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A highly selective voltammetric sensor for nanomolar detection of mercury ions using a carbon ionic liquid paste electrode impregnated with novel ion imprinted polymeric nanobeads

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ABSTRACT

This work reports the preparation of a voltammetric sensor for selective recognition and sensitive determination of mercury ions using a carbon ionic liquid paste electrode (CILE) impregnated with novel Hg^{2+}-ion imprinted polymeric nanobeads (IIP) based on dithizone, as a suitable ligand for complex formation with Hg^{2+} ions. The differential pulse anodic stripping voltammetric technique was employed to investigate the performance of the prepared IIP-CILE for determination of hazardous mercury ions. The designed modified electrode revealed linear responses in the ranges of 0.5 nM–10 nM and 0.08 μM–2 μM with a limit of detection of 0.1 nM ($S / N = 3$). It was found that the peak currents of the modified electrode for Hg^{2+} ions were at a maximum value in phosphate buffer of pH 4.5. The optimized preconcentration potential and accumulation time were to be −0.9 V and 35 s, respectively. The applicability of the proposed sensor to mercury determination in waste water samples is reported.

1. Introduction

Heavy metals which remain in ecological and food chain systems are not biodegradable [1]. Mercury has been considered as a human health hazard and is one of the most harmful pollutants in the environment. Mercury may cause kidney toxicity, neurological damage, paralysis, chromosome breakage, and birth defects [2]. However, the Hg toxicity is highly dependent on its chemical form; in fact, its organic materials such as methylmercury are more toxic than its inorganic and elemental species [3]. The main part of mercury contamination in humans usually comes from food chain systems [4]. The elemental mercury and inorganic mercury from global anthropogenic sources are converted into organic forms including monomethylmercury, dimethylmercury, ethylmercury (EtHg) and phenylmercury, by biogeochemical transformation processes and, owing to their bioaccumulative and persistent properties, are accumulated in fish through food chain in ecosystems [3]. The main sources of exposure to organic mercury are by the consumption of the fish or seafood and the most common exposure to inorganic mercury is by the inhalation of Hg vapor released from dental amalgams or from gold mining activities [5]. Thus, due to the high toxicity of low levels of Hg^{2+} ion, the development of new selective and sensitive methods for determining and removing mercury ions from pollutants is still a challenging task.

Instrumental methods such as atomic absorption spectroscopy (AAS) [6], atomic fluorescence spectrometry (AFS) [7], inductively coupled plasma mass spectrometry (ICP-MS) [8] and X-ray absorption spectroscopy [9], which have been widely used for measuring Hg^{2+} ions are usually time-consuming, need expensive and complicated instruments and possess no capability for on-site mercury monitoring. Moreover, a number of fluorescence methods on the basis of a nile blue-based chemodosimeter [10], a conjugated polymer based fluorescent probe [11], a nanocomposie-based luminescence sensor [12], a DNA-functionalized monolithic hydrogel [13] and catalytic gold nanoparticles [14] have been developed. However, most of these methods possess a poor selectivity and moderate sensitivity [15].

Meanwhile, due to their good portability, high sensitivity with low cost and simple instrumentation, the electrochemical methods have been accepted as an alternative of the spectroscopic techniques for the detection of heavy metal ions [16].

Since the determination of mercury at sub-microgram per liter levels suffers from the matrix interferences, separation and preconcentration procedures are required before the determination step [17]. Recently, solid-phase extraction (SPE) is being utilized for the preconcentration of heavy metals. However, in the SPE methods, when solid supports such as active carbon [18], ion-exchange resins [19], chelating fibers [20] and chelating resins [21] are used, the selectivity needs to be improved for a specific element. Thus, in this respect, the chemically modified electrodes have attracted an increased attention for the electroanalytical determination of various trace metals after their selective

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preconcentration. These electrode surfaces may be modified by a given chemical reaction in an open circuit to accumulate a selected analyte prior to its voltammetric quantification [22,23].

Among different molecular recognition materials reported in the past decade [24–26], the ion imprinted polymers (IIP) containing inorganic cation selective sites, have been used as highly selective sorbents [27–32]. One of the wide applicability of IIPs is their use for pretreatment and enrichment of low concentration analytes in complex matrices [33]. In fact, the introduction of IIPs in trace and ultratrace analyses opened a new era in the field of preconcentration/separation chemistry. The use of IIPs for SPE (IIP–SPE) provided a high potential in trace and ultratrace analyses. Beside the high selectivity, the other advantages of IIPs are their high adsorption capacities which provide improved sensitivity and lower detection limit. In addition, IIP materials usually show high stability and durability against harsh chemical environments. Due to the vital importance of selective separation, removal, preconcentration and detection of traces of highly toxic Hg^{2+} ion from environmental and biological samples several mercuric IIPs have already been reported in the literature [34–42].

The principle of ion imprinting is based on complex formation between an imprint metal ion and suitable ligands (either polymerizable or non-polymerizable) in the liquid phase prior to polymerization and then initiation of the polymerization process in the presence of cross-linking monomers and initiator [27–32]. After polymerization, the imprint metal ion is removed from the polymeric particles by leaching with mineral acid that leaves cavities or “imprinted sites” in the polymeric particles that are complementary in shape and size of the imprint metal ion. The resultant polymeric particles can be used as extractants for selective separation and enrichment of imprint metal ion from dilute aqueous solutions by batch or column experiments.

In recent years, the use of electrodes modified with IIPs in the preparation of metal ion electrochemical sensors has received an increasing attention [43–49]. These electrodes have brought together the advantages of different kinds of modifying agents in a single modified electrode. We have recently reported a number of nanosized ion imprinted polymeric beads with enhanced selectivity and sensitivities [29,30,29,30,41,46,48].

