the voltammetric signal during the determination of Pb^{2+} using MOF-235(10%)/CPE. Experimental conditions: $[Pb^{2+}] = 150 \text{ ng L}^{-1}$, pre-concentration potential: -0.9 V, volume of solution: 10 mL.

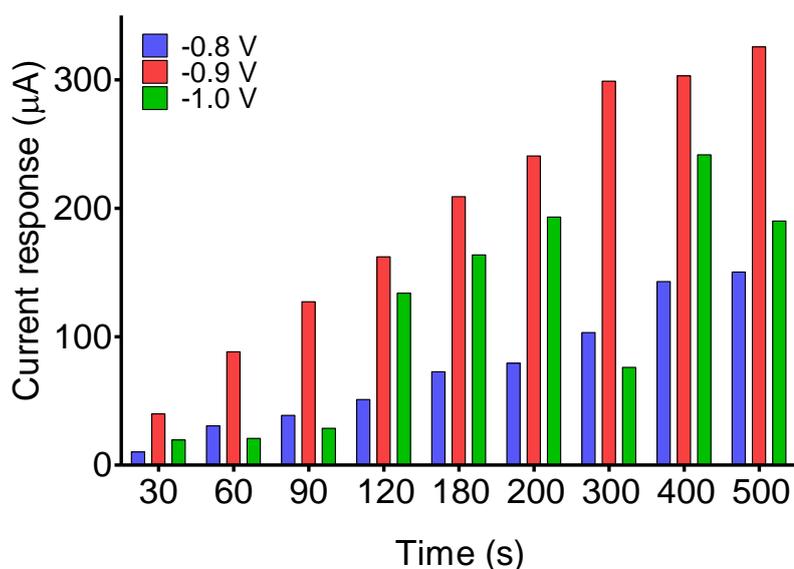


Figure 6. Effect of potential and deposition time on differential pulse voltammetry signal for determining Pb^{2+} with MOF-235(10%)/CPE. Experimental conditions: $[Pb^{2+}] = 150 \text{ ng L}^{-1}$, supporting electrolyte = acetate buffer (0.2 mol L^{-1} , pH = 4.6), volume of solution: 10 mL.

As illustrated in Fig. 6, in all cases, an increase on the deposition time favored an increase on the sensitivity of the MOF-235(10%)/CPE. The data also show that over 300 s the surface of the electrode modified with 10% MOF - 235 is saturated, and shorter times decrease the sensitivity of the determinations. Thus, the best deposition potential was registered as -0.09 V, and consequently, these conditions being selected to obtain the calibration curve.

3.3. Calibration

After the optimization of all parameters, the anodic redissolution voltammetric response was evaluated, using acetate buffer at pH 4.6, deposition time of 300 s and potential of -0.9V, to determine the analytical curve. Different Pb^{2+} concentration solutions were used to obtain the analytical curve, as shown in Figure 7. As can be observed, the current peak had a good linear relationship with the Pb^{2+} concentration. Results also showed that after the expected linear tendency at the lower concentration levels, the slope diminished up to reach an asymptotic value (data not showed). The calibration plot was linear between 50 – 300 ppb (inset, Fig. 7a). At lower concentration values the reproducibility of the response was poorer. A well-established number of analytical curves were achieved using CPE, evaluating the peak intensity, as a function of the Pb^{2+} concentration, and considering at least six analyte concentrations. The functional relationship was $i = (0.24 \pm 0.01) [\text{Pb}^{2+}] - (3.87 \pm 1.84)$ (slope and intercept were the average of four independent calibrations) where I and the Pb^{2+} are expressed in μA and ppb, respectively.

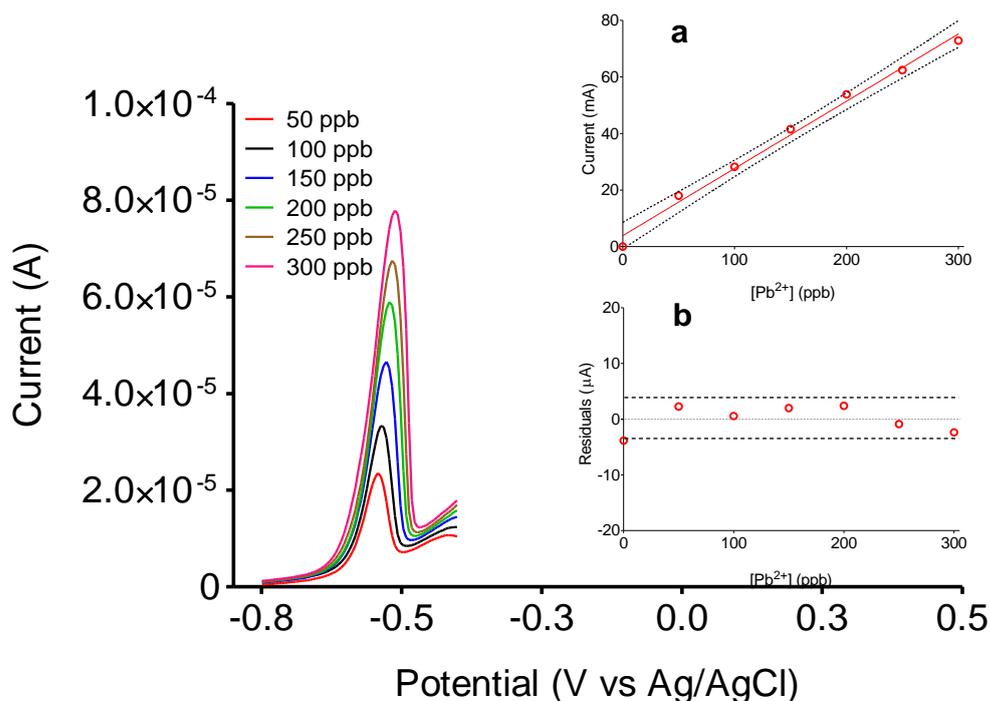


Figure 7. Anodic redissolution voltammetric curves performed with MOF-235(10%)/CPE, varying the Pb^{2+} concentration from 50 to 300 ppb. Insets: (a) typical calibration plot, current response, as a function of Pb^{2+} concentration ($n = 6$; $r^2 = 0.9951$; $P = 95\%$) and (b) residuals plot with 5% of confidence lines.

