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Synthesis, characterization and application of novel lead imprinted polymer nanoparticles as a high selective electrochemical sensor for ultra-trace determination of lead ions in complex matrixes

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ABSTRACT

We report on the design of a lead(II)-selective electrode based on the use of lead(II) imprinted polymer nanoparticles (IP-NPs), and its application for the differential pulse voltammetry determination of lead ions. The IP-NPs were obtained by precipitation polymerization of 4-vinylpyridine (the functional monomer), ethylene glycol dimethacrylate (the cross-linker), 2,2'-azobisisobutyronitrile (the initiator), 4-(2-pyridylazo)resorcinol (the lead-binding ligand), and lead ions (the template ion) in acetonitrile solution. After polymerization, the Pb(II) in the polymer nanoparticles were leached out with dilute hydrochloric acid to create cavities for hosting Pb(II). The new sensor showed high selectivity for lead ions in the presence of common potential interferences according to the specific recognition nature of the synthesized material. A carbon paste electrode was modified with the IP-NPs, and differential pulse stripping voltammetry was applied as the detection technique after open-circuit sorption of Pb(II) ions and its reduction to the metallic form. An explicit difference in the response was observed between the electrodes modified with IP-NPs and electrodes modified with non-IP-NPs. The modified electrode responds to Pb(II) was linear in the 0.1 nM to 10 nM (with sensitivity of 49.179 nA/nM) and in the 10 nM to 10 μM (with sensitivity of 30.305 μA/μM) concentration range. The limit of detection (LOD) of the sensor was 30 pM (at S/N =3). The sensor was successfully applied to the trace determination of Pb(II) in spiked environmental water samples.

1. Introduction

The contamination of the environment by heavy metals, including lead, remains a serious problem because of their non-biodegradability and high toxicity, yet their continued exposure in the environment from mining, natural sources and enrichment and release from human technological uses. The toxic heavy metals are incorporated into water and various food chains where they can gain entry into, for example, human bodies via drinking water, food, and breathing airborne particles. Therefore, a highly sensitive method for the determination of ultra-trace heavy metals is required. Lead is classified as prevalent toxic metal, which constitutes a major environmental health problem. Because lead and their compounds are widely used as chemical materials in modern society, they are widespread in environmental sample. Among them, lead has extensively been used in industry in the production of pigments, anticorrosion coatings, alloys, batteries, etc. and thus it is widely spread in different areas of the environment. High toxicity of lead is due to chronic poisoning resulting from trace exposure and leads to several organs disruption particularly kidneys and nervous system. The European Union has set the maximum allowable concentrations in food to be from 0.02 to 1 mg L^{-1} and World Health Organization has set 10 mg L^{-1} for drinkable water [1]. Several methods based on atomic absorption spectrometry (AAS) [2], inductively coupled plasma optical emission spectrometry (ICP-OES) [3,4] and inductively coupled plasma mass spectrometry (ICP-MS) [5–8] graphite furnace atomic absorption spectrometry (GFAAS) [9,10] have been successfully applied to the determination of trace elements in real samples. However, voltammetric methods are highly favorable techniques for the determination of metal ions because of its low cost, high sensitivity, easy operation and

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the ability for portability. In order to enhance the sensitivity and selectivity of the electrochemical determination of lead(II), chemically modified electrodes have received increasing attentions in the past decades. The modifiers used include bismuth [11–15], PAN-incorporated nafion [16], organic chelating groups [17–21], clay nano particles [22], zeolite [23], SiO_2–Al_2O_3 mixed-oxide [24], and silica [25]. Anodic stripping deferential pulse voltammetry (ASDPV) is the most attractive electrochemical technique for the determination of trace heavy metals due to its high sensitivity and selectivity with modified electrodes. Advantage of ASVDPV over the other three methods (AAS, ICP-AES or ICP-MS) is the simplicity of the required instrumentation, which is relatively inexpensive, low electrical power consumption, portable as well as suitable for automation [26–28]. On the other hand, ion-imprinted polymers (IIPs) are recognizing metal ions after imprinting, while retaining all the virtues of MIPs. The production of polymers exhibiting selective binding of a specific cation, involves the formation of cavities equipped with complexing agents so arranged as to match the charge, coordination number, coordination geometry and size of the target cation.

In the present work, combining the advantages of high selectivity from the IIP nanoparticles technique and high sensitivity from CPE detection, a IIP-CPE sensor has been developed for the determination of lead ion. Some advantages of this work are simplicity, rapidity, high selectivity, being operative and cheap, easy to usage and sensitive determination of low levels of lead ions in aqueous solution.

