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Electrochemical Detection of Lead Ions with Ordered Mesoporous Silica–Modified Glassy Carbon Electrodes

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Abstract The development of methods for lead ion determination in various biological and environmental samples is both necessary and challenging. In this context, considering the properties of both SBA-15 and MCM-41 mesoporous materials and the role of NH_2-functional groups grafted on the silica surface (SBA-15-NH_2 and MCM-41-NH_2), the aim of the study was to investigate the electrochemical detection of Pb^{2+} by means of silica-modified glassy carbon electrodes (GCEs). The square wave anodic stripping voltammetry (SWASV) was used to characterize the modified electrodes with four different samples of ordered mesoporous silica (OMS) powders, mentioned above. Additionally, scanning electron microscopy (SEM) was used to characterize these modifiers. Pb^{2+} exhibits a well-defined oxidation peak (around − 0.5 V vs. Ag/AgCl/KCl_{sat}) and high peak current at either bare or OMS-modified glassy carbon electrodes, but the best response was recorded in the case of GC/SBA-15-NH_2-modified electrode in 0.1 M acetate buffer. The performance of the prepared electrodes is highlighted by good analytical parameters (satisfies the requirements of low cost and rapid results), which recommends them to be used for real sample analysis.

Keywords Ordered mesoporous silica · Silica-modified glassy carbon electrodes · Square wave anodic stripping voltammetry · Lead ion detection

1 Introduction

Heavy metals are environmental priority pollutants, especially in developing countries with rapid industrialization of the economy (Chu et al. 2019). Many heavy metal ions (HMIs) are known as toxic and carcinogenic. HMIs of particular concern such as Cd^{2+} (Awual et al. 2018), Cu^{2+} (Cao et al. 2013), Hg^{2+} (Hazra et al. 2019), Ni^{2+} (Li et al. 2013), Pb^{2+} (Kang et al. 2017), and their compounds are widely used in industries and, unlike organic contaminants, are not biodegradable leading to contamination of natural water, tending to accumulate in living organisms and threatening the health of human beings. It is worth mentioning that Cd^{2+}, Cu^{2+}, Hg^{2+}, and Pb^{2+} are the most common HMIs present in our daily lives. The importance of controlling the level of environmental pollutants in natural waterways and

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potable water has generated increasing interest in the development of novel sensors for the detection of HMIs such as lead ions.

Lead has several uses, such as in accumulators, ammunitions, piping, paints, anti-radiation screens, and tin-based welding alloys, as well as the industrial processing of other metals, for example silver, gold, and bismuth (Sadiq and Alan 1997). A medical condition caused by elevated levels of the lead metal in the blood is lead poisoning. The detection of Pb^{2+} becomes an important concern of the research, because humans accumulate elevated levels of lead in the blood stream, which affect seriously their one health (kidney, liver, cardiovascular, brain functions, reproductive and immune system) (Afkhami et al. 2013) and its detection becomes an important concern of the research. Therefore, this led to increasing demands to develop reliable methods that can rapidly detect Pb^{2+} in a sensitive and selective manner (Awual et al. 2018).

For the detection of trace amount of lead, many standardized methods have been used, such as atomic absorption spectrometry (AAS) (Fayazi et al. 2016), atomic fluorescence spectrometry (AFS), and inductively coupled plasma mass spectroscopy (ICP-MS) (Sánchez Trujillo et al. 2013) or atomic emission spectrometry (ICP-AES) (Wuilloud et al. 2002). However, electrochemical methods are often preferred due to their simplicity, efficiency, high selectivity, excellent sensitivity, short analysis time, portability, and low cost (Cunci and Cabrera 2011).

In order to determine Pb^{2+}, the electrochemical properties of various modified glassy carbon electrodes were investigated by other authors and previously reported (Xiong et al. 2013; Zhou et al. 2016). Among the modifiers, silica-based materials deserve special attention for a number of reasons. The siliceous mesoporous materials, mainly SBA-15 and MCM-41, have attracted the scientists' interest due to their large specific surface areas (200–1200 $m^2\ g^{-1}$), ordered structure (El-Salamony et al. 2017), inert framework, non-toxicity (Hudson et al. 2008), and hydro/thermal stability (Mesa et al. 2008), which allow them to be used as catalyst and enzyme supports (Pitzalis et al. 2017), as well as adsorbents (Llewellyn 2014; Lachowicz et al. 2019), sensing devices (Buica et al. 2013), or drug delivery systems (Nairi et al. 2017; Wang 2009). Recently, we used OMS-modified glassy carbon electrodes (GCEs) for the electrochemical detection of malachite green (MG) (Sacara et al. 2017) and Cd^{2+} ions (Sacara et al. 2019). It was found that OMS modification of GCE to obtain GC/OMS/Nafion significantly improved the sensitivity and the detection limits of either MG or Cd^{2+} respect to GC/Nafion electrodes.

