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Electrochemical detection of lead (II) at bismuth/Poly(1,8-diaminonaphthalene) modified carbon paste electrode

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Abstract A new sensor based on carbon paste electrode modified with Poly(1,8-diaminonaphthalene) and bismuth film (Bi-Poly1,8-DAN/CPE) was prepared and characterized with cyclic voltammetry and electrochemical impedance spectroscopy. The sensor was found to exhibit an electroactivity toward the sensing of lead using square wave voltammetry in acidic medium. Various operational parameters, such as concentration of Bi(III), square wave voltammetric parameters, deposition potential and deposition time were investigated. Under the optimized conditions, a linear range was achieved over concentration range from 0.5 μg L^{-1} to 50 μg L^{-1}, with a detection limit of 0.3 μg L^{-1} offering a good repeatability and reproducibility. Finally, the Bi-Poly1,8-DAN/CPE was applied for the analysis of lead in water samples with satisfactory results.

1. Introduction

Excessive levels or even small doses of very toxic metals (i.e. lead, cadmium, mercury) can cause several damages on the environment and human health. Therefore sensitive and selective methods for the detection of heavy metals especially lead have become a priority in environmental monitoring. During the last decades, different approaches have been used to develop high-performance electrochemical sensors based on bismuth film or conducting polymers (Hwang et al., 2008a,b; Kefala and Economou, 2006; Yi et al., 2012). Since the pioneering work of Wang (Wang et al., 2000), Bismuth film electrode called environmentally friendly electrode has been widely used in organic, biological and pharmaceutical analysis (Chatzitheodorou et al., 2004; de Lima and Spinelli, 2013; Jain and Sharma, 2012; Pierini et al., 2013). Detections of heavy metals especially lead using voltammetric techniques and bismuth film electrodes have been reported in some excellent reviews (Arduini et al., 2010; Baldrianova et al., 2007; Lezi et al., 2012; Švancara et al., 2010; Wang, 2005). Consequently, Bismuth has been introduced as an alternative working electrode material, and it has a property to form binary or

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multi-component alloy with some heavy metals commonly known as fused alloy, facilitating the nucleation process during deposition of heavy metal ions.

The modification of the electrode by organic conducting polymers has also been a very active area of research. Organic conducting polymers received great attention due to their potential application as electrochemical sensors (Ates and Sarac, 2009; Bai et al., 2009; Shahrokhian et al., 2015). Philips et al., demonstrated that the chelating cyano group containing polyaniline derivative could be an effective electrode for ultrasensitive electrode for detection of lead and cadmium (Philips et al., 2012). The electrochemical modification of glassy carbon with electropolymerized form of 1,10-phenanthronine for voltammetric determination of cadmium was reported by Oztekin et al. (2011). The sensitivity of Poly(1,8- diaminonaphthalene) to heavy metal ions such as Ag^+, Hg^{2+} and Cu^{2+} has been studied using electrochemical and spectroscopic methods. The ability of conducting polymer matrices to complex heavy metals was studied by different groups. It has been proved that metal ions form complexes with amino groups of the polymer (El Rhazi and Majid, 2014; Nguyen et al., 2011).

More recently, the combination of metallic ions with polymers has been investigated to improve the properties of these materials for electroanalytical purposes. Ojani et al., reported that the combination of 1,5-diaminonaphthalene and Nickel particles improves the oxidation of methanol (Ojani et al., 2008). In another study, Hathoot et al., prepared and characterized the Poly1,5-diaminonaphthalene on the surface of carbon electrode using cyclic voltammetry. After electropolymerization, the transition metal ions of Ni (II) were incorporated to the polymer for the electrocatalytic oxidation and simultaneous determination of glucose, ascorbic acid and dopamine (Hathoot et al., 2012). A Bi/Nafion/overoxidized 2-mercaptoethanesulfonate-tethered polypyrrole/glassy carbon electrode has been developed to simultaneous determination of cadmium and lead (Chen et al., 2014). The composite film is of great interest because of their strong electronic interactions between the metallic particles and the polymer matrices (Henríquez et al., 2012; Kokkinos and Economou, 2011; Li et al., 2009; Piankova et al., 2011; Yang et al., 2014). It has been reported that the electrocatalytic properties of nanoparticles could be improved by the conductive polymeric matrices (Balazs et al., 2006; Švancara et al., 2006; Wang et al., 2013; Yang et al., 2013).

Motivated by the striking properties of Poly1,8-diaminonaphthalene into carbon paste electrode and the wide uses of bismuth film electrode in electroanalysis, we decided to combine the advantageous feature of our conducting polymer and bismuth film for a detection of lead. At our best knowledge, the combination of 1,8-diaminonaphthalene (1,8-DAN) and bismuth was not studied. Herein, for the first time facile approaches for synthesis of Bi-Poly1,8-DAN were proposed. At the first step, the electropolymerization of 1,8-DAN into carbon paste electrode was conducted in acidic media free of monomer. The electrode surface could be renewed by simple extrusion of a small amount of paste from the tip of the electrode and the polymer could be renewed very easily. Then, the bismuth film electrode was deposited at negative potential. For determination of lead, the Poly (1,8-DAN) was modified with *in situ* plated bismuth film electrode and the performance of prepared sensor was then evaluated in real water samples using square wave anodic stripping voltammetry.

2. Experimental section

2.1. Reagents and materials

The chemical reagents used in the preparation of stock solutions were of analytical reagent grade. 1,8-Diaminonaphthalene (1,8-DAN) was obtained from Sigma Aldrich. All solutions were diluted by distilled water. Supporting electrolyte was solution of hydrochloric acid. Bismuth Stock solution of 100 mg L^{-1} was prepared from $Bi(NO_3)_2$š$5H_2O$ (Sigma Aldrich), whereas $Pb(NO_3)_2$ (Riedel–Dehaen) was employed in the preparation of metal-ion stock solution with concentration of 100 mg L^{-1}.

2.2. Instrumentation

Voltammetric measurements (cyclic voltammetry (CV), square wave voltammetry (SWV)) and Electrochemical Impedance Spectroscopy (EIS) were performed using AUTOLAB PGSTAT302 N (EcoChemie, Utrecht, Netherlands) Potentiostat/Galvanostat controlled by GPES 4.9 software. The three-electrode system configuration includes a carbon paste as the working electrode, saturated calomel electrode (SCE) as the reference electrode, and platinum disk as the counter electrode. The pH was adjusted by addition of NaOH or HCl solution using a Fisher Scientific Accumet AB15 Basic pH meter.

2.3. Preparation of working electrode

A 1,8-Diaminonaphthalene doped carbon paste electrode (1,8-DAN/CPE) was fabricated as follows: 1% (w/w) of 1,8-DAN dissolved in a small quantity of acetonitrile, thoroughly homogenizing with 1 g graphite powder and 30% (w/w) paraffin oil using a mortar and pestle. The paste mixture was packed into electrode cavity 2 mm (Teflon-PTFE tube, $\phi = 3$ mm) and electrical contact was established with a copper rod. The surface of the 1,8-DAN/CPE was polished on a piece of white paper. The bare carbon paste electrode (CPE) was fabricated with the same way without addition of the monomer. The Bi-Poly1,8-DAN/CPE and BiF-CPE were prepared by *in situ* plating bismuth in the detection step.

2.4. Procedures

Electropolymerization was performed at a constant potential of 0.7 V (vs. SCE) for 80 s in 0.1 M HCl solution. Following the polymerization, the electrode was cycled in 0.1 M HCl solution free of monomer for five scans until a stable voltammogram was obtained. The conditions employed will be reported in the discussion.

In square wave anodic stripping voltammetric (SWASV) measurements, the modified electrode by Poly1,8-DAN was dipped into 0.1 M HCl solution containing 500 μg L^{-1} Bi (III) and predetermined concentration of target Pb(II). A deposition potential of −1 V (vs. SCE) and a deposition time of 120 s were applied to the working electrode under stirring conditions. The stirring was stopped and after 10 s equilibration time, the square wave anodic stripping voltammograms (SWASV) were recorded between −0.7 and −0.3 V (with a step increment of 5 mV and amplitude of 50 mV). For repetitive

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