Recently, the carbon ionic liquid electrodes (CILEs), first introduced by Safavi and co-workers [50,51], in which the IL playing a great role in increased conductivity, wide electrochemical windows, antifouling effect, renewable surface of the electrode, and providing the ability to lower the over potential of electroactive compounds, have found wide applications in the field of electrochemical sensing [52,53]. CILE can be prepared by substituting the non-conductive organic binder with high conductive ionic liquids, which exhibit superior electrochemical performances over the traditional working electrodes [51].

Dithizone (Dz) is well known to form fairly stable 1:2 (metal to ligand) complexes with a variety of metal ions in some non-aqueous solvents [54]. Dithizone can react with mercury(II) to form a violet complex, with a binding constant of $\log \beta 2 = 42.5$ [55], which is insoluble in water and soluble in benzene, chloroform or carbon tetrachloride [54,55]. In this paper, we report the first synthesis and characterization of novel ion-imprinted polymeric nanoparticles by using dithizone (Dz) as a non-polymerizable ligand for quantitative and selective separation and enrichment of imprint Hg^{2+} ions in aqueous solutions. The obtained Hg^{2+} imprinted polymer nanoparticles were then used as a modifying agent in order to prepare a novel sensitive and selective CILE as a voltammetric sensor for low level detection of Hg^{2+} ions in aqueous solutions.

2. Experimental

2.1. Chemicals

Ethyleneglycol dimethacrylate (EGDMA) and 1,5-diphenylthiocarbazone (dithizone; Dz) were supplied by Merck (Darmstadt, Germany). 2,2′-Azobis(isobutyronitrile) (AIBN) was obtained from Aldrich (St. Louis, MO, USA). Analytical grade $Hg(NO_3)_2 \cdot H_2O$, $Hg(CH_3COO)_2$, $Pb(CH_3COO)_2 \cdot 3H_2O$, $Pb(NO_3)_2$, $Cu(NO_3)_2 \cdot 3H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, $Cd(NO_3)_2 \cdot 4H_2O$, and $NaH_2PO_4 \cdot 2H_2O$ were obtained from Merck and used as received. Graphite fine powder (extra pure, particle size ≤50 μm) and other chemicals were of analytical grade from Merck. Doubly distilled water was used throughout the work. The ionic liquid 1-octyl-3-methylimidazolium hexafluorophosphate ($OMIMPF_6$) was synthesized and purified according to the literature [56]. Doubly distilled water was used throughout the work.

2.2. Apparatus

All voltammetric studies were carried out using a Metrohm electroanalyzer model 757 VA Computrace. The software used was 757 VA Computrace, version 2.0 with a three-electrode system. The carbon paste electrodes modified with Hg^{2+}-IIP was used as a working electrode. A platinum wire and an Ag/AgCl electrode were used as the counter and reference electrodes, respectively.

A Varian Vista Pro (CCD simultaneous) model inductively coupled plasma (Palo Alto, CA, Australia) was used for the determination of all metal ions. The operational conditions for ICP-AES and wavelength of analytical lines were in accordance with manufacturer's instructions. The IR spectra (4000–500 cm^{-1}) were recorded on a 460 model IR spectrometer (Shimadzu, Kyoto, Japan) after drying of polymeric nanoparticles at 80 °C for 5 h. A model 713 digital pH meter (Metrohm, Switzerland) was used for pH adjustments. Elemental analyses were performed on a Vario El III CHN analyzer (Elementar, Hanau, Germany). All absorption spectra were recorded on a UV–visible spectrophotometer (S-2100 series, SCINCO Co. Ltd., Korea), equipped with a thermostated cell compartment. A Frigomix thermostat (Compiegne, France) was used to keep the solution temperature constant at 25.00 ± 0.05 °C. Scanning electron micrographs of dried and ground polymers were obtained using a model XL30 scanning electron microscope (Philips, Holland).

2.3. Preparation of Hg^{2+}-imprinted polymeric nanoparticles

The mercury(II) ion-imprinted nanoparticles were prepared by a thermal precipitation polymerization technique. The procedure for the synthesis of poly(EGDMA-Dz/Hg(II)) colloidal nanoparticles was achieved in two steps. In the first step, dithizone (0.250 mmol) and $Hg(CH_3COO)_2$ (0.125 mmol) were added to dimethylsulfoxide (10 mL) as a complexation and co-solvent in a 25 mL vial to interact with each other in order to produce a pink Hg^{2+}-Dz. In the second step, EGDMA (5 mmol), AIBN (0.1 mmol) and tetrahydrofuran (10 mL) were added as a cross-linker, free radical initiator and polymerization solvent, respectively, to the first step solution, and then stirred at room temperature. Argon gas was bubbled trough the prepolymerization mixture for 5 min to remove molecular oxygen from the mixture, as it traps the radicals and retards the polymerization.

Then the reaction vial was sealed and heated in an oil bath at 60 °C for 24 h under magnetic stirring at 500 rpm to complete the thermal polymerization. After polymerization, the excess amount of solvent was removed by centrifugation of the resulting suspension solution. The prepared polymer was washed several times with 1:4 (v/v) methanol/water to remove the unreacted materials and then by 0.1 M HNO_3 for the leaching of the imprint metal ions until the wash solution was free from Hg^{2+} and, finally, by doubly distilled water until neutral pH is reached. The polymer material was dried overnight. Because of the high adhesion of particles to each other, the dried polymer was ground to get particles in nano scale. The achieved colloidal nanoparticles were applied for next sorption and desorption studies. The synthesis of non-imprinted polymer (NIP) or poly(EGDMA-Dz) was carried out the same as that of Hg(II)-IIP preparation procedure, but without addition of $Hg(CH_3COO)_2$ (template).