This work is aiming to establish the optimal conditions for the analysis of Pb^{2+} by square wave anodic stripping voltammetry (SWASV), using glassy carbon electrodes drop-casted with a composite layer containing one of four different types of OMS (pristine SBA-15 and MCM-41 and amino-functionalized silica (SBA-15-NH_2 and MCM-41-NH_2) (McManamon et al. 2012; Guo et al. 2015), immobilized in an ion-exchange polymer (Nafion).

2 Experimental Section

2.1 Apparatus

The electrochemical experiments were conducted using an Eco Chemie Metrohm Autolab PGSTAT302N 30 V/2 A (Utrecht, The Netherlands) connected to a PC for control and data storage. A classical three-electrode cell (10 mL volume, Princeton Applied Research, USA) containing a glassy carbon (GC) electrode (inner diameter of 3 mm, polyether ether ketone isolation, ALS Ltd., Japan) as the working electrode, a silver/silver chloride electrode in saturated potassium chloride solution (Ag/AgCl, KCl_{sat}) as reference electrode, and a platinum plate (Radiometer Analytical M241Pt, USA) as counter electrode was employed for the electrochemical studies. The pH measurements were made using a glass electrode connected to a Hanna Instrument HI2002 pH meter.

For morphological analysis, the samples deposited on glassy carbon electrodes were coated with a 10-nm gold layer and performed using a Hitachi SU8230 High Resolution Scanning Electron Microscope (SEM) equipped with a cold field emission gun.

Standard measurements by inductively coupled plasma optical emission spectrometry (ICP-OES) were performed with a Spectro CirosCCD (Spectro Kleve, Germany) apparatus.

2.2 Reagents

All reagents were of analytical grades and used without further purification. Deionized water was used to prepare all solutions. Working solutions were freshly prepared before use by diluting stock solutions. Tetraethoxysilane (TEOS, 98%),

hexadecyltrimethylammonium bromide (CTAB, > 99%), Pluronic copolymer 123 (EO_{20}-$PO_{70}EO_{20}$), sodium hydroxide, anhydrous toluene (99.8%), 3-aminopropyltriethoxysilane (APTES, > 98%), triethylamine (> 99%), and hydrochloride acid (37%) were purchased from Sigma-Aldrich (Milan, Italy). A 0.1 mol L^{-1} acetate buffer solution with pH 4.4 was prepared by mixing $C_2H_3NaO_2$ with CH_3COOH (Merck, Darmstadt, Germany). Sodium dodecyl sulfate (SDS) and Nafion (5% wt. ethanol) were purchased from Sigma-Aldrich (Milan, Italy). $ZnSO_4 \cdot 7H_2O$ (Sigma-Aldrich, Milan, Italy), $Cd(CH_3COO)_2 \cdot 2H_2O$ and $Pb(CH_3COO)_2 \cdot 3H_2O$ were purchased from Reactivul Bucuresti, Romania.

2.3 Synthesis of OMS Samples

MCM-41, MCM-41-NH_2, SBA-15, and SBA-15-NH_2 samples were synthesized according to a previously reported procedure and their physico-chemical characterisation (TEM, SAXS, TGA, etc) are described thoroughly by Salis et al. (2010, 2016).

2.4 Preparation of the Modified GC Electrode

Prior to any modification, the GC electrode was polished to a mirror-like surface on a piece of felt with alumina slurry (0.3 nm), rinsed thoroughly with deionized water after each step, then washed successively with ethanol and deionized water for 2 min in an ultrasound bath separately and dried. In order to obtain a homogeneous suspension and to prevent precipitation and aggregation of silica particles, 1% of SDS was used to prepare 2.0-mg/mL OMS suspensions. The cleaned GCE surfaces were covered by drop-casting with 5.0 μL suspension and dried at room temperature (RT). To improve the stability of samples, 5.0 μL of Nafion 2.5% (prepared by dilution with ethanol from a 5% wt. solution) was added on the electrode surface. The coating was allowed to dry at RT for 20 min. Before use, the electrodes were equilibrated for 10 min in the supporting electrolyte solution. The GC/Nafion electrode was compared with all other electrodes being the reference. The investigated GCEs were Nafion-modified with or without OMS (namely GC/Nafion; GC/SBA-15/Nafion; GC/SBA-15-NH_2/Nafion; GC/MCM-41/Nafion; GC/MCM-41-NH_2/Nafion).

