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Preparation and application of nanocomposite based on imprinted poly (methacrylic acid)-PAN/MWCNT as a new electrochemical selective sensing platform of Pb^{2+} in water samples

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ABSTRACT

This paper describes the development of an electrochemical sensor highly selective to Pb^{2+} ions based on drop-coated glassy carbon electrode (GCE) with a suspension of ion imprinted polymer (IIP) loaded with 1-(2-pyridylazo)-2-naphthol (PAN) (IIP-PAN) and multi-walled carbon nanotubes (MWCNT). The polymer has been characterized by SEM and TGA. The electrochemical method is based on open-circuit preconcentration of Pb^{2+} onto modified electrode in 0.05 mol L^{-1} Tris-HCl buffer solution at pH 6.0 during 20 min. The reduction of Pb^{2+} was than performed on closed circuit at − 1.2 V during 60 s in a 0.05 mol L^{-1} HCl solution, followed by subsequent differential pulse anodic stripping voltammetric determination in the range from − 0.8 to − 0.3 V. Electrode modified provided a better analytical response than those modified with its respective non imprinted polymer (NIP), IIP without PAN and MWCNT alone, which clearly demonstrates the synergic effect of recognition sites of IIP-PAN and MWCNT. Competitive adsorption studies for the binary Pb^{2+}/Cu^{2+}, Pb^{2+}/Cd^{2+}, Pb^{2+}/Ni^{2+}, Pb^{2+}/Ni^{2+}, Pb^{2+}/Zn^{2+} mixtures revealed the respective relative selective coefficients (k') 301, 13.3, 9.5, 63.0 and 133.3, thus indicating that IIP-PAN is much more selective than NIP. Presence of potential interfering metal ions was also studied and the proposed electrode proved to be very tolerable. Limits of detection (LOD) and quantification (LOQ) were found to be 0.16 μg L^{-1} and 0.50 μg L^{-1}, respectively. The inter-day method precision was found to be 1.72 and 1.86% (relative standard deviation) and the intra-day precision was found to be 1.68 and 2.53% for 5.0 and 10.0 μg L^{-1} of Pb^{2+}, respectively. The developed sensor was effectively applied to water samples and synthetic urine with satisfactory recovery values from 95 to 103%. The accuracy of method was checked by analysis of standard reference material 1643e Trace Elements in Water NIST.

1. Introduction

Lead is one of the most hazardous metal and is widely spread in environmental resources, mainly in water and food causing damage for human health [1]. Lead ions are non-biodegradable and tend to bioaccumulate in cells of living organisms by binding strongly to sulfhydryl groups on enzymes or proteins, thus affecting metabolic processes. Moreover, lead can cause kidney problems, damage in brain, bones and central nervous system, as well as increase blood pressure [2]. Due to these facts, international agencies such as United States Environmental Protection Agency (EPA), Agency for Toxic Substances and Disease Registry (ATSDR) and International Agency for Research on Cancer (IARC) have classified lead as a carcinogenic element for human beings [1,3,4]. Since lead has an unquestionable toxicity, some legislation establishes maximum levels of heavy metals. The World Health Organization (WHO) recommends a maximum allowable limit of 10.0 μg L^{-1} of lead in drinking water [5].

Although some traditional spectroanalytical techniques, such as Graphite Furnace Atomic Absorption Spectrometry (GF AAS) [6], Inductively Coupled Optical Emission Spectrometry (ICP OES) [7] and

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Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) [8] possess adequate detectability for lead determination at trace and sub-trace levels, they present high cost of acquisition and maintenance and training of special skills. In this sense, due to their portability, low cost and easy operation, the electrochemical methods, mainly the voltammetric ones, have been widely used for determination of lead ions [9–11]. However, it is well-known that the choice of a proper electrode is of paramount importance for obtaining voltammetric methods with high sensitivity, selectivity, stability and reproducibility.

Among electrode materials, metallic electrodes either in bulk or in film form, such as mercury [12], silver [13], gold [14–16], bismuth [17] and antimony [18] have been employed for lead determination. Although widely used, some of these electrodes, in general, may suffer from important drawbacks, such as lack of reproducibility due to intermetallic compounds depending upon nature of analysed sample and fouling of the electrode after measurements [19].

Therefore, different approaches for obtaining chemically modified electrodes (CMEs) aiming at enhance the sensitivity and the selectivity for voltammetric determination of lead have been widely proposed. The chemical modifiers may be integrated in the electrodic material through film formation onto surface of bare electrode by using carbonaceous materials as electrode paste. Some modifiers/approaches such as crown ethers [20], Langmuir-Blodgett (LB) film of a *p-tert*-butylcalix [4]arene derivative [21], diphenylthiocarbazone [22] and bismuth/poly(1,8-diaminonaphthalene) [23], gold cysteamine self-assembled monolayer, in situ functionalized with ethylenediaminetetraacetic acid (Au–CA–EDTA SAM) [24], magnetic nanoparticles modified with diethylenetriamine pentaacetic acid (DTPA) [25] and graphene oxide/carbon nanotube/poly(*O*-toluidine) nanocomposite [26] have been reported in the development of chemically modified electrodes for lead ions determination.

