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Trace level voltammetric determination of lead and cadmium in sediment pore water by a bismuth-oxychloride particle-multiwalled carbon nanotube composite modified glassy carbon electrode

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ABSTRACT

Two multiwalled carbon nanotubes-based composites modified with bismuth and bismuth-oxychloride particles were synthesized and attached to the glassy carbon electrode substrate. The resultant configurations, Bi/MWCNT-GCE and BiOCl/MWNT-GCE, were then characterized with respect to their physicochemical properties and electroanalytical performance in combination with square-wave anodic stripping voltammetry (SWASV). Further, some key experimental conditions and instrumental parameters were optimized; namely: the supporting electrolyte composition, accumulation potential and time, together with the parameters of the SWV-ramp. The respective method with both electrode configurations has then been examined for the trace level determination of Pb^{2+} and Cd^{2+} ions and the results compared to those obtained with classical bismuth-film modified GCE. The different intensities of analytical signals obtained at the three electrodes for Pb^{2+} and Cd^{2+} vs. the saturated calomel reference electrode had indicated that the nature of the modifiers and the choice of the supporting electrolyte influenced significantly the corresponding stripping signals. The most promising procedure involved the BiOCl/MWCNT-GCE and the acetate buffer (pH 4.0) offering limits of determination of 4.0 μg L^{-1} Cd^{2+} and 1.9 μg L^{-1} Pb^{2+} when accumulating for 120 s at a potential of -1.20 V vs. ref. The BiOCl/MWCNT electrode was tested for the determination of target ions in the pore water of a selected sediment sample and the results agreed well with those obtained by graphite furnace atomic absorption spectrometry.

1. Introduction

The trace determination of Cd^{2+} and Pb^{2+} with different metallic-film electrodes that now often replace toxic mercury based electrodes is a challenge in many electroanalytical laboratories [1–3]. One of the first examples of this kind is the bismuth-film electrode (BiFE) in combination with anodic stripping voltammetry (ASV) [1] that has been introduced nearly fifteen years ago and, since then, becoming apparently the most popular working electrodes due to its environmentally friendly character. The ability of bismuth to form intermetallic alloys with different elements, as well as its insensitivity towards dissolved oxygen are just some of remarkable electrochemical features of bismuth-based electrodes that stay behind their widespread use [4,5].

Up until now, many types of bismuth-film or bismuth modified electrodes have been proposed and most of them also proven to be useful for different target analytes, first of all, for selected metals at the very low concentration level [1,6–31], but also for various organic compounds [32–38], in batch [1,6–25,29–31] and in flow injection [26–28] working regimes. Carbon-based electrode materials are well-known substrates for modification with bismuth as glassy carbon [1,9,13], carbon paste [7,8,12,17,18,29,30] and boron-doped diamond [10,11], but some metal electrodes like gold [19,22], platinum [13] and silver-amalgam [35] are convenient for modification with bismuth, too. In fact, bismuth-based configurations represent a specific type of chemically or physically modified electrodes that can be obtained by various methods, ranging from simple electrodeposition, via the adding of various Bi^{3+}

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compounds (e.g.: Bi_2O_3 [18], BiF_3 [29] or NH_4BiF_4 [30], etc.) as bulk-modifiers, up to the preparation of templates by screen-printing [26,27,39] and sputtering [31], etc.

Different designs were elaborated to improve the adhesion of bismuth particles onto / into the substrate, especially those based on carbonaceous materials, which expands the applicability of the respective electrodes at various pH, or to enhance the stability, sensitivity and/or selectivity of the electrode surface [40–52]. There were numerous efforts to improve the sensitivity of bismuth-based working electrodes, including the expansion of the sensor surface via the synthesis of mesoporous bismuth-based materials [41,42], the enlargement of the substrate electrode surface before modification with bismuth [43] and the incorporation of micro/nanoparticles of bismuth or bismuth-composite nanoparticles [20,44–53]. Nafion® protective layers [15,20,21,23–25,27,48,51], or other compounds like surfactants [15,21] or complex-forming agents (e.g. α,α′-bipyridyl [25], crown ethers [27] etc.) were found to improve the sensitivity and/or selectivity of the methods.

Multiwalled carbon nanotubes (MWCNTs), especially in their functionalized forms, are widely used as building blocks of electrodes because of their unique electrical conductivity, large surface area, and high affinity towards certain target analytes. It is well-known that bismuth-modified carbon nanotube-based electrodes are excellent with respect to electrochemical detection of ultratrace metals [45–52]. Also, it is known that the combining MWCNTs with Bi_2O_3 gives rise to composites appropriate as the modifiers of choice for the determination of H_2O_2 [44], anticoagulant acenocoumarole [53] and antidepressant drug escitalopram [54], as well.

Electrochemical techniques have often been used to study environmental processes related to water and sediment quality either in the field or in the laboratory [10,55–63]. Frequently measured target analytes are usually various elements, such as Fe, Mn, Cr, Co, Pb, etc., and sulphur or phosphorus in its different form in the water as well as in the sediment samples. Related to the sediment characterization is the "sediment pore water" (or also "interstitial water") whose quality is being considered as important parameter, indicating the actual processes/equilibria between the sediment and bulk water phases [64].