The limit of detection was estimated from the equation $LOD = 3.3S_b/m$, where S_b is the standard deviation of the measurements and m is the coefficient of the calibration curve. The limit of detection (LOD) was approximately 18 ppb. This approach allows to control both false positive and false negative errors ($\alpha=\beta=0.05$), as recommended by IUPAC [18-21] as well as already established by experts in the field [22,23]. Additionally, the residuals of the regression are randomly distributed around the zero (inset, Fig. 7b), allowing a visual verification of the absence of a significant non linearity [24]. Another feature is that no noteworthy alterations in calibration curves were recorded in different days, confirming the good stability of the MOF-235(10%)/CPE. The above results allow us to conclude that good repeatability and reproducibility of analytical measurements can be achieved by using MOF-235(10%)/CPE with no electrochemical cleaning or pre-treatment of the electrode surface. In fact, the performance of the novel MOF-235/CPE was superior to other ones, in terms of LOD, as showed in Table 1. In other cases, the modification proposed is time-consuming, several steps are required or expensive reagents/materials are used, which is a disadvantage respect to the electrochemical sensor recommended here. For example, the 1,3,5-tris(4-aminophenyl)benzene–2,5-dimethoxyterephthaldehyde–covalent organic framework/CPE, which has a significant LOD ($0.39 \mu\text{g L}^{-1}$) but the preparation is relatively more complex than that MOF-235(10%)/CPE.

Finally, the proposed electrochemical sensor was used to determine lead in 05 drinking water samples. When the samples were adjusted in pH (by using buffer acetate) and consequently analyzed, no significant amount of lead was detected (lower than LOD). Therefore, the same samples were spiked with well-known concentration of lead (approx. 50 ppb), and pH conditions were also adjusted by using buffer acetate as supporting electrolyte. After that, the Pb^{2+} concentration was determined for each one of the samples spiked. According the results, no matrix effects were observed due to the composition of each one of the drinking water samples. Pb^{2+} concentrations estimated using the analytical curve obtained by anodic dissolution procedure are reported in Table 2. The samples analyzed, with both anodic dissolution procedure and AAS, to quantify the concentration of Pb^{2+} provided similar outcomes, with modest discrepancies.

Table 1. The comparison of the proposed method with other electrochemical sensors developed for determining Pb^{2+} ions.

Electrode materials (modifier/electrode)	Linear range ($\mu\text{g L}^{-1}$)	Detection limit ($\mu\text{g L}^{-1}$)	Ref.
Sb/CPE	50–201	0.9	[25]
Tripolyphosphate-kaolinite/CPE	62.6–1450.4	17.4	[26]
Salicylic acid/glassy carbon spheres	207.2–2072	37.3	[27]
Poly(diphenylamine-co-2-aminobenzonitrile) film/glassy carbon electrode	259–58730	165.8	[28]
MOF-5/CPE	2.1–207.2	1.01	[2]
Black Rice/CPE	50–200	14.58	[29]
crosslinked chitosan with glutaraldehyde/carbon nanotube paste electrode	20.72–414.4	11.81	[30]
Bi-Poly1,8- diamionaphthalene/CPE	0.5–50	0.3	[31]
Calixarene bulk modified screen-printed electrodes	100–2400	38	[32]

1,3,5-tris(4-aminophenyl)benzene–2,5-dimethoxyterephthaldehyde–covalent organic framework/CPE	1–414	0.39	[33]
MOF–235	50–300	18	This work

Table 2. Determination of Pb²⁺ concentrations by using the anodic dissolution and ASS procedures as well as the recovery.

Sample	Electrochemical/ppb	ASS/ppb	recovery(%)
1	51.6	51.0	100.3
2	49.5	50.5	99.0
3	48.9	49.8	97.8
4	49.7	49.7	99.4
5	51.2	50.1	102.4

4. CONCLUSION

An easy and rapid cost-effectiveness sensor for determining Pb²⁺ was carried out using CPE modified with metal-organic framework composite. From the results reported in this work, the use of different MOF-235 ratio demonstrated that 10% of MOF-235 in CPE was enough to obtain a higher and a rapid voltammetric response during detection of lead ions. This sensor is a novel alternative respect to more toxic or expensive modification materials (such as nanotubes, mercury polarography and so on, as showed in Table 1). The electroanalytical modified MOF electrode can be considered as a less time-consuming and a less expensive tool than other analytical methods. This electrode was very favorable for its use in acidic determination of Pb²⁺ as well as this procedure is precise, with a quantification limit of 18 ppb and quite reproducible. Although the difference between Pb concentrations determined with anodic dissolution and AAS is on average around 10%, the electroanalytical method can be used with acceptable confidence, ensuring precision of quantification and a good sensitivity; in addition, it is cheaper than the commonly used spectroscopic ones, which also require the use of more toxic and expensive reagents. At present, our results demonstrate the potential of electroanalytical techniques for monitoring the course of environmental interventions.

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