2.5 Electrochemical Measurements

All experiments were performed at room temperature (RT, 22 ± 2 °C), and by pumping argon gas in solution, the dissolved oxygen was removed. All potentials reported in this paper were referenced to Ag/AgCl (in saturated KCl solution). SWASV was used to study the electrochemical behavior of Pb^{2+}.

SWASV conditions were as follows: potential range, from − 0.7 V to − 0.4 V vs. Ag/AgCl, KCl_{sat}; frequency, 25 Hz; amplitude, 0.07 V; and step potential, 0.005 V; after equilibration, 5 s; electrode conditioning, 0 V vs. Ag/AgCl, KCl_{sat}; duration, 60 s; deposition time, 120 s; deposition potential, − 1 V vs. Ag/AgCl, KCl_{sat}.

3 Results and Discussion

3.1 Electrochemical Determination of Pb^{2+}

As a highly sensitive and low detection limit electrochemical method, SWASV was used to detect the Pb^{2+} ions. The role of –NH_2 functional groups grafted on the silica surface on the electrochemical behavior of the modified electrodes was also investigated. Starting from the literature data (Xiong et al. 2013), 0.1 M acetate buffer was chosen as electrolyte.

3.2 Influence of Silica Type

The results presented in Fig. 1 are in line with those obtained for the determination of surface area of the working electrode (GC). A difference of the Pb^{2+} signal strength between the SWASV represented in Fig. 1a (GC/Nafion, GC/SBA-15/Nafion, and GC/SBA-15-NH_2/Nafion) and Fig. 1b (GC/Nafion, GC/MCM-41/Nafion, and GC/MCM-41-NH_2/Nafion) is seen. Besides the unique properties of OMS, the highest I_p and the less positive E_p result from their large surface areas.

Figure 2 a shows the SWASV of the GC/SBA-15-NH_2/Nafion electrode in 0.1 M acetate buffer (pH 4.4) containing various concentrations of Pb^{2+} (0.5–6.0 μM), and from Fig. 2b, it could be seen that the peak current height varied linearly with Pb^{2+} concentration in the same range. In Table 1, the electroanalytical parameters of the various GC modified electrodes with mesoporous silica and Nafion are presented, and it can be seen that the best analytical performance belongs to the electrode with GC/SBA-15-NH_2/Nafion, where the