Another possibility of modifying bare electrodes for lead determination is based on the use of ion imprinted polymer (IIP). High selectivity of IIP can be most explained from the selective binding sites created through interaction between the metallic ion used as template and the monomer that will survive the synthesis process [27,28]. Literature data have reported that the most important approach for the synthesis of highly selectivity IIP is based on the use of nonvinylated chelating ligand trapped into the polymeric network [29]. In such approach both functional monomer and chelating ligand provides interaction with the metallic ion and conduces to higher selective sites of recognition with better fit between the cavities and the template due to the cavities generated with the specific coordination geometry and number and size of template ion [30].

Several ligands have been widely applied in the IIP synthesis for forming a ligand-metal complex, such as acetate-picolinamide [31], dimethylglyoxime [32], diazoaminobenzene [33], dithizone [34], morin [35] diphenylcarbazone [36], 8-hydroxyquinoline [37,38] for a wide variety of metals. In spite of outstanding selective performance of IIP synthesized in the presence of chelating ligand, their application has been mostly focused on the development of solid phase preconcentration methods.

According to literature data few studies have been devoted to the use of IIP as an electrochemical sensing device for metal ions determination and the most common strategy for sensor preparation involves the incorporation of IIP into carbon paste electrode [39–44]. However, as it is well-known, the adequate integration of modifier element on the transducer electrode play a fundamental role on the performance of electrochemical sensing device and the main limitation of carbon paste electrode modified with IIP is the low amount of polymer regarding the carbon, which may provide low selectivity of electrochemical sensing. In this sense, the integration of IIP with a conductive nano-carbonaceous, such as carbon nanotubes, on the surface of transducer electrode by drop casting method seems to be a better way for obtaining IIP-based electrochemical sensor. When appropriately prepared, the suspension of IIP and carbon nanotubes may be very stable and the amount of IIP may be greater than carbon nanotubes. Although interesting, at the best of our knowledge, the preparation of IIP-based electrochemical sensor drop casting method is still sparse [45].

According to aforementioned, in this study we have synthesized an ion imprinted poly(methacrylic acid) loaded with chelating 1-(2-pyridylazo)-2-naphthol selective towards Pb^{2+} and evaluated its use as modifier element of glassy carbon electrode in the presence of multiwalled carbon nanotubes (MWCNT) for the development of a new voltammetric method for detection of Pb^{2+} using differential pulse anodic stripping voltammetry (DPASV). Herein, it has been chosen the cross-linked poly(methacrylic acid) since it is well-known that the functional monomer is able to form metal ion complexes with cations [46], while azo compounds, such as the 1-(2-pyridylazo)-2-naphtol, have ability to form stable and colored complex with metals [47].

Characterization of IIP (without PAN), IIP-PAN and its respective non-imprinted polymer (NIP) was carried out by TGA (thermogravimetric analysis), SEM (scanning electron microscopy) and their selectivity was studied.

By virtue of achieved results, such as simplicity, stability of suspension, and synergic effect of IIP and MWCNT towards electrochemical Pb^{2+} detection, the use of drop casting method can be highly recommended for the integration of IIP on the surface of transducer electrode when associated with conductive nano-carbonaceous.

2. Experimental

2.1. Apparatus

For selectivity studies, concentration of lead was determined by a Shimadzu AA-6601 (Kyoto, Japan) flame atomic absorption spectrometry (FAAS) equipped with a lead hollow cathode lamp operated at 10.0 mA and wavelength of 217 nm. Flame was composed by acetylene-air in a flow rate of 2.0 and 15.0 L min^{-1}, respectively. All pH measurements were performed utilizing a Metrohm 827 digital pH meter (Herisau, Switzerland). Voltammetric measurements were performed with a potentiostat/galvanostat Autolab® PGSTAT-101 at room temperature. Differential pulse anodic stripping voltammetry (DPASV) experiments were performed in an electrochemical cell with 15.0 mL capacity containing a platinum wire as the auxiliary electrode, an Ag/AgCl electrode as the reference and the modified glassy carbon electrode as the working electrode. Before modification, the glassy carbon electrode (Metrohm, 3.0 mm in diameter) was carefully polished with 0.5 μm alumina slurry on a flat surface, rinsed thoroughly with deionized water, and then sonicated immediately using in deionized water for 2 min. The morphological features of polymers were evaluated by SEM, using a microscope JEOL JSM-6360 LV equipped with dispersive energy microscopy. Thermal stability of polymers was evaluated from TGA using a TGA 4000 Perkin Elmer (Waltham, USA) thermobalance. For analysis, ~10 mg of sample was heated from 30 to 900 °C at a rate of 10 °C min^{-1}, under nitrogen flow of 20 mL min^{-1}.

2.2. Materials and reagents

All reagents used in this work were of analytical grade without previous purification. Dimethylsulphoxide (DMSO) was purchased from F. MAIA, 2,2′-Azobis(2-methylpropionitrile) (AIBN) and ethylene glycol dimethacrylate (EGDMA) from Sigma-Aldrich, methacrylic acid (MAA) from Acros, 1-(2-pyridylazo)-2-naphthol (PAN) and lead nitrate [$Pb(NO_2)_3$] from Vetec, Tris hydrochloride (Tris-HCl) from Invitrogen and acetate from MERK, multi-walled carbon nanotubes (MWCNTs; of 10–40 nm in diameter and 5–20 μm in length; purity: 93%) from CNT Co. Ltd., Korea and Nafion® (5%) from Sigma-Aldrich. Values of pH were adjusted with sodium hydroxide solutions (Merk) and hydrochloric acid (Panreac). All solutions were prepared using ultrapure water purified by a Milli-Q® system (Millipore, Bedford, MA, EUA). In