In the present work, we have combined the benefits of bismuth-based modifiers, BiOCl/MWCNT and Bi/MWCNT, with the outstanding electronic properties of MWCNT enhancing the sensitivity of the traditional BiFE based anodic stripping voltammetric method for the determination of toxic heavy metal ions, namely: Pb^{2+} and Cd^{2+}. Finally, the methodical procedure intended for the trace analysis was optimized with both types of electrodes, being compared with the BiF-GCE. The applicability of the method was tested on the determination of both Cd^{2+} and Pb^{2+} in the pore water of a real sediment sample from the river basin Great Backa Canal (Veliki Bački Kanal, R. Serbia). In the case of pore water sample, comparative graphite furnace atomic absorption spectrometric (GF-AAS) measurements were performed.

2. Experimental

2.1. Chemicals

Analytical grade *N*,*N*-dimethylformaldehyde (DMF), Nafion® (wt. 5%), $NaBH_4$, NH_3OHCl, CH_3COONa, cc. HCl and cc. CH_3COOH were purchased from Merck (Darmstadt). The multiwalled carbon nanotubes used in this study were synthesized from ethylene using chemical vapor deposition over Co–Fe/alumina catalyst. ICP stock solutions (all in concentration of 1000 ± 1 mg L^{-1}) of Bi^{3+}, Pb^{2+}, Cd^{2+}, and $BiCl_3$ were purchased from Sigma Aldrich. The sediment was sampled from the Great Backa Canal (R. Serbia).

2.2. Methods

An Autolab electrochemical analyzer operated via the GPES 4.9 software (Metrohm Autolab, Utrecht, The Netherlands) was used for all electrochemical measurements. The cell stand included a three-electrode system with GCE (⌀ 3 mm, Amel, Italy) substrate electrode surface modified with BiOCl/MWCNT, Bi/MWCNT or BiF as working, a platinum wire (Amel) as auxiliary electrode and a saturated calomel electrode as a reference.

Powder X-ray diffraction (XRD) patterns for the synthesized materials were obtained using a Rigaku Miniflex II instrument using Cu *K*α radiation. Surface morphology characterization and semi-quantitative chemical analysis of the BiOCl/MWCNT and Bi/MWCT nanomaterials were performed in a HITACHI S-4700 Type II cold field emission scanning electron microscope with an integrated Röntec QX2 EDS detector.

A graphite furnace atomic absorption spectrometer (Perkin Elmer Aanalyst 700) was applied for comparative sediment sample analysis. A Sonorex digitec (Bandelin) ultrasonic bath was used for the synthesis of bismuth-based materials and an ISCRA centrifuge for the separation and washing steps of the synthesized composite materials.

All pH measurements were made using a digital pH-meter (Radiometer, Nederland) and a combined glass electrode (Jenway, England).

2.3. Working electrode material preparation

2.3.1. BiOCl/MWCNT and Bi/MWCNT electrodes

The BiOCl/MWCNT-GCE and Bi/MWCNT-GCE were prepared *ex situ* by simple drop-coating of the appropriate suspensions of target modifiers on the freshly polished glassy carbon electrode surface. The synthesis of modifier materials is based on our recently published procedure of Sb/MWCNT preparation with $NaBH_4$ reduction and surface coating [65]. Briefly, in the case of both composites $BiCl_3$ (20 mg), MWCNT (16.4 mg) and 5%Nafion® solution (100 μL) were dispersed in DMF (10 mL) using an ultrasonic bath for 30 min. For Bi/MWCNT, 0.25 mL of a freshly prepared 1.8 mol L^{-1} aqueous solution of $NaBH_4$ was added to the dispersion and stirred for 10 min, while in the case of BiOCl/MWCNT 0.25 mL of 1.8 mol L^{-1} NH_3OHCl was added. The solid part was precipitated using a centrifuge (600 rpm for 15 min) and decanted. The precipitate was washed with ethanol (2 ×) and acetone (1 ×), and then transferred to a hot air oven and dried at 220 °C for 20 min. 0.5 mg from each sample was dispersed in a mixture of ethanol (0.9 mL) and Nafion®0.5% (0.1 mL), and sonicated for 20 min. 5.0 μL aliquots of the resulting suspensions were dropped on the glassy carbon electrode surfaces and dried at room temperature.

2.3.2. Bi particles

The Bi nanoparticles were obtained using the Bi/MWCNT synthesis procedure but without adding any nanotubes. The obtained particles served for the comparison of XRD characteristics.

2.3.3. BiF-GCE

A cell containing the aqueous solution of a Bi^{3+} (0.50 mg L^{-1} in acetate buffer at pH 4.0) was electrolyzed under continuous stirring at the cathodic potential of -1.20 V for 120 s similarly as was elaborated earlier [1].