2. Experimental

2.1. Materials

4-vinyl pyridine with high purity was purchased from Merck (Darmstadt, Germany, www.merck.de). Ethylene glycol dimethacrylate (EGDMA) and 4-(2-pyridylazo) resorcinol were obtained from Fluka (Buchs SG, Switzerland, www.sigmaaldrich.com). 2,2′-Azobisisobutyronitrile (AIBN) was obtained from Acros Organics (New Jersey, USA). NaOH, HCl, HNO_3, acetic acid (HOAC) and methanol were purchased from Merck (Darmstadt, Germany). The acetate buffer solutions (0.15 mol L^{-1}) were prepared with CH_3COONa and CH_3COOH. All the other reagents used were of analytical grade and purchased from Merck (Darmstadt, Germany, www.merck.de). Stock solutions of Cu^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}, Ni^{2+} and Co^{2+} were prepared from Titrisol solutions (Merck, Darmstadt, Germany, www.merck.de). Ultrapure water was prepared using a Milli-Q system from Millipore (Bedford, MA, USA). Ore polymetallic gold Zidarovo-PMZrZ (206 BG 326) from Bulgaria was used as the reference material.

2.2. Apparatus

All electrochemical measurements were performed with a Palm-Sens (EN 50081-2) potentiostat. A personal computer was used for data storage and processing. The three electrode electrochemical cell used was equipped with a modified (Pb^{2+} ion imprinted polymer) carbon paste electrode (MCPE) as a working electrode, a saturated calomel electrode (SCE) as a reference electrode and a platinum electrode as an auxiliary electrode (Azar Electrode Co, Iran). All potentials in the text were reported versus this reference electrode. The pH measurement was performed with a Metrohm model 691 pH/mV meter. Heidolph heater stirrer model MR 3001 (Germany) was employed for heating and stirring of the solutions. Fourier Transform Infrared (FT-IR) spectra (4000–200 cm^{-1}) in KBr were recorded using Bruker IFS66/S FT-IR spectrometer. High angle X-ray diffraction patterns were obtained on a Philips-PW 17 C diffractometer with Cu K_α radiation. Scanning electron microscopy (SEM) was performed by gently distributing the powder sample on the stainless steel stubs, using SEM (KYKY, EM3200) instrument. The thermal properties of synthesized polymers were determined using a BAHR-Thermoanalyse GmbH (Germany) with employing, heating and cooling rates of 10 °C min^{-1} and using a condenser as the coolant. The samples were weighed as a thin film and carefully packed into a clean aluminum pan (11.5-12.5 mg), and sealed by crimping an aluminum lid on the pan (Shimadzu universal crimper). An Al_2O_3 empty pan sealed with a cover pan was used as a reference sample. A scanning range of 10 to 800 °C was used for samples at 10 °C min^{-1} in nitrogen gas.

2.3. Synthesis of Pb^{2+} ion imprinted polymer (IIP) and non-imprinted polymer nanoparticles (NIP)

The nanosized lead-imprinted polymer was prepared by precipitation polymerization technique. In the first step, 3 mmol of 4-vinyl pyridine (functional monomer) and 1 mmol of 4-(2-pyridylazo) resorcinol (the lead-binding ligand) were dissolved in 50 mL of acetonitrile in a 100 mL glass flask. Subsequently, as the second step, 1 mmol of $Pb(NO_3)_2$ as an imprinted metal ion (template) was added slowly to a glass flask and the resulted mixture was stirred for 5 h at room temperature. In the third step, 18 mmol of EGDMA and 75 mg of AIBN were added as cross-linker and initiator. The oxygen of the sample solution was removed by bubbling nitrogen through the sample for 10.0 min. Polymerization was performed in an oil bath at 65 °C for 24 h in the presence of nitrogen under magnetic stirring at 400 rpm. The prepared polymer was washed several times with 1:4 (v/v) methanol/water to remove the unreacted materials and then with HCl (1 mol L^{-1}) for leaching the imprinted metal ions until the washing solution was free from lead ions. Finally, it was washed with double distilled water until reached a neutral pH. (Fig. 1 provides the images of synthesized nanosized IIP after each step). The resulting fine powder was dried under vacuum in a desiccator before studies. In the same way, the non-imprinted polymer (NIP) was also prepared without lead ions.

2.4. Preparation of IIP-MCPE

Based on optimized conditions, ion imprinted polymer modified carbon paste electrode (IIP-MCPE) was prepared. A mixture of IIP (15% w/w), graphite powder and paraffin oil (55:30% w/w) was blended by hand in a mortar with a pestle to construct the IIP-CPE. The body of the carbon paste working electrode was a Teflon rod with a hole (2 mm in diameter and 5 mm deep) bored at one end for paste filling. The electrical connection was made with a copper wire through the center of the rod.

2.5. Real sample pretreatment

The polyethylene bottles filled with the samples were cleaned with detergent, water, diluted nitric acid and water in sequence. The samples were immediately filtered through a cellulose filter membrane (pore size 0.45 μm), and were acidified to pH of 2.0 for storage. Tap water samples (50 mL) were taken from our research laboratory without pretreatment (pH adjusted to 5.0). Before analysis, the water samples (50 mL) which were taken from Caspian Sea, river (Siahrood river (Ghaemshahr, Iran)) and waste (water fish ponds) were adjusted to pH of 5.0 according to optimized experimental conditions.