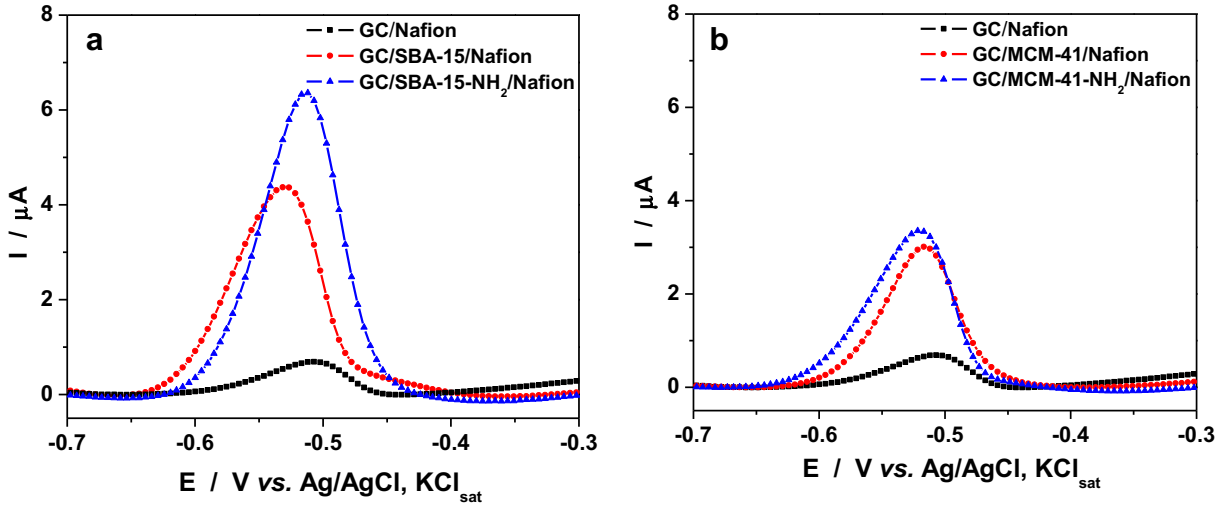

Fig. 1 SWASV measurements for GC bare and modified with OMS electrodes in 0.5 µM Pb^{2+} solution at pH 4.4. Experimental condition: electrolyte, 0.1 M acetate buffer; starting potential, − 0.7 V vs. Ag/AgCl, KCl_{sat}; frequency, 25 Hz; amplitude, 0.05 V; step potential, 0.001 V, deoxygenation using Ar for 5 min before measurements and 60 s between each measurement

calibration curve and correlation coefficient for Pb^{2+} was: I_{peak} (µA) = 1.33 C (µM) + 4.81 (R = 0.9983 for 12 experimental points).

3.3 Calibration Curves and Electroanalytical Parameters

Calibration curves for the silica-modified GC electrodes were drawn for all silica-modified electrodes by plotting the peak current, I_{peak}, versus the lead ion concentration (Fig. 3), and the corresponding electroanalytical parameters are listed in Table 1.

In Table 1, the detection limits (DLs) were calculated for a signal-to-noise ratio of 3, using the formula DL = 3SD/slope, where the slope and standard deviation (SD) correspond to the parameters of the fitting equation.

It can be seen that all silica powders immobilized on GC surface have a good impact on metal ion detection due to their good adsorption properties.

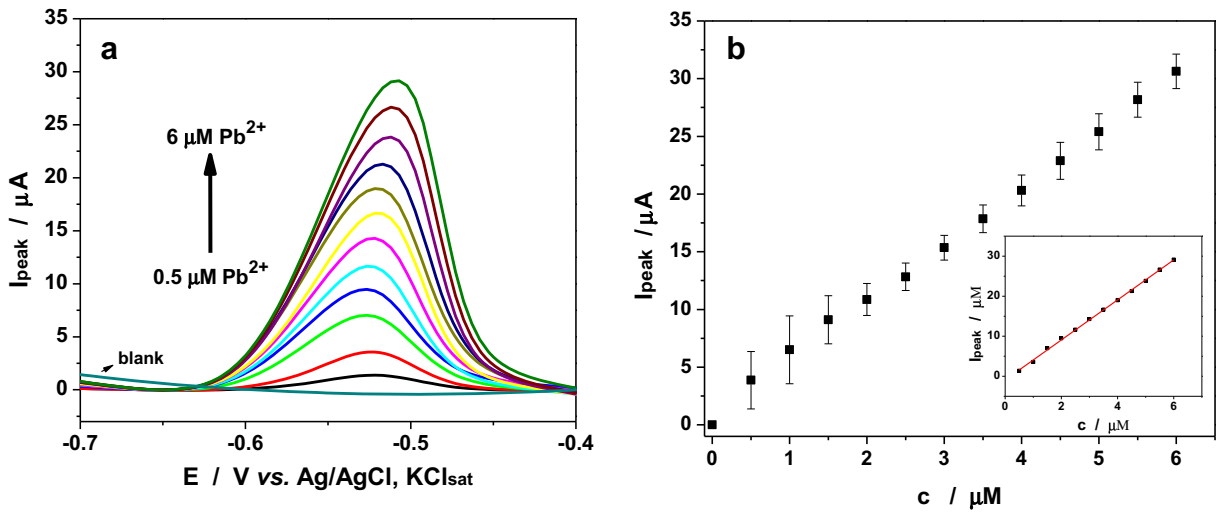

Fig. 2 SWASV measurements recorded for Pb^{2+} detection at GC/SBA-15-NH_2/Nafion modified electrode in acetate buffer of pH 4.4 (**a**). Calibration curve and the corresponding linear region of the polarization curve (inset) (**b**). Experimental conditions: electrolyte, 0.1 M acetate buffer; starting potential, − 0.7 V vs. Ag/AgCl, KCl_{sat}; frequency, 25 Hz; amplitude, 0.05 V; step potential, 0.001 V, deoxygenation using Ar for 5 min before measurements and 60 s between each measurement. The error bars correspond to the mean of three successive measurements with three different electrodes

Table 1 Electroanalytical parameters of the various GCEs modified with OMS and Nafion

Electrode	Sensitivity (A/M)	Detection limit (μM)	Linear domain (μM)	R^2/N^*
GC/Nafion	1.35 ± 0.069	1.68	0.5–4	0.9861/8
GC/SBA-15/Nafion	3.36 ± 0.037	0.72	0.5–5	0.9993/10
GC/SBA-15-NH_2/Nafion	4.81 ± 0.063	0.23	0.5–6	0.9983/12
GC/MCM-41/Nafion	2.92 ± 0.049	1.17	0.5–4	0.9985/8
GC/MCM-41-NH_2/Nafion	2.39 ± 0.051	1.26	0.5–5	0.9898/10

N^* represents the number of experimental points

Despite their smaller specific surface area, silica powders SBA-15 (S_{BET} = 880 m^2/g) and SBA-15-NH_2 (S_{BET} = 373 m^2/g) were proven to perform more than MCM-41 (S_{BET} = 1061 m^2/g) and MCM-41-NH_2 (S_{BET} = 894 m^2/g), in which the detection limit of the electrodes is concerned, suggesting that the surface area is not the only characteristic of the silica powders that should be taken into consideration. The best results were obtained with the GC/SBA-15-NH_2/Nafion electrode (lowest detection limit and highest sensitivity). The presence of the –NH_2 group has a beneficial effect on electrodes' performances, being probable that amino groups bind metal ions, thus increasing their concentration at the interface during the accumulation step (Dai et al. 2014) and hence lowering the detection limit. Moreover, considering that the SBA-15 structures are synthesized from non-ionic templates and show thicker walls, they usually are more stable than the MCM-41 structure. Similar results were previously obtained for Cd^{2+} detection through OMS-modified GCEs. In that case, besides an effect due to surface area and surface functionalization, an additional effect due to solution pH was observed. Indeed, while at pH 4.4 the GC modified with MCM-41 (the material with the highest surface area) gave the highest sensitivity; at pH 6, this was obtained with the SBA-15-NH_2-modified electrode. It is hence likely that the GCE performances, expressed by the slopes of the electrochemical calibration curves, are the outcome of several contrasting effects involving OMS surface area and functionalization, as well as metal ion species, the nature, and the pH values of buffer solution (Sacara et al. 2019).

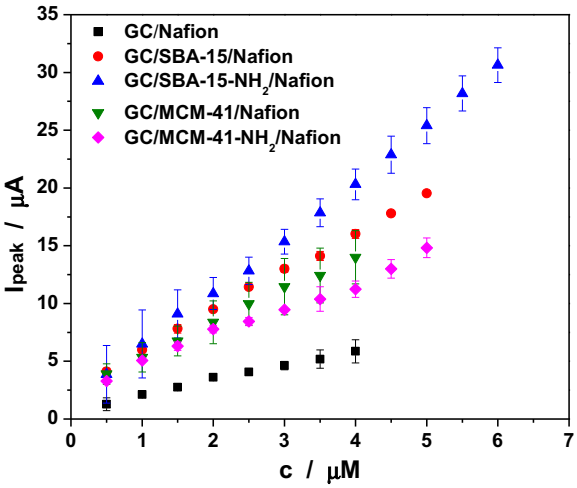

Fig. 3 Graph depicting the calibration curves for Pb^{2+} detection at different silica-modified GCEs. Experimental conditions: as in Fig. 1

3.4 Morpho-structural Analysis

In Fig. 4, the SEM micrographs of GC electrodes modified with amino-functionalized OMS (SBA-15-NH_2 Fig. 4a, and MCM-41-NH_2 Fig. 4b) and Nafion are presented.

It is seen that GC/SBA-15-NH_2/Nafion (Fig. 4a) has a looser structure than GC/MCM-41-NH_2/Nafion (Fig. 4b) allowing an easier accumulation of the Pb^{2+} ions in the pores and channels of the coating.

3.5 Selectivity and Interference Studies

In order to evaluate the possible interference of other HMIs with the detection of lead, two heavy metal ions, Zn^{2+} and Cd^{2+}, were tested. Figure 5 presents the SWASVs at the bare GCE (Fig. 5a), the GCE/SBA-15-NH_2/Nafion (Fig. 5b) by using the concentration of 50 μM of the three heavy metal ions. Figure 5 c displays SWASVs at GCE/SBA-15-NH_2/Nafion by peak currents of Pb^{2+} which increase linearly with concentrations in the range of 50–300 μM and peak currents of Cd^{2+} maintaining constant with concentration of 50 μM. All the electrodes were tested in 0.1 M acetate buffer (pH 4.4).

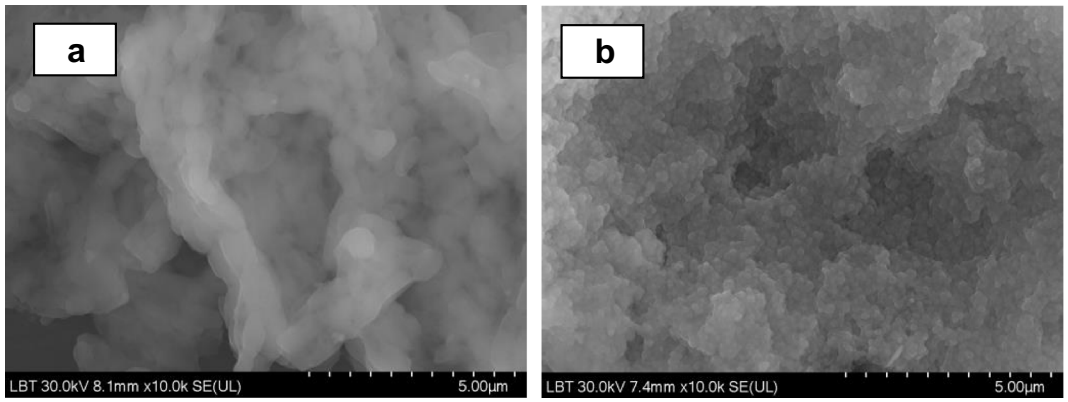

Fig. 4 SEM micrographs of GC/SBA-15-NH_2/Nafion (**a**) and GC/MCM-41-NH_2/Nafion (**b**) electrodes prepared by drop-casting with 5.0 µL suspension of 2.0 mg/mL OMS in 1% SDS and dried at room temperature

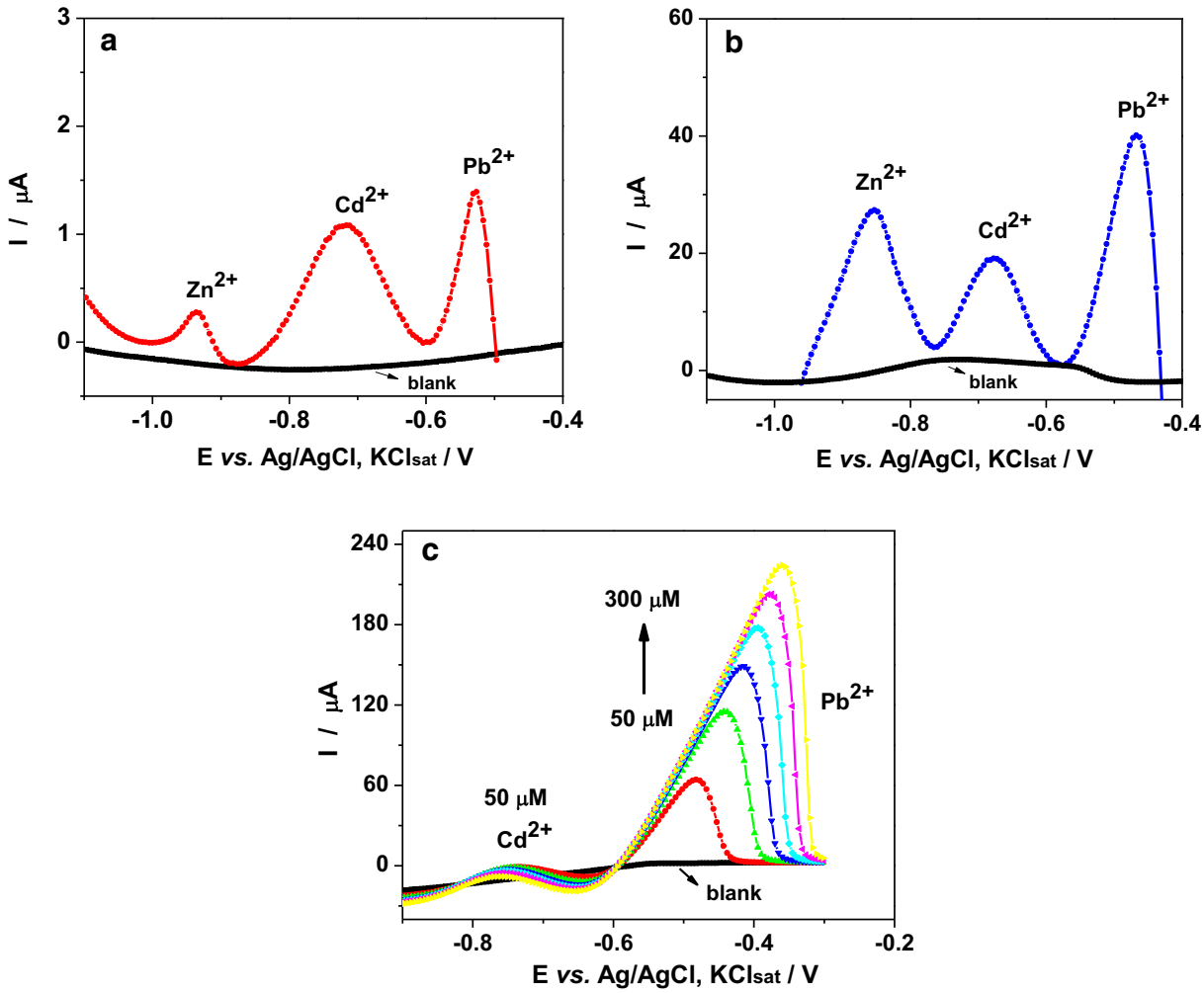

Fig. 5 SWASVs for the simultaneous additions of 50 µM of Zn^{2+}, Cd^{2+}, and Pb^{2+} at GCE/Nafion (**a**) and at GCE/SBA-15-NH_2/Nafion (**b**), and additions of 50 µM of Cd^{2+} and from 50 µM to 300 µM of Pb^{2+} at GCE/SBA-15-NH_2/Nafion (**c**) to 0.1 M acetate buffer solution (pH 4.4), following deposition at − 1.2 V for 120 s. Experimental conditions: as in Fig. 1

Table 2 ICP-OES and electrochemical methods for Pb^{2+} detection

Concentration Pb^{2+} (mg/L)		Recovery (%)
ICP-OES	GC/SBA-15-NH_2/Nafion	
0.035 ± 0.001	0.029 ± 0.003	98.8

Three distinct and well-separated peaks were obtained for Zn^{2+}, Cd^{2+}, and Pb^{2+}, indicating that no interference exists in the case of these ions.

3.6 Repeatability and Reproducibility of GC/SBA-15-NH_2/Nafion Electrode

Repeatability and reproducibility were tested by SWASV and expressed for current peak intensities. Repeatability was found to be 4% for a single electrode GC/SBA-15-NH_2/Nafion with four consecutive measurements and reproducibility (RSD%) was found to be 5.1% for five electrodes following identical measurement procedures.

3.7 Real Sample Analysis

Determination of Pb^{2+} concentration was performed by SWASV, with GC/SBA-15-NH_2/Nafion electrode from a natural water sample (pH 5) situated in Sălaj region, Romania. The measurements were repeated three times and the peak height values mediated, then interpolated on a premade calibration curve for the estimation of the unknown concentration. Working conditions (see Fig. 1) were the same as for all SWASVs measured before, and the calibration curve was done in 0.5–6 μM Pb^{2+} concentration range, at pH 4.4. In Table 2, the results of the standard ICP-OES method compared with the value obtained with GC/SBA-15-NH_2/Nafion-modified electrode are presented. As can be seen, the obtained results by both methods are in good agreement.

4 Conclusions

Ordered mesoporous silica immobilized on GCE improves the electroanalytical parameters of GCEs/Nafion due to their large surface area and to their adsorption ability.

The electrodes exhibited a linear response over a wide concentration range with a selective response to lead ion, and they are easy to prepare and is a rapid method of determination.

The analytical parameters of the prepared electrodes determined by square wave anodic stripping voltammetry were very promising, recommending the use of the modified electrode for determination of trace amount of Pb^{2+} ions in real sample